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Message from the President of the Association of Researchers of Thailand

Dear All Members

The Association has successfully held the 2020 general meeting with the request for the amendment of the regulations of the association to provide flexibility in the administration in the digital age which has been unanimously approved by the meeting.

The Association has established the working party for cannabis research for the public by gathering people in the cannabis industries across the country to collaborate on research in various fields including education, agricultural technology and innovation, medicine, integrated medicine, economy, industry, and social and cultural services, and in media and public relations. This will be achieved by conducting research and publishing into a special edition of the journal of the Association. And we have a plan to hold a conference on cannabis in the next year. If any member has research work on hemp cannabis, you are invited to publish your articles in our journal.

Lastly, we hope all of our members of the Association of Researchers of Thailand will go through this difficult time together.

Associate Professor Dr. Phiphat Nonthanathorn
the President of the Association of Researchers of Thailand

This International Journal of Science and Innovative Technology (IJSIT) is volume 3 and issue 2 which is still continuously honored by academics and researchers who have continuously submitted the research works for publication which works can be further extended to innovations in order to propel Thailand to international acceptance and towards sustainable development.

There are many activities of the Association of Researchers of Thailand in collaboration with external agencies, to lead the research cooperation and various academic disciplines, such as The Council of Science and Technological Association of Thailand (COSTAT) whose the Association is a member to meet and discuss with the Minister of higher education, research, science and innovation, special seminar on “Applying holistic innovation with Global Digital Farmers to stimulate the market demand”, Academic discussion and exhibition booth of Thailand Research Expo2020 and ASE2020, the Contest award of Green school and learning the green for a sustainable world 2020, the Association as Certified Body (CB) organization to certify personal according to professional standards in the field of researcher service, the Certification organization code CB-0271-A and Training Workshop “Science Communication Workshop Serie 2”

The editorial team would like to thank the professors, academics, and researchers for this occasion in submitting important articles for further development into innovation for the actual application. The International Journal of Science and Innovative Technology (IJSIT) will play an important role in disseminating research knowledge that can be used to solve problems and continue to develop Thailand and make sustainable international connections accordingly.

Assistant Professor Dr. Sujinna Karnasuta
Editor in Chief


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The Effects of Silica/Carbon Black Hybrid Filler Contents on Natural Rubber Composite Properties Using Conventional Vulcanization System

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Abstract

The physical properties and mechanical properties of rubber composite were improved by reinforcing with silica and carbon black (S/CB) hybrid filler. The amounts of S/CB hybrid filler were varied from 30 to 60 phr of NR. Maximum torque and minimum torque of NR compound grew continuously with increasing the amount of hybrid filler. The NR compounds were vulcanized for 90 % of cure time at 150 °C. Physical and mechanical properties, e.g., hardness, volume change, abrasion loss, tensile strength, tensile modulus, elongation at break, tear strength and compression set of NR composite were investigated. The overall properties of the NR composite went up with increasing S/CB hybrid filler until 50 phr but they decreased after increasing S/CB hybrid filler of > 50 phr. This is mainly due to the agglomeration of S/CB hybrid filler. Moreover, hybrid filler content loaded NR composites hardly affects properties of aged NR composites. The results reveal that the optimum amount of S/CB hybrid filler added 50 phr in NR composites is suitable for application.

Keyword: Natural rubber; Hybrid filler, Physical properties; Mechanical properties; Aging resistance

1. Introduction

Natural rubber (NR) is one of the bio-based polymers which is used to prepare compounding rubber for many applications and products, including automobile tires, outdoor sealing and aerospace engineering. The properties of NR is known to exhibit outstanding such as good oil resistance, high strength and low gas permeability and it can be improved for specific applications (Heinrich et al., 2002; Pal et al., 2010; Schué, 2000). NR plays a major role in rubber industry, especially for the production of truck tyres, because it strengthens the rubber in highly strained regions and, therefore, impedes the formation of cracks (Nair & Joseph, 2014). One of the most important NR design is the fillers which commonly is added into rubbers as a reinforcing agent to improve mechanical properties (tensile strength, tear strength, abrasion resistance, and aging resistance). For example, the carbon blacks (CB), silica (S) and resins

reduce material costs and improve mechanical properties. The carbon black and silica are used as the main reinforcing-fillers that increase the usefulness of rubber (Al-Hartomy et al., 2016; Flanigan et al., 2012; Kato et al., 2013; Rattanasom et al., 2009; Rattanasom et al., 2007; Ulfah et al., 2015). Production of some mechanical rubber goods requires rubbers with multifunctional properties, such as strength, barrier properties, resistance to oxidative aging.

The properties of rubber compounds are strongly influenced by the incorporation of carbon black and silica. Although the carbon black-reinforced rubber exhibits higher modulus, strength and abrasion resistance when compared to a silica-reinforced one, silica provides a unique combination of tear strength, aging resistance and adhesion properties. To improve the properties of NR product, silica was used as an important reinforcing agent in rubber composite together

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with carbon black (Li et al., 2008; Sae-Oui et al., 2014; Thappong et al., 2014). The surfaces of both reinforcing fillers are very different. It is known that silica contains predominantly the hydroxyl group on the surface, which results in highly polar or hydrophilic and strong filler-filler interaction via hydrogen bonds. Intramolecular hydrogen bonds of silica are very strong and it can form a tight aggregate (Wang et al., 2016; Xu et al., 2015). Therefore, the surface of silica was modified by using two coupling agents, polyethylene glycol (PEG) and bis(3-triethoxysilylpropyl) tetrasulfide (Si-69), as previously reported in numerous studies. Each coupling agent has a different function. PEG can be used as a permanent buffer between silica and the ingredients coated on the surface of silica to remove the cure hindering adsorptions. The added PEG improves the properties of NR including cure rate, scorch, viscosity, hardness, trouser tear, compression set, heat buildup and abrasion index (Kralevich & Koenig, 1997). The Si-69 is needed to improve the filler-to-rubber bonds or interaction between the particles of silica and elastomer (Pal et al., 2010; Kralevich & Koenig, 1997; Fröhlich et al., 2005; Kaewsakul et al., 2014; Kaewsakul et al., 2016). It was reported that the presence of Si-69 simultaneously worked as the surface capping agent at the mixing temperature between 50 to 110 °C (Rattanasom et al., 2009; Rattanasom et al., 2007; Choi & Park, 2001; Tabsan et al., 2010).

The ratio between carbon black and silica as the hybrid filler of NR was previously studied in order to determine the optimum proportions (Rattanasom et al., 2009; Rattanasom et al., 2007). The results showed that the composite containing carbon black and silica of 30:20 and 20:30 in hybrid filler had the better overall mechanical properties and, therefore, these ratios were chosen for the subsequent study. The degree of reinforcement depends on the amount of the hybrid filler. In this study, the S/CB ratio of hybrid filler was kept condition of proportions at 3:2, when the total hybrid filler to NR composite was varied from 30 to 60 phr. The effects of the filler content on the physical properties, mechanical properties, morphology property and aging resistance of rubber composite were investigated. The NR composite would be potentially used to produce a

rubber corner guard to protect wall corners from accidental damage. It is suitable for parking garages, basement parks and commercial warehouses.

2. Materials and Methods

2.1 Materials

Natural rubber (STR 5L) has Mooney viscosity (ML_{1+4} at 100 °C) of 81.3. Properties of carbon black N220 are iodine adsorption 121 mg/g, DBP adsorption 114 cm³/100g and pour density 350 g/dm³. Silica US-M were investigated by BET surface area as 175 m²/g, bulk density 0.19 g/cm³. The silicon dioxide (SiO₂, Hydrated Base) was 93.0%. The other additives such as zinc oxide (ZnO), stearic acid, poly(ethylene glycol) bis(3-triethoxysilylpropyl) tetrasulfide (Si-69), N-(1,3-di methyl)-N'-phenyl-*p*-phenylenediamine (6-PPD), gum resin, naphthenic oil, 2,2,4-Trimethyl-1,2-Dihydroquinoline polymer (TMQ), Tetramethyl thiuram Disulfide (TMTD), N-tert-butyl-2-benzothiazole sulfenamide (TBBS), and sulfur (S₈) were also of commercial grades. STR 5L rubber and all mixing additives were obtained from suppliers in Bangkok, Thailand.

2.2 Preparation of S/CB hybrid filler NR composites

All composites were prepared at the same composition of NR and additives, except for the amount of silica (US-M) and carbon black (N220), that were varied based on the formulation shown in Table 1. In this research, reinforcement of NR with silica/CB hybrid filler at various ratios was maintained constantly at 3:2 and the total amount of hybrid filler was varied from 30 to 60 phr. The formulations were named as S/CB30, S/CB40, S/CB50, S/CB55 and S/CB60. Silica surface was modified with a silane coupling agent as 8% wt. of silica. Then, NR was masticated in an internal mixer (Brabender Plasticorder, Yongfong) firstly at 70 °C for 5 min and rotor speed of 60 rpm. After that, the other ingredients, except the curatives: TBBS, TMTD and S₈, were added and mixed for 8 min at the same temperature and rotor speed. Finally, the curatives were poured and admixed for 5 min using the two roll-mill to prepare NR compound. NR compound of each formulation was kept at least 16 h at room temperature before testing. The curing time (tc90), maximum torque and minimum torque

for preparing the NR composites or NR vulcanizates the NR composites experiment procedure was shown in Figure 1. were measured using the moving die rheometer (MDR) on the cure curve at 150 °C. The schematic diagram of

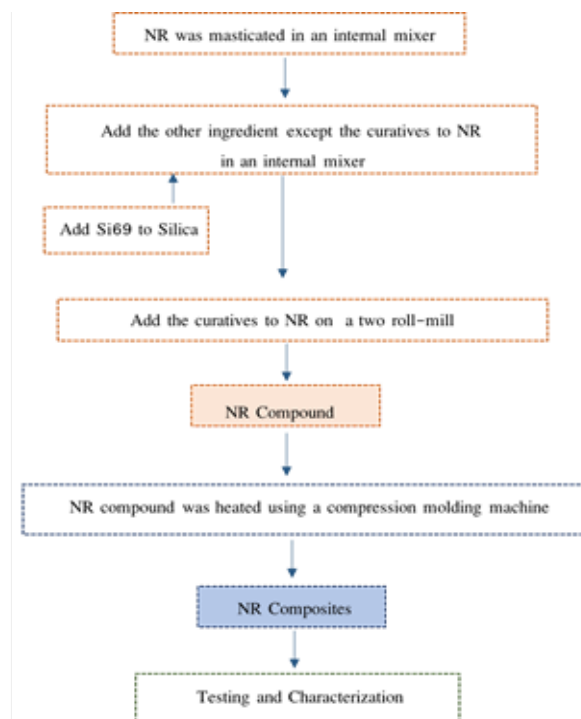


Figure 1. The schematic diagram of NR composites experiment procedure.

Table 1. Formulation of the rubber composites (in phr of total rubber content)

Ingredients	Composition (phr)				
	S/CB30	S/CB40	S/CB50	S/CB55	S/CB60
STR 5L	100	100	100	100	100
ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2
Carbon Black N220	12	16	20	22	24
Silica US-M	18	24	30	33	36
Si69 (8 % wt. of silica)	1.44	1.92	2.4	2.64	2.88
PEG4000 (5 % wt. of silica)	0.9	1.2	1.5	1.65	1.8
Naphthenic Oil	6	6	6	6	6
Gum Rosin	5	5	5	5	5
6 PPD	2	2	2	2	2
TMQ	1	1	1	1	1
TBBS	1	1	1	1	1
TMTD (Sulfur donor)	0.2	0.2	0.2	0.2	0.2
Sulfur	2	2	2	2	2

2.3 Testing and Characterization

2.3.1 Maximum torque and minimum torque

Maximum torque and minimum torque of NR composites were determined using Moving Die Rheometer (Monsanto, MDR2000) at 150 °C. The 10 g of samples were used with a 0.5° arc. The cure time (tc90) of the cure samples was used to measure the total torque change on the cure curve.

2.3.2 Hardness and Volume change tests

Hardness values were conducted using a Shore A type from universal hardness tester (Bareiss Digi test II) under conditions according to ISO 7619 Part 1. Additionally, the volume change of products in water was carried out following ISO 1817.

2.3.3 Tensile tests

The tensile modulus values at 100% (M100) and 300% (M300) of elongation at break, tensile strength and elongation at break were tested on dumbbell-shaped specimens using a universal mechanical testing machine (Shimadzu Intron Universal Testing Machine) following ISO 37:2011 (Type 1) at a crosshead speed of 500 mm/min.

2.3.4 Compression set and Tear properties tests

Compression set values were measured using the compression set test fixtures according to method B specified in ASTM D395-03 (2008) at 70 °C for 24 h. Tear strength of specimens was carried out on die B shaped specimens using a universal mechanical testing machine (Shimadzu Intron Universal Testing Machine) according to ISO 34 (Method B)

2.3.5 Abrasion loss tests

Abrasion loss of cylinder specimens was carried out using abrasion tester following DIN 53516. Abrasion loss is measured by moving a test piece of rubber composite across the surface of an abrasive sheet mounted on a revolving drum. It is expressed as a volume loss in cubic millimeters.

2.3.6 The aging properties

The aging properties of samples were measured by placing dumbbell-shaped five specimens in the air circulating oven at 70 °C during 96 h. After that,

the samples were cooled at room temperature for at least one day before the measurement of hardness and tensile properties of samples. The tensile and hardness properties of aged samples were investigated in the same method as the unaged samples. Tensile strength retention was calculated from the equation⁹:

$$\text{Tensile retention (\%)} = [(T_u - T_a)/T_u] \times 100,$$

where T_u and T_a are tensile strength of unaged and aged specimens, respectively

2.3.7 Scanning electron microscopy

The morphology of fracture surfaces of NR composites was investigated using scanning electron microscopy (SEM JEOL 6340F) at an accelerating voltage of 10 kV. The specimens were sputter-coated with gold to prevent charging on the surface before the examination.

3. Results & Discussion

3.1 Maximum torque and minimum torque

Maximum torque and minimum torque at various S/CB hybrid filler contents are displayed in Figure 2. The minimum torque of NR compound grows up continuously with increasing the amount of hybrid filler up to 60 phr due to the increase of NR compound viscosity. Furthermore, the maximum torque dramatically increased when S/CB hybrid filler content went up from 30 phr to 60 phr. It is already reported that maximum torque depends on the three-dimensional crosslinking density and chain entanglements. This result can be explained that S/CB hybrid filler affects the crosslinking density by reacting with the chemical ingredients of formulation thus leading to a higher torque²⁵.

3.2 Physical properties

3.2.1 Hardness and volume change of NR composites

Figure 3. presents the effect of S/CB hybrid filler contents on the hardness of NR composites. The hardness of NR composite increased upon raising the content of S/CB hybrid filler because the increment of hard phase from silica and carbon black were more loaded in NR composites thus leading to a decrease of NR matrix phase. The volume change of NR composites

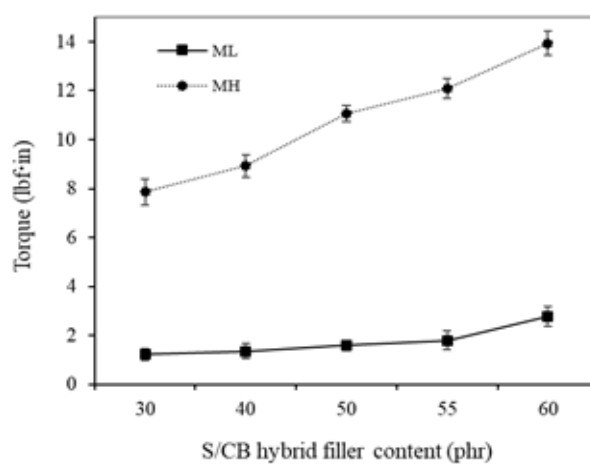


Figure 2. Maximum torque and minimum torque of NR compound with various S/CB hybrid filler contents

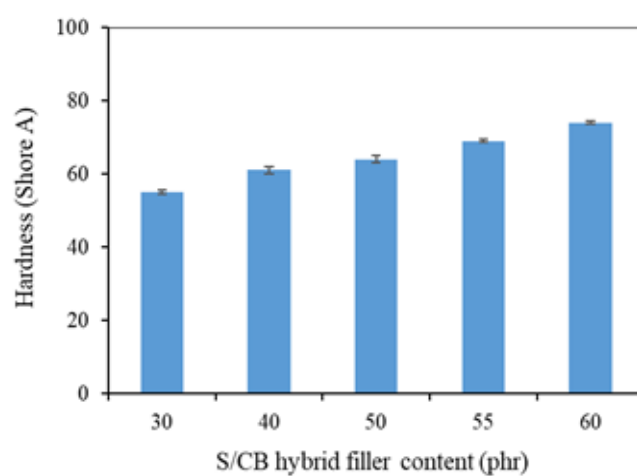


Figure 3. Hardness of NR composites with various S/CB hybrid filler contents

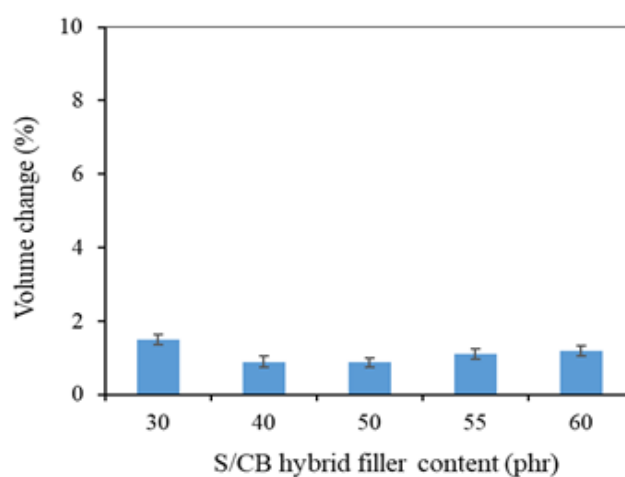


Figure 4. Volume change of NR composites with various S/CB hybrid filler contents

with different loading of S/CB hybrid filler are shown in Figure 4. The volume change of NR composite is slightly changed as the contents of S/CB hybrid filler increased from 30 to 60 phr. This means that adding S/CB hybrid filler in the range of 30 to 60 phr less affected the volume change of NR composite. This is due to cross-link bond density in NR composites after curing NR compound.

3.3 Mechanical properties

3.3.1 The modulus of NR composites

Figure 5. is presented the modulus of NR com-

posites at various S/CB hybrid filler content. The modulus is the force at a specific elongation value, ie 100% or 300% elongation. The increase of S/CB hybrid filler content was affected continuously increase the 100% and 300% modulus. This is due to the increment of the hard phase from the added silica and carbon black. Moreover, the increase in modulus with S/CB hybrid filler content is explained by the stiffening effect caused by the interaction between the filler and rubber particles. Additionally, the hardness properties of NR composites also follow the same trend as the modulus.

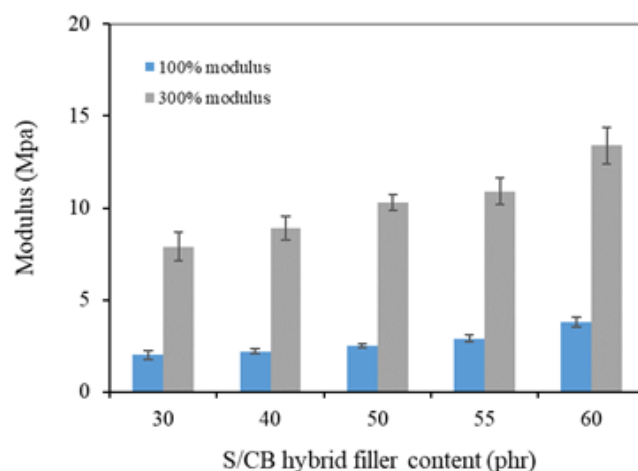


Figure 5. 100 % and 300 % Modulus of NR composites with various S/CB hybrid filler contents

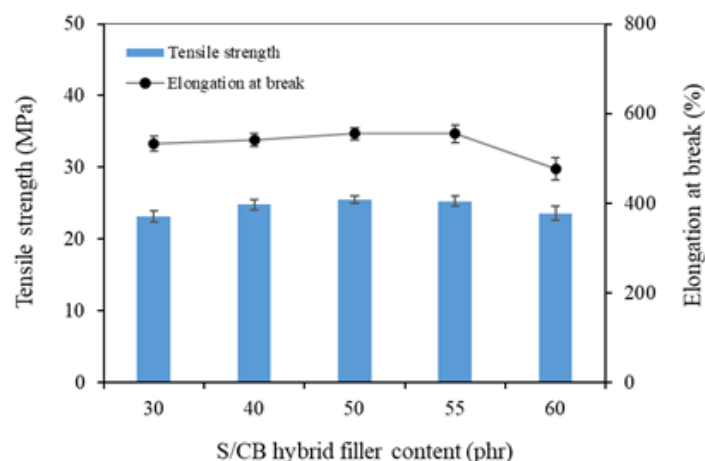


Figure 6. Tensile strength and Elongation at break of NR composites with various S/CB hybrid filler contents

3.3.2 The tensile strength and elongation at break

The comparison of results between the tensile strength and elongation at break with various S/CB hybrid filler contents is shown in Figure 6. The tensile increase with increasing S/CB hybrid filler up to 50 phr and then they slightly decrease when silica content is

further increased. On the other hand, it appears that elongation at break does not significantly change with increasing S/CB hybrid filler from 30 phr to 55 phr. Both results are started to decrease as the content of S/CB hybrid filler at 55 phr. This is due to the high S/CB hybrid filler at > 50 phr tended to coalesce leading to poor dispersion. This could restrict molecular chain mobility

when NR composites were stretched which lowered the tensile strength and elongation at break.

3.3.3 Tear strength and the abrasion loss

The tear strength and the abrasion loss of NR composites at various amounts of S/CB hybrid filler are shown in Figure 7. The tear strength first increased when adding S/CB hybrid filler to 50 phr. After that, tear strength decreased with further loading S/CB hybrid filler up to 60 phr. It is significantly seen that the tear strength drop with increasing S/CB hybrid filler over 50 phr because of formation of hybrid filler agglomer-

ation in NR composite. This result that the interaction between hybrid filler and NR is weak, so the increment in the filler loading has further reduced this interaction. Moreover, the hybrid filler agglomerated also prevent molecular chains movement of NR. Furthermore, the decline of abrasion loss could be explained by the increase in hard phase filler thus leading to high abrasion resistance of NR composite. This result supports the slightly decreased abrasion loss with increasing S/CB hybrid filler content from 30-60 phr. Moreover, it corresponded with hardness properties.

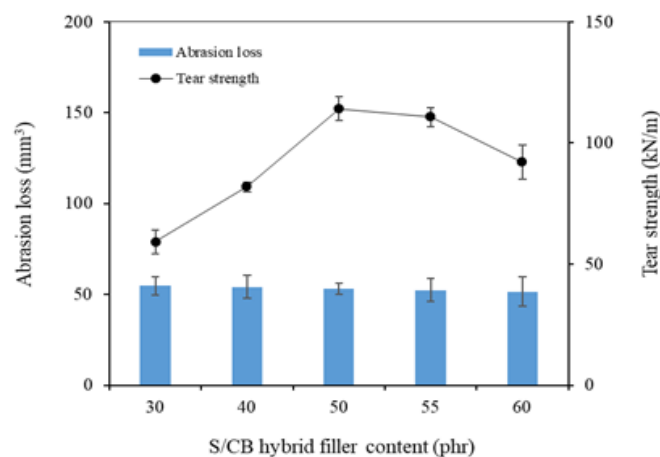


Figure 7. Tear strength and Abrasion loss of NR composites with various S/CB hybrid filler contents

3.3.4 Compression set

Figure 8. is shown the compression set of the NR composites. The compression set is a test of the ability of the rubber to retain their elastic properties after extended compression at a constant strain under a specified set of conditions (Smith, 1993; Othman, 2001). The compression set value of NR composite was varied upon the amount of hybrid filler. Low amounts of hy-

brid filler from 30 to 40 phr give a low compression set of NR composite but compression set of NR composite slightly increased with increasing hybrid filler content over 40 phr. The result suggests that the increase in compression set values confirms that the elasticity of cured NR composite is impaired in the presence of hybrid filler at higher contents. It could be resulted from the agglomeration of hybrid filler, leading to the loss of

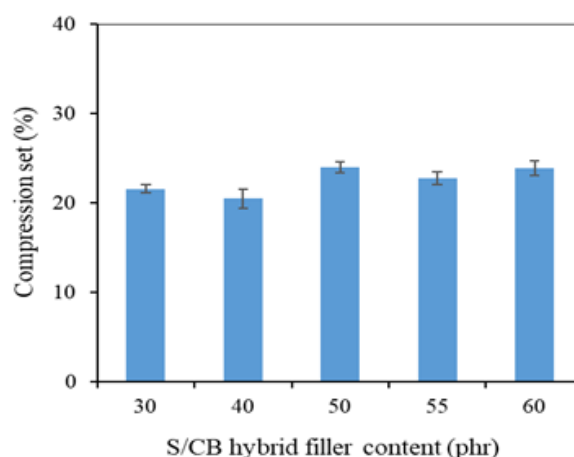


Figure 8. Compression set of NR composites with various S/CB hybrid filler contents

the NR composite elasticity.

3.4 Morphology property

The fractured surfaces of NR composites loaded with S/CB hybrid filler are shown in Figure 9. It indicates that hybrid filler was well dispersed in NR composite and no critical agglomeration of hybrid filler was visible at low loading level. Nevertheless, the increase

of hybrid filler content more than 50 phr, the particles tended to agglomerate. It can be seen that good dispersion of S/CB hybrid filler is considered as a factor to achieve good mechanical properties (Ghari & Azam, 2016) which according to the results of the mechanical properties of NR composites.

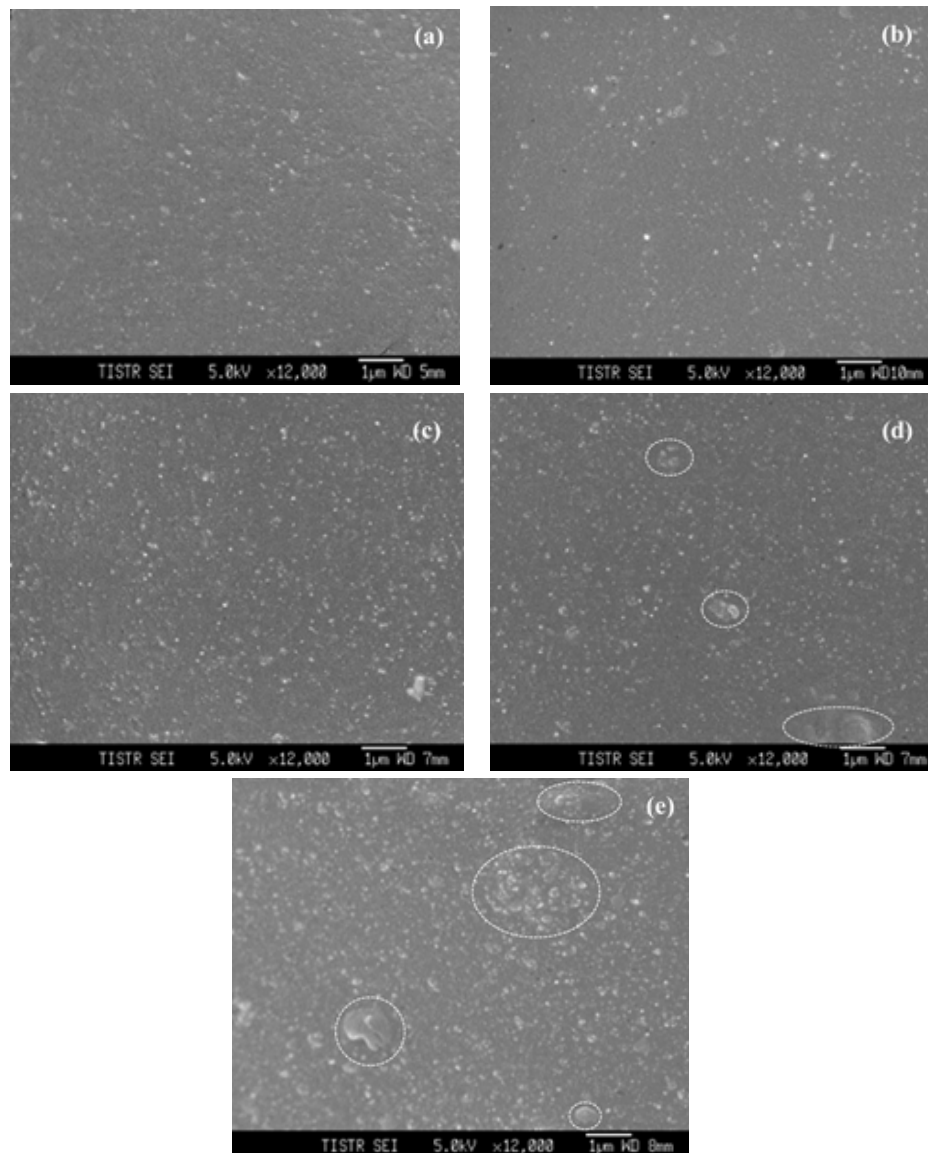


Figure 9. The fractured surfaces of NR composites with various S/CB hybrid filler contents; (a) 30 phr, (b) 40 phr, (c) 50 phr, (d) 55 phr and (e) 60 phr

3.5 Aging resistance

Aging is the degeneration of desirable properties during storage or usage that it is a phenomenon common of NR because it is susceptible to thermal-oxidative ageing due to unsaturated carbon-carbon double bonds in molecular structure. Moreover, various changes can occur in rubber component as a result of the conditions under which it is used or stored. This research studied changing properties of NR composites under accelerated aging.

The hardness change with various S/CB hybrid filler contents is shown in Figures 10. The hardness of all NR composites formulation slightly increased as the heat aging temperature grew at 70 °C for 168 h. Besides, the loading of hybrid filler increases the hardness retention of NR composites hardly changed. The tensile test results for the heat-aged specimen at 70 °C for 168 h

are presented in Figures 11 and 12. It can be seen that the tensile strength and elongation at break of aged NR composites at 70 °C for 168 h less went up when they were compared with tensile strength and elongation at break for unaged NR composites (virgin). Moreover, tensile strength retention, elongation at break retention of NR composites slightly increase when the hybrid filler content increase because the heating effect could destroy the remaining molecular chain of unsaturated NR and initiates the movement of the filler within the matrix. Hence, degradation occurred inside of the NR matrix thus leading to the breaking of filler-rubber and rubber-rubber bonding. Nevertheless, they are also evident that hybrid filler content added NR composites hardly affect hardness change, tensile strength retention and elongation at break retention of aged NR composites.

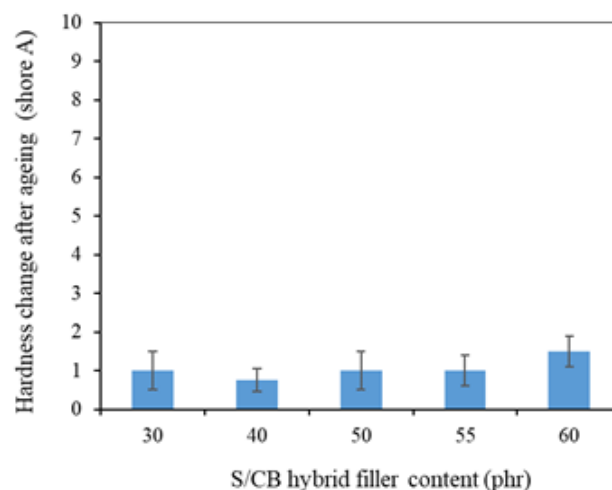


Figure 10. Hardness change after aging of NR composites with various S/CB hybrid filler contents at 70 °C for 168 h.

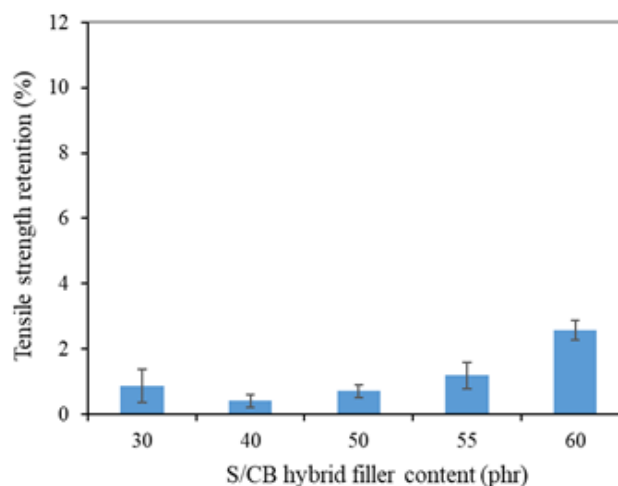


Figure 11. Tensile strength retention of NR composites with various S/CB hybrid filler contents at 70 °C for 168 h.

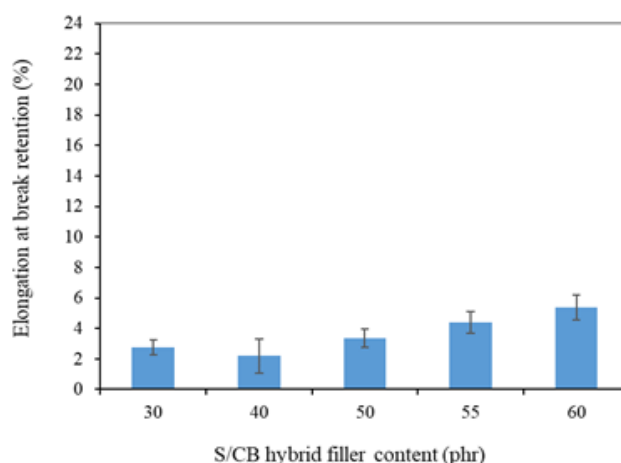


Figure 12. Elongation at break retention of NR composites with various S/CB hybrid filler contents at 70 °C for 168 h.

4. Conclusion

It can be concluded that maximum torque and minimum torque of NR compound increases continuously with increasing the amount of hybrid filler. The mechanical properties, physical properties of NR composites can be improved by using silica/carbon black hybrid filler. The properties of NR composites were dependent on the amount of hybrid filler. The results reveal that high S/CB hybrid filler content over 50 phr resulted in poor dispersion and the more large agglomeration formed. This non-uniform mixture could affect the mechanical and physical properties by increasing

hardness, modulus and lowering of elasticity. Nevertheless, the amount of S/CB hybrid filler hardly affects the physical and mechanical properties of aged NR composites. The results suggest that the optimum amount of hybrid filler is suitable at 50 phr on the application of NR composites.

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The development in the innovation of the research-based instruction model in the curriculum development course for students of the teaching profession

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Abstract

The R&D research is aimed to: develop an instructional model: curriculum development course by using research-based learning for pre-service teachers. The four steps taken were 1) analyzing, 2) designing and developing, 3) trial, and 4) evaluation. The samples were 60 Thai-major students in the 1st year students from the Faculty of Education, Chaiyaphum Rajabhat University, while enrolled in the second semester of the academic year 2020 who were selected by using multistage random sampling. The research instrument were: 1) a curriculum development knowledge test; 2) an ability evaluation test on the performance of curriculum development. The statistics for the data analysis were percentages, mean, standard deviation, t-test dependent, and content analysis.

The results of this research were as follows:

1. The development of instructional model. The ALDRE Model which comprised : 1) Analyze needs for learning, 2) Learning planning, 3) Develop learning skill, 4) Reflect & knowledge summary and 5) Evaluate & apply. The result of the efficient criterion was 83.56/81.86
2. The differences of students' learning outcomes of students' knowledge before and after being taught by this model were statistically significant at the .01 level. The students' learning outcomes after instruction were higher than before the instruction.
3. The students' ability in project work as a whole is at a high level.

Keywords: Instructional model, research-based learning

Background and the Importance of the Problem

A new paradigm in tertiary education has focused on developing potential learners where knowledge is used to solve problems and to develop professional practices with quality. Higher Education Institute defining the vision and objectives of teaching and learning that in favor of such development has the conceptual framework for changing the critical teaching and learning paradigms that is to focus on the university of research by formulating a strategic plan for the development of higher education institution, which are summarized as follows (Committee of Higher Education, 2006);

- 1) Promote and support research strengthening
- 2) Promote and support teaching and learning excellence
- 3) Stimulate and develop the ability to participate in academic activities of those involved both inside

and outside the higher education institution.

- 4) Expand educational opportunities of the population in a higher education institution
- 5) Seek and develop opportunities for academic cooperation
- 6) Develop infrastructure that mainly facilitates and supports the academic objectives of higher education institutions
- 7) Increase the international role of higher education institutions

According to the goal of the educational strategy of higher education institutions, it has strengthened the connection between research and teaching which will result in higher quality education because it has the potential to use research to solve problems and improve the operation more effectively. The development of teaching and learning process in higher education institutions and educational management today

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have changed the teaching process from content-oriented to the balanced development of learners in all areas including knowledge and understanding of the subject content, professional practice skills, thinking process skills, problem-solving skills, morality and ethics and development of positive attitude towards the profession.

The development of instructional model in favor of the development of tertiary learners regarding the research-based learning styles, the research process and the learning process are related to higher education institutions that focus on research which will be an institution with outstanding contributions to knowledge creation and will focus on learning management based on research. This is based on the belief that the research process and learning process have common characteristics that are the creation of a culture of searching for knowledge which is the learning process of a person. The research is to gain experience in applying knowledge into practice to create new knowledge which is a process that helps develop the advanced intellectual skills of the researcher. Intellectual process and research process will help learners to develop their learning styles which will benefit the learners for their ability to learn both while studying and after graduation which will make them the learners with continuous learning skills (Ministry of Education, 2002)

Research-based learning management, research-based approach or research-based instruction learning management is a technique in creative teaching that focuses on developing learners to be more creative (Paitoon Sinlarat, 2014) because research is a human development process, especially in the development of researcher resulting the researcher to feel confident in asking questions, questioning, being knowledgeable and creative. Because research is to seek knowledge or to solve problems, the researcher must have initiatives in considering issues or information. The result of this action makes the researcher curious, energetic, rational, in making academic progress since the result of the research or the knowledge gained makes it possible to understand, predict or control the phenomenon while increasing the ability to solve problems (Somwang Phi-

thianuwat and Tassanee Boonterm, 1994). Therefore, research-based learning management should be the learning management that allows learners to learn and practice in seeking knowledge systematically and step by step making students find knowledge by themselves. Or in other words, it is a teaching and learning process that utilizes the research paradigm as a teaching process. The atmosphere of teaching and learning is organized in a way that allows students to use the research process or research results as a tool in learning the content. The research processing may be used to teach the content while the research results can be used as content for learning and the research process may be used for studying the content or allowing students to practice the research directly or to help train students' research skills (Thissna Khammanee, 2012; Paitoon Sinlarat, 2014). It is a teaching method that enables students to do their research so as they know how to solve problems, being analytical, and having skills in seeking knowledge by themselves. It is a learning method that supports the concepts of student-centered teaching and learning that focuses on students to directly search and discover for knowledge by themselves (Paitoon Sinlarat, 2014).

The researcher as a teacher encounters many problems that obstruct the learning the curriculum development subject because the researcher lacks student-centered learning management techniques, and the researcher acts on transferring knowledge to students instead of allowing them to practice. Most of the teaching methods are lectures, explanations through presentation programs while learning of curriculum development is a course that focuses on theoretical content where students need to have the foundation of curriculum, the design and curriculum development, and concentration when studying in the class. Besides, learners need to read more, exploring more additional knowledge, doing a lot of exercises. As a result, some students feel bored, not interested in the class, lack of enthusiasm for study, lack of responsibility in the work and submission of work, or learning productivity of students has poor quality, less cooperation in teaching and learning while they do not dare to express opinions nor

answering questions while studying and having a negative attitude in learning this course resulting effects on academic achievement. Due to these circumstances, it can be concluded that the students' behaviors do not support learning to their full capabilities. As a result, students have relatively low learning development with problems in learning, lack of problem-solving skills which should be developed to increase learning potential. However, problems in the classroom can be solved systematically along with learning management using Research-based Learning and Teaching approach according to the concept of Somwang Phithiyanuwat and Tassanee Boonterm, 1994; Paitoon Sinlarat, 2014) which state the teaching strategies or teaching and learning styles where teachers can use to make the research to involve in the teaching method which can be classified into 4 groups as follow ; Group 1: Research methodology as a teaching method for students to practice the research at various levels. Group 2: Having students to join a research project with a teacher or as a research assistant in the research work of a teacher. Group 3: Teaching by having students study the research of teachers and leading researchers in a particular field to learn what the frontier of knowledge in one's science. Learn how to solve problems, research results, the principles, and theories used in that research. Learn to apply research results and further research, and; Group 4 Teaching by using research results in teaching for the learners to know that what the current theory and new knowledge of their subjects are. And it is also to build faith for the students towards the teachers. Besides, teachers will have the opportunity to regularly change and develop their teaching methods to be up-to-date.

From the aforementioned reasons, the researcher, therefore, realizes the importance in the development of the research-base instructional model for the curriculum development course for students of the teaching profession with the objective in developing a research-based instructional model for curriculum development for students of the teaching profession and to study the effectiveness of the instructional model based on research. And this research is to encourage learners to acquire knowledge and basic skills for life-

long learning.

Research Objectives

1. To develop the research-based instructional model for the curriculum development course for students of the teaching profession to be 80/80 effective.

2. To study the effectiveness of the research-based instructional model for the curriculum development course for students of the teaching profession, as follows;

2.1 Comparison of knowledge in curriculum development before and after the implementation, according to the teaching and learning process, using research-based curriculum development for teachers.

2.2 Study the capability in developing the curriculum of schools during the instruction according to the learning using research-based curriculum development for teachers.

Hypothesis of the Research

In this research, the researcher assumes the research in the process of model development and the experiment of teaching and learning model as follows:

1. The research-based instructional model for the curriculum development course for students of the teaching profession is developed with the efficiency of 80/80

2. Knowledge regarding curriculum development of teachers before and after implementing research-based instructional model has the statistically significant difference at 0.01 level.

Scope of the Research

This study is the research and development where the scope of research is defined as follows;

1. Population and Sample

1.1 Population

The population in this research consists of 371 students of the teaching profession in the bachelor degree of Bachelor of Education program, Faculty of Education of Chaiyaphum Rajabhat University, the academic year 2019 from 7 programs including Science,

English, Computer, Early Childhood Education, Thai Language, Physical Education program, and Social studies programs.

1.2 Sample used in this research is the first-year students of the teaching profession, the Faculty of Education, Chaiyaphum Rajabhat University, in the semester 2 in the academic year of 2019, and the Multistage Random Sampling method is used for sampling as follows:

Step 1 A random selection for students from 1 of 7 subject areas obtains students from the Thai program.

Step 2 A random selection for a number of students from 2 groups in the Thai program obtains 30 students from 1 group.

2. Scope of Variable

Variables used in this research consist of

1.1 Independent variable is the research-based instructional model, "ALDRE model"

1.2 The dependent variables are;

1.2.1 Knowledge in course development of the curriculum development subject.

1.2.2 Capability to develop the school curriculum.

3. Research Process

3.1 Step 1 Research (R) Analysis (A), the researcher proceeds as follows

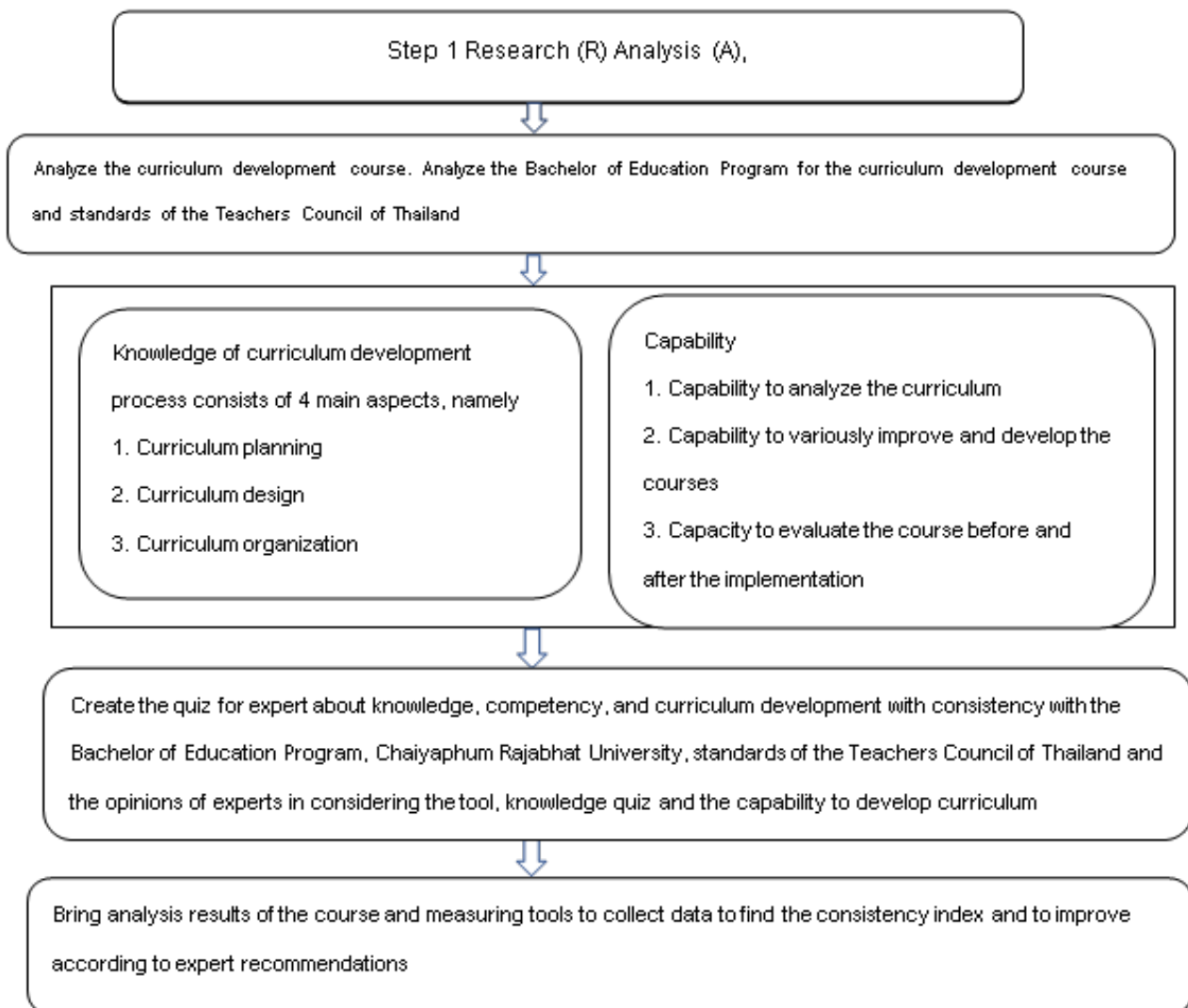


Figure1: Step 1 Research: R, Analysis: A

Step 2 Design and development of the research-based instructional model for the curriculum development course for students of the teaching profession (Design and Development), the researcher proceeds as follows

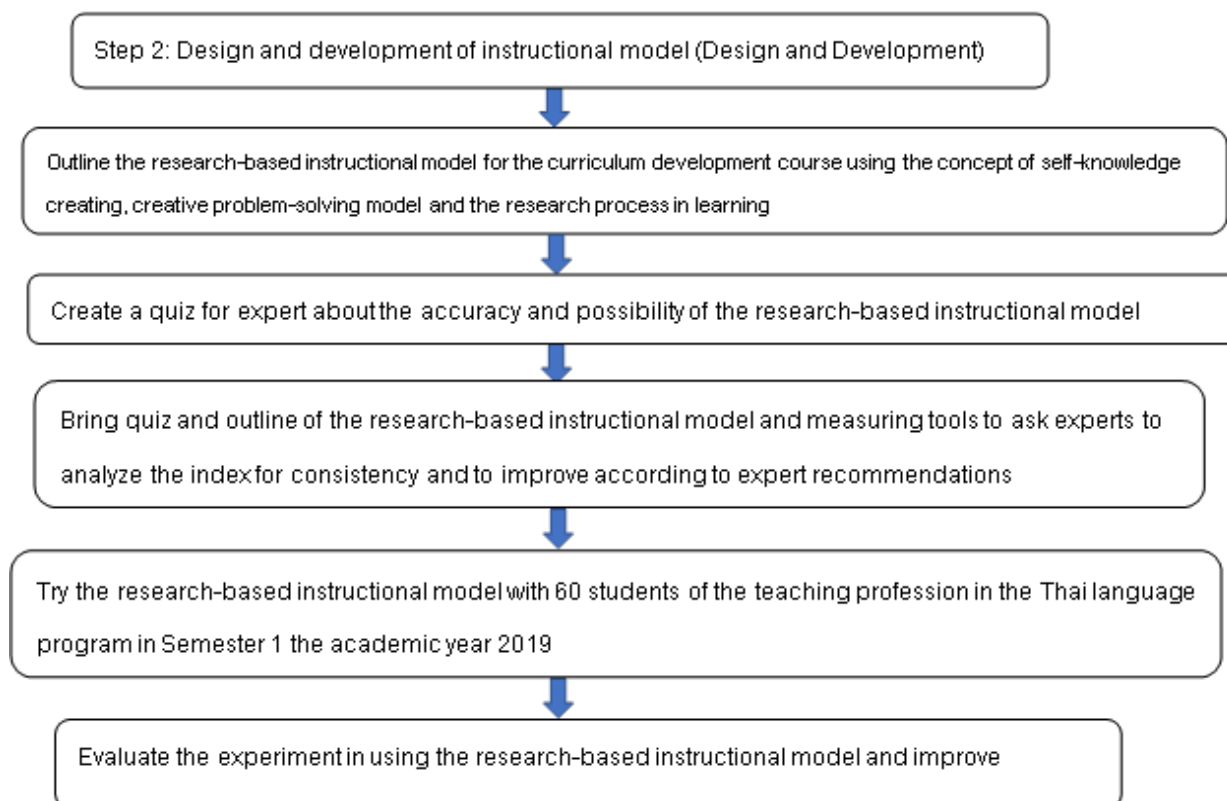


Figure 2 Design and development of the research-based instructional model for the curriculum development course for students of teaching profession (Design and Development)

Step 3 The implementation of developed instructional model (Implementation).

Research methodology.

This research is a pre-experimental research process conducted the 2nd semester of the academic year 2019, 16 weeks, 4 periods per week, during 13.00 - 17.00 hrs as follows

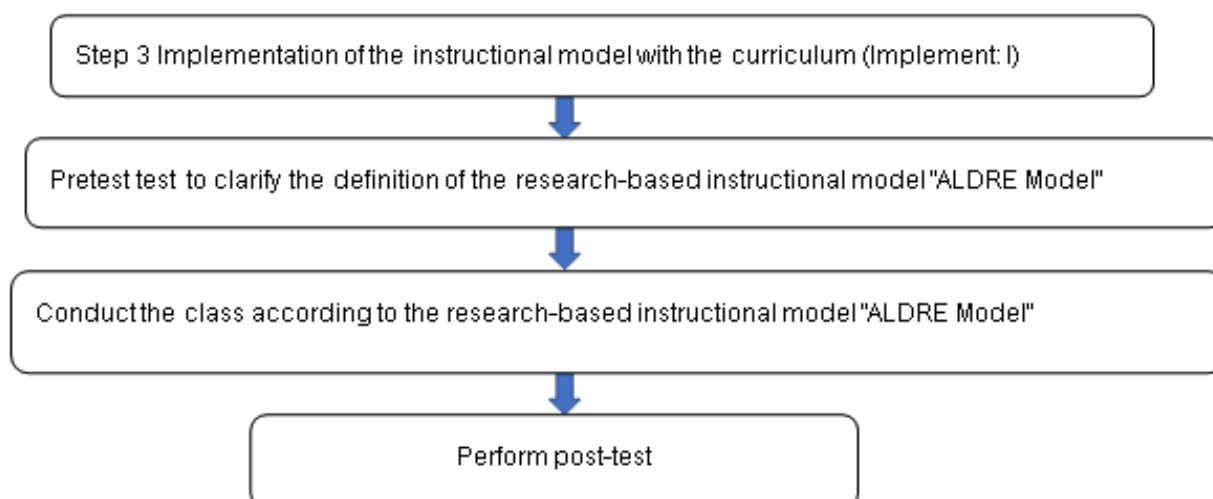


Figure 3: Step 3 Implementation

Step 4: Assessing the research-based instructional model "ALDRE Model" of the curriculum development course for students of the teaching profession (Evaluation: E) the researcher proceeds as follows

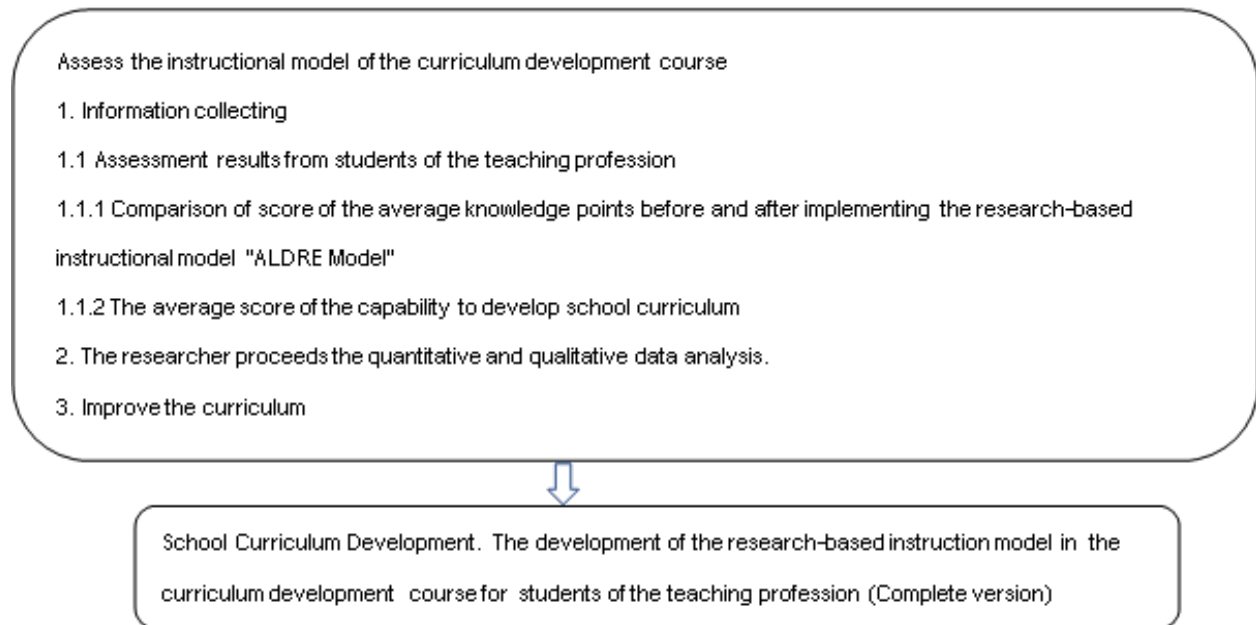


Figure 4 Assessment of the research-based instructional model "ALDRE Model" of the curriculum development course (Evaluation)

4. Tools used for research and data collection

Tools used in the research consist of

4.1 Learning Management Plan for the curriculum development for research-based learning management, "ALDRE Model" consisting of principles, objectives, content, teaching procedures, media/learning resources, measurement, and evaluation including supporting activities.

4.2 Quizzes to test the knowledge of curriculum development in the form of a 4-choice test totaling 40 items.

4.3 Assessment form for the curriculum development, a checklist for items that are graded according to rubric basis.

5. Data collection

The researcher collects data for study according to school curriculum development in the experiment process for the research-based instructional model, the curriculum development course for students of the teaching profession in actual condition by experimenting with pre-experimental research design

which consists of learning activities according to the research-based instructional model for students of the teaching profession called the ALDRE Model, as detailed in the following learning steps.

Step 1: Analyze learning needs to determine the learning objectives of the curriculum development subject and to define the objectives of the curriculum that students must develop.

Step 2: Learning planning: learners plan the learning by themselves, namely;

2.1 Defining self-development strategies or performing activities that help learners learn about the curriculum development process.

2.2 Build calendars and tools for monitoring and self-assessment.

Step 3: Develop learning skills

For the development of learning skills, students study by seeking and using learning resources both in a cooperative learning style and learning in cooperation, using various methods in learning and verifying knowledge related curriculum development process, as follows;

3.1 Finding and using learning resources

3.2 Using various methods for learning

3.3 Knowledge verification.

Step 4: Reflection and knowledge summarization

For reflection and summary of knowledge, teacher encourages students to explain concepts, the process of curriculum development using their language, asking about the evidence and clarity of the student's explanation that uses previous knowledge or previous experience of the student as a basis in explaining. As for knowledge critique, the teacher encourages the learners to expand their knowledge and understanding of the curriculum development process through new experiences. Students are encouraged to apply knowledge to adapt to real-life experiences through the curriculum development process.

Step 5: Evaluate & Apply

As for the assessment of knowledge and understanding, students are encouraged to assess their knowledge and capability, to assess learning progress and to evaluate the achievement of educational goals and students further apply their knowledge and understanding with the development of more new courses.

Data Collection

In this research, the researcher collects data to study the effectiveness of the research-based instructional model, "ALDRE Model" in the curriculum development course for students of the teaching profession as follows;

1. Conduct the test before studying using the test for curriculum development knowledge in the form of a 4-choice test with the sample students and collect data for further analysis

2. The researcher conducts learning management according to the learning management plan for the research-based curriculum management "ALDRE Model" for 16 weeks, 4 periods per week from 13.00 - 17.00 hrs.

3. Once the learning management is completed, perform the test for knowledge of curriculum development using a 4-choice test totaling 40 items, and then collect the data for further analysis.

4. The researcher uses all the obtained data to

analyze using the statistical method and process

6. Data Analysis and Statistics used in the research

6.1 Data derived from the knowledge test is analyzed to compare the values of the median, standard deviation, percentage, and T-test dependent samples

6.2 Data from the assessment of institutional curriculum development is evaluated using a Rubric Checklist for assessing the competency in developing the institutional curriculum into the following scores. 1 point refers to low capability, 2 points refer to middle capability, 3 points refer to a high level of capability.

7. Research Summary

7.1 As for the result of the research-based instructional development "ALDRE Model" for the curriculum development subject for students of teacher profession, the teaching and learning model development is conducted by analyzing for the curriculum development process, the description of curriculum development subject of Bachelor of Education program, Faculty of Education, Chaiyaphum Rajabhat University and the standard 2 of Teachers Council of Standards for the curriculum development. Curriculum development using the curriculum development process to develop into the research-based instructional model for the curriculum development subject for students of the teaching profession consists of 5 issues, namely; 1) Concept and theory about curriculum development 2) Curriculum planning 3) Curriculum design and development 4) Curriculum organization and 5) Curriculum evaluation. And the research-based instructional model for the curriculum development course for students of teacher profession consists of 5 steps as follows: 1) Analyze learning needs 2) Learning planning 3) Develop learning skills 4) Reflect & knowledge summary and 5) Evaluation & Apply, the results of this research reveal that the instructional model is developed with the efficiency of. 83.56 / 81.86 according to the first assumption

7.2 The effectiveness of the research-based instructional model, the results reveal that;

7.2.1 Knowledge of students before

and after learning following the research-based instructional "ALDRE Model" of the curriculum development course for students of the teaching profession, after the teaching, students have higher learning performance than before studying at the statistical significance level of .01, which is in accordance with the 2nd assumption.

7.2.2 The overall capability of students in curriculum development is at a very good level. For each step in the curriculum development consisting of the workload, the presentation, the self-assessment, and the operation according to the curriculum development process, the scores obtained are; 7 students obtain a low level, 14 students obtain a middle level, and 9 students obtain a higher level.

8. Discussion

8.1 The research-based instructional model for the curriculum development course for students of teacher profession ALDRE Model consists of 5 steps as follows:

1) Analyze learning needs 2) Learning planning 3) Develop learning skills 4) Reflect & knowledge summary and 5) Evaluation & Apply. The results of this research reveal that the developed instructional model has an efficiency of 83.56 / 81.86 according to the first assumption. However, this may be due to, firstly, the research-based instructional model for the curriculum development course for students of teacher profession is derived from the analysis in the essence of the curriculum development process that researcher applies the results of the course development program based on the concepts of Tyler (1949), Taba (1962), Saylor & Alexander (1981), Oliva (1992) and Wichai Wongyai (1980). It can be said that the research-based instructional model for the curriculum development course for students of teacher profession that the researcher has designed and developed can help gain knowledge and capability in completing the steps of curriculum development in accordance with the results that the researcher has studied in the curriculum planning model of Kember (2005) and then applied for the course which consists of 5 development processes, namely (1) fundamental data analysis (2) curriculum design (3) curriculum develop-

ment (4) curriculum implementation and (5) curriculum evaluation. In adopting the research-based instructional model for the curriculum development course for students of the teaching profession, it relies importantly on the student-centered instruction concept consisting of steps in learning by creating knowledge by oneself. The instructor encourages students to clarify the knowledge by searching for knowledge from several media both in the form of documents, books, journals, and web-based learning sources, then choose to receive and understand new information. In this process, students will summarize the knowledge into their knowledge and understand that knowledge. Then, students will review, revise, and use new knowledge to reflect and summarize knowledge. The instructor encourages students to expand their knowledge and understanding of the curriculum development process of students through new experiences. There is an evaluation of knowledge and understanding of learning. And students are encouraged to apply knowledge to adapt to real-life experiences through the curriculum development process, to be applied for further curriculum development.

8.2 Knowledge of students before and after learning following the research-based instructional "ALDRE Model" of the curriculum development course for students of the teaching profession, after the teaching, students have higher learning performance than before studying at the statistical significance level of .01, which is in accordance with the 2nd assumption. This may be due to the results that the research-based instructional model allows students to learn the essence of research topics including research design, to study quality research samples, reading the research work conducted from the actual condition of instructional management in the classroom, in schools and communities, applying the learning theory to instructional management, samples of research used in practice for guiding in organizing teaching and learning conditions that support linking between education, research and practice by bringing process and knowledge gained from the research into action and integrate the research process with learning management for use as media for students to learn about teaching to be consistent with the theory. In or-

ganizing instructional activities, the researcher designs to allow students to identify the problems of teachers' research, examine the importance of the problem, and find the answer that leads to the changing by searching for relevant research documents. Once students obtain the answers or guidelines, it will lead to the creation of tools used for learning management and measurement and evaluation of instructional management allowing students to practice good quality research, providing students the opportunity to brainstorm ideas for practical learning, focusing on group work. The teacher plays a facilitator role to monitor students to conduct learning activity smoothly encouraging students to be enthusiastic about their participation. This is consistent with the research results of Thanakhon Phuangkham and Ladda Sila Noi (2011) which found that academic achievement for History subject 2 gained from the research-based instructional management has an achievement score of 70 percent or higher. This is due to students follow the research-based instructional management and students search for information, being enthusiastic to learn, interested in group activities, gaining knowledge from direct experience, gain knowledge that is more permanent beyond memorization alone.

8.3 The overall capability of students in curriculum development is at a very good level. For each step in the curriculum development consisting of the workload, the presentation, the self-assessment, and the operation according to the curriculum development process, the scores obtained are; 7 students obtain a low level, 14 students obtain a middle level, and 9 students obtain a higher level. This may be due to the researcher has obtained the research-based instructional model for the curriculum development course for students of teacher profession that has been developed which has the essence according to the curriculum development process following the development process in 5 steps including (1) basic data analysis (2) curriculum design (3) curriculum development (4) curriculum implementation and (5) curriculum evaluation. This is consistent with Saylor & Alexander (1981) and Ornstien & Hunkins (1998) Since the researcher has tested the quality in accordance with the self-knowledge generation mod-

el (The Constructivist Learning Model (CLM) consisting of 3 steps which are 1) Clarify knowledge by searching for knowledge from various media in the form of documents, books, journals, and web-based learning, 2) Choose to receive and understand new information, and 3) Review, revise, and use new knowledge, such learning approach is consistent with Kember (2005) research that utilizes the curriculum planning model and instructional model of desired outcomes that focus on the mutual agreement in learning activities to achieve desired learning outcomes evaluated by the Student Engagement Project). And the researcher has studied documents related to curriculum development and course description according to the Standard 2 of the Teachers Council of Thailand standards for curriculum development course in the following aspects: 1) Philosophy, Theoretical Concepts of Education 2) Curriculum Theory 3) Curriculum Model 4) Curriculum Type 5) Fundamental Data of Curriculum Development 6) Design and Development of School Curriculum 7) Curriculum Implementation 8) Curriculum Assessment 9) Problems and Trends of Curriculum Development and in the aspect of capability as follows; 1) Capability to analyze courses 2) Capability to variously improve and develop the courses 3) Capability to evaluate the course before and after implementation 4) Capability to create school curriculum. And from attending activities, students learn together that helps to enhance knowledge and understanding even more. There is an exchange of knowledge from the presentations of each group, learning how to define issues from learned situations, being able to analyze issues, knowing how to find suitable methods to obtain the solution, capable to gather information from learning sources while interpreting data and summarizing the learning results to understand. This is the development of students' learning methods resulting in effective understanding and learning.

9. Suggestions

9.1 Suggestions in using research findings

9.1.1 For the effective implementation of the instructional model, teachers should be well prepared to plan activities following mutual learning characteris-

tics. And it should be an atmosphere of encouragement from one another which will make students more interested in studying. And in implementing the instructional model for schools, qualified personnel with knowledge and experience in conducting research must be provided along with the support that facilitates teaching and learning according to the instructional model. And the manual in using the instructional model for a teacher should be also provided that allows participated students to study and understand easily including the guideline for teachers to organize activities and to strengthen good attitudes towards using the instructional model

9.1.2 For the design of research-based learning activities at the tertiary level, the teacher should provide basic knowledge of the research process in the classroom before learning during the orientation so that learners can link to the content of the course. And for the design of measurement and evaluation in learning management, the assessment based on actual conditions should be provided to emphasize students to practice, using the scenarios of good quality research results, study from learning sources, collect data, summarize the result, and perform the presentation. In the assessment, students should be evaluated in many dimensions such as skills, knowledge, capability, thinking, and other characteristics. The methods used for assessment based on actual condition should be varied, in-

cluding observation, interviews, work inspections, student self-reporting.

9.1.3 In the research-based instructional management, the instructor should create a challenging atmosphere, stimulating and encouraging learners with curiosity to solve problems and find the answer. This is to encourage students to feel that they are capable of solving problems or doing activities. And the teacher should encourage them to do or respond including providing examples of success or what students have done before so as students to become confident in their capability and feel proud of themselves resulting in no fear of continuing to do other activities.

9.2 Suggestions for future research

9.2.1 The research and study for the research-based instructional model should be conducted along with the problem-based instructional model for curriculum development and other courses by allowing relevant people to participate since students have to spend time researching additional information outside the class hours.

9.2.2 The research on the research-based instructional model for the curriculum development course for students of the teaching profession should be conducted using other concepts such as online education development, development of subject formats in the form of e-learning, etc.

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Low-Cost Remote-Sensing-Node based on LoRa Mesh Network for Smart Agriculture

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Abstract

The advanced technology of the internet of things (IoT) is currently a low-cost and low power solution, and able to transmit data remotely, resulting in the transformation of traditional agriculture into smart agriculture. Therefore, this paper presents the development of low power and low-cost remote communication system based on the Heltec WiFi LoRa 32 microcontroller for smart agriculture. The proposed system divides into two parts: (i) the wireless network (Mesh network) is to communicate data between three sensor-nodes and server-node at a distance no more than 100 meters, (ii) the radio frequency signal at band 868.125 MHz on the device itself is to communicate between server-node and gateway that is far more than 500 meters. Then send data via the internet service provider (ISP) on the CloudMQTT to monitor the required data. The development of this remote communication system can apply to large-scale agriculture that is far from the ISP to know environmental data such as the temperature and humidity. The experiments determine the test area covering an area of 1,200 square meters. Discussions present the data of distances that can send data from the signal station (LoRa-Node-Server) to the receiving station (LoRa-Gateway) then send data via the ISP to the cloud server in another area, at 710 meters, especially.

Keywords: IoTs, LoRa, CloudMQTT, Heltec WiFi LoRa 32

I. INTRODUCTION

The internet of things (IoT) can help and allow monitoring of the information that submitted, as well as can control from anytime and anywhere in the world where the internet connected. The LoRa IoTs is quite a hot issue in many industries and agriculture like the smart city and smart farm. Large-scale agriculture has introduced many IoTs technology, depending on the application, especially the intelligent agriculture and the precision agriculture that has introduced IoTs technology. It depends entirely on communication between devices, allowing data to transmit and receive or transfer quickly. Cycleo (Slats, 2020) was developed the LoRa and released in 2012 as a non-licensed technology. While it is also considered as non-3rd Generation Partnership Project (3PPP) standard which is not the same as

NB-IoT, EC-GSM, etc. Recently, in Hayati & Suryanegara (2017)'s study was proposed the tracking and monitoring the patient with mental disorder by using LoRa as the main communication platform of devices which showed the feasibility of LoRa network performance, power of the battery and the scalability. In Huh & Kim (2019)' study analyzed LoRa-based mesh networks for IoT by a modified LoRaWan that supports mesh network and TEDS to detect the collision rate in the network. In Andrade & Yoo (2019)'s work presented the LoRa in field of smart city by analyzed the qualitative that carried out about the development of the smart city solutions such as transportation, health monitoring, and pollution level measurements. In Ray (2017);s study proposed a comprehensive review of IoT deployment for smart agriculture based agriculture framework to leverage full-fledged combination between agriculture and IoT. An

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IoT solution to control and manage irrigation proposed in Fernandez et al. (2019) that related to connectivity and energy availability in the rural areas. However, the challenges of LoRa for agriculture have many solutions led to a high reliability, low-cost and low power solutions either in terms of investment or operation. This paper presented low-cost remote-sensing-node based on LoRa mesh network for smart agriculture to measure temperature and relation humidity of soil and ambient on the crop area.

The paper consists of five sections. Section I is the introduction. Section II presents the overview of the system. Section III provides the proposed system design while Section IV discusses the evaluation of the proposed system. The conclusion and the future work show in Section V, respectively.

II. OVERVIEW OF THE SYSTEM

A. Heltec WiFi LoRa 32

The heltec WiFi LoRa 32 board shown in Figure 1, is recommended for this project due to its capability is adequate and lowest-cost for the price comparing with the other board devices. Furthermore, the board incorporates a 0.96-inch OLED display. Their features are CP2102 that includes USB to UART converter, Flash memory 32 MB, and Lithium battery charger, etc. The power supply for the Heltec WiFi LoRa 32 board is another important point in the design of equipment selection for this project. Must know, how much power the device needs? By considering (Fernandez et al., 2019) the needs of the board, can divide into three modes: (i) Running mode, microprocessor read sensor, (ii) transmitting mode, data sent to the controller or gateway. When

the data transmission process is complete, the device will select the operation to be in the low-power mode until it instructs to send it again. During this time, the device will be in (iii) Deep sleep mode. In this mode, the device's CPU, LoRa module and WiFi module will stop connecting.

Table I. The electric parameters for Running Mode, Transmitting Mode, and Sleeping Mode (Fernandez et al., 2019).

I_r (mA)	I_{tra} (mA)	I_{ds} (mA)	T_{tra} (sec)
50.1	71.7	11.9	0.2384

That are

- I_r = Running Mode Current (mA),
- I_{ta} = Transmitting Mode Average Current (mA),
- I_{ds} = Deep Sleep Mode Current (mA), and
- T_{tra} = Transmitting Time (sec).

B. Temperature & Humidity Sensors

There are many types of measuring devices or sensors using to measure the environmental factors, such as temperature and humidity, depending on the option in conjunction with the control equipment or controller. In this project, the sensor IC number SHT10 has used, considering the price and durability of the device to monitor temperature and humidity values. It can divide into two types according to the usage characteristics. Figure 2 shows the form of the waterproof encapsulating material container of the soil temperature and humidity sensor that can be measured both

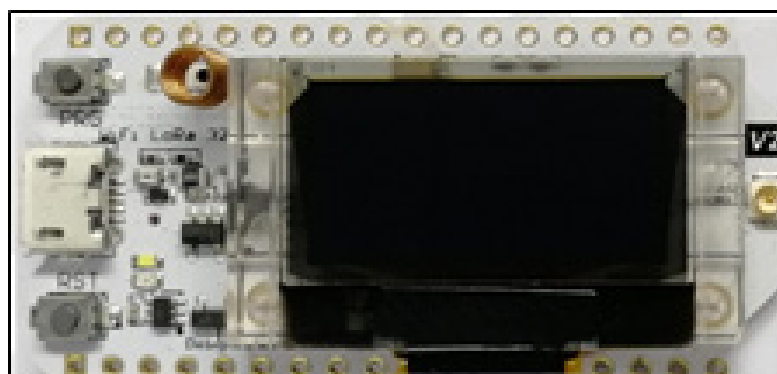


Figure 1. Heltec WiFi LoRa 32



Figure 2. The IC sensor number SHT10 encased with the waterproof metal container.



Figure 3. The IC sensor number SHT10 encased with the plastic container.

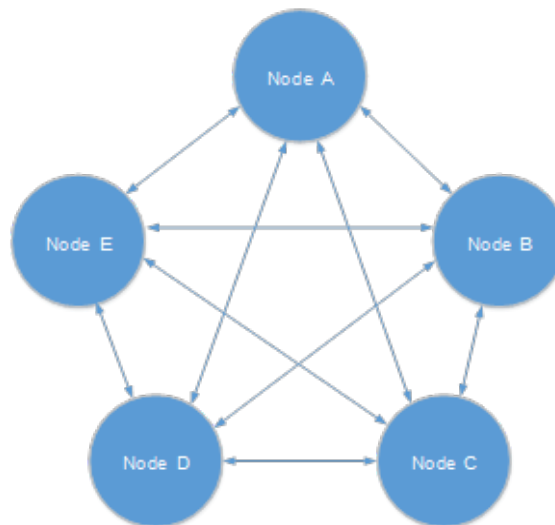


Figure 4. The Mesh Network

in ambient and in non-flooded soil. The SHT10 is in a plastic material container as shown in Figure 3. The SHT10 is a low-cost integrated sensor that measures relative humidity and ambient temperature. It provides the measurements using a proprietary two-wire serial communication protocol. The accuracy of relative humidity and ambient temperature provide $\pm 4.5\%RH$ between 0 and 100%RH and $\pm 0.5^{\circ}C$ between $-40^{\circ}C$ and $+123.8^{\circ}C$, respectively. The response time is 8 second of relative humidity and 5-30 second of ambient

temperature. The operating supply voltage is between 2.4 volts and 5.5 volts.

C. The Mesh Network (Huh & Kim, 2019)

A wireless network known as a mesh network protocol is using with the wide-area-network, in which communication is the path between data between all nodes and all other nodes, resulting in data routes. Multiple paths of the mesh network will safe from the occurrence of system failures, as shown in Figure 4. All node devices are both a data receiver and a data trans-

mitter.

III. THE PROPOSED SYSTEM DESIGN

The design and the programming of the remote-sensor-node connected with the LoRa-Gateway to bring data to MQTT Cloud Server and send to recipients. The details of the remote-sensor-node development project has shown in Figure 5.

- Determine three Sensor-nodes (Heltec WiFi LoRa 32+SHT10)
- Define one LoRa-server-node (Heltec WiFi LoRa 32)
- Set one LoRa-gateway (Heltec WiFi LoRa 32)
- Set Wi-Fi Router to connect data over the internet to MQTT Cloud Server

The project has considered an outdoor agriculture area of 1,200 square meters. This crop area is divide into three plots, each plot spanning 400 square meters. In agriculture, the soil and ambient environmental parameters play an important role in crop yield. The soil moisture and soil temperature sensors have used for measuring the soil parameters. Their parameters measured include relative humidity (%RH) and ambient temperature (°C). Each plot has only one sensor-node. Three node sensors interface with the LoRa-server-node based on the mesh network and then will send their

data to the LoRa-server-node, which will then upload their data by using the radio frequency, band 868.125 MHz to a LoRa-gateway through the internet to the Cloud MQTT server. The real-time hardware implementation of the network has discussed in the next section.

A. The SHT10 Sensor Deployment

The SHT10 encased with the two material containers have been chosen that encapsulated in a sintered metal enclosure protecting electronics from direct contact with water to measure temperature and humidity of soil. The SHT10 encased with the plastic container is used for measuring ambient. The proposed project measures four environmental parameters, namely soil temperature, soil relative humidity, ambient temperature and ambient relative humidity. The SHT10 is the sensor measuring the temperature and relative humidity, accurately and environmentally resistant. The deployment of the SHT10 divided into two features: (i) By using IC sensor number SHT10 contain in the encapsulated waterproof metal material as shown in Figure 2. (ii) By using the IC sensor number SHT10 contain in the plastic container as shown in Figure 3.

B. The Hardware Deployment

The proposed network for monitoring agriculture is consisted of the spatial distribute three sensor-nodes shown in Figure 6, and a LoRa node server based on the mesh network of wireless platform.

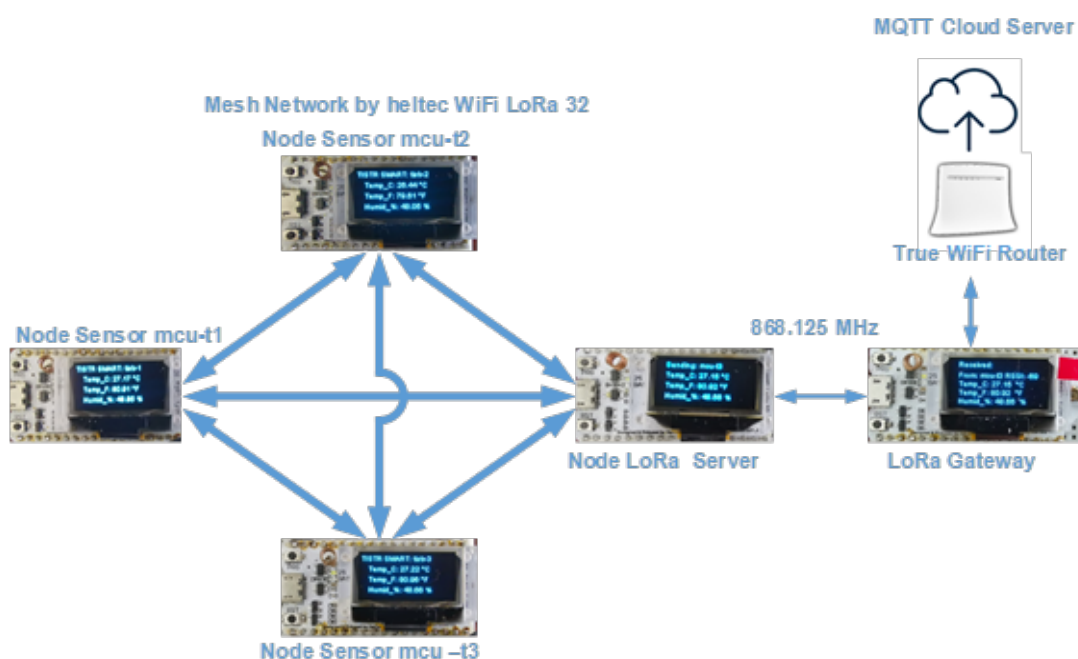


Figure 5. The Design of the Proposed System



Figure 6. Three Sensor-Nodes.

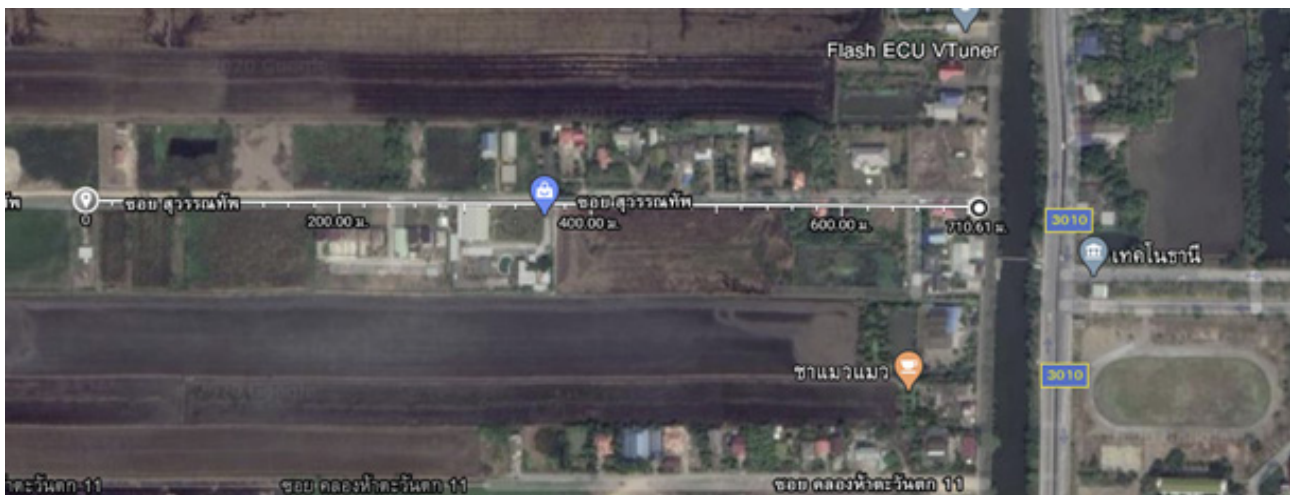


Figure 7. The devices installed in the crop area and data transmission distance.



Figure 8. The soil sensor-node deployed in the crop area.



Figure 9. The ambient sensor-node deployed in the crop area.

The sensor-nodes is a line of sight range of about 50 meters, which means that the sensor-node of transmission range covers the whole crop area and can easily reach the LoRa-server-node. The data of their sensor-nodes send via the mesh network protocol to the LoRa- server-node every 30 minutes and then go to the sleep state to conserve the power consumption. The LoRa-server-node is always on and transfers the collected data through the radio frequency band 868.125 MHz to the LoRa-Gateway, which then pushes the data to the internet into the cloud MQTT server with the help of the ISP True 4G Router. Since the experimental area is in a location without the ISP, the project is using the ISP True 4G Router to connect the node-LoRa-server to the internet. The LoRa-Gateway has powered on since it requires 7-12 volts' supply installed far from the crop area 710.61 meters, as shown in Figure 7. The soil sensor-node deployed in the crop area has shown as Figure 8, and the ambient sensor-node deploys in the crop area have shown as Figure 9, respectively.

IV. EVALUATION OF THE PROPOSED SYSTEMS

The evaluation of the proposed system presents low power, low-cost and long-range transmission data by measuring the power consumption, cost and the data transmission distance. In the following section

For evaluating, the power consumption of sensor-node has considered the electrical current. The

power consumption of sensor-node has included of the Heltec WiFi LoRa 32 board and SHT 10 sensor measured by FLUKE 289 TRUE RMS multimeter. The electrical current parameters of running mode (I_r), transmitting mode (I_{tra}), and deep sleep (I_{ds}) mode have shown in Table 2.

Table 2. The electric current parameters of sensor-node.

I_r (mA)	I_{tra} (mA)	I_{ds} (mA)
54.3	75.2	15.5

Next, the battery of sensor-node has used the alkali battery size AA, 1.5 volts, 3,000 mAh and 3 units. They connected in series to get a total of 4.5 volts. The formula for calculating the lifetime of the battery for sensor-node has the following:

$$\text{Battery Life} = \frac{\text{Battery Capacity in mAh}}{\text{LoadCurrent in mA}}$$

Running Mode;

$$\text{Battery Life} = \frac{3,000 \text{ mAh}}{54.3 \text{ mA}} = 55 \text{ Hrs } 24 \text{ Min}$$

Transmitting Mode;

$$\text{Battery Life} = \frac{3,000 \text{ mAh}}{75.2 \text{ mA}} = 39 \text{ Hrs } 8 \text{ Min}$$

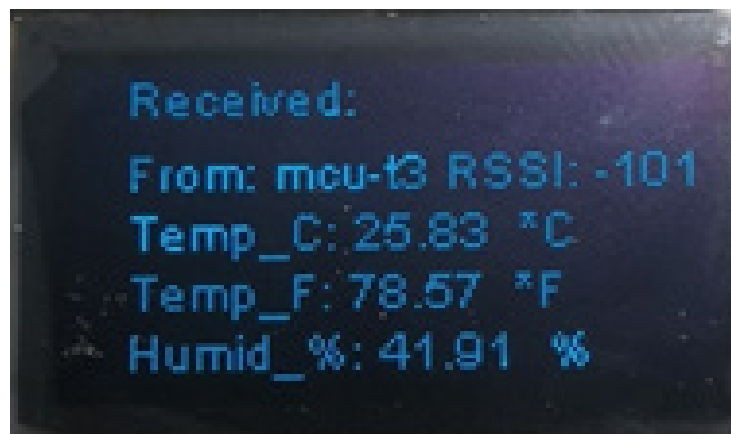


Figure 10. Show the received signal strength indicator (RSSI) of LoRa Gateway.

Deep Sleep Mode;

$$\text{Battery Life} = \frac{3,000 \text{ mAh}}{15.5 \text{ mA}} = 193 \text{ Hrs } 54 \text{ Min}$$

The maximum distance of data transmission has measured the line of sight about 850 meters from LoRa server-node to LoRa Gateway through the radio frequency band 868.125 MHz. The received signal strength indicator (RSSI) is -101 dBm as shown in Figure 10. According to the characteristic of the board, the best RSSI of the board is -98 dBm

V. CONCLUSION AND THE FUTURE RESEARCH

This paper presents the development of low power, low-cost and long-range communication systems with the Heltec Wi-Fi LoRa 32 microcontroller board and the SHT 10 sensor. The wireless frequency network design called Mesh network has used for data communication between each sensor-node and LoRa server-node. Then transmits a long-range communication by using the radio frequency band 868.125 MHz to enable remote communication devices between LoRa server-nodes and LoRa gateway. The development of this remote communication system can apply for large-scale agriculture that far from the internet, which needs to monitor environmental data such as temperature and humidity of soil and ambient. Specifically, the crop area for the test system, we install equipment consisting of sensor-nodes 1, 2, and 3, and install LoRa server-nodes covers 1,200 square meters of agricultural plot. The LoRa server-nodes can send data to the receiving

station (gateway) and transmit data through the internet service provider to the MQTT cloud server in other areas installed at a distance of 710 meters. According to the experimental results of the long-range transmission, using the radio frequency band 868.125 MHz, with the capability of the proposed system can transmit and receive data, clearly at a distance of 850 meters at the received signal strength indicator (RSSI): -101 dBm. All devices use the default IPEX antenna. The data transmission distance depends on the characteristics like transmitted power, and the type of antenna.

The future work will develop the antenna to enable the devices to transmit signals farther than the original server-node or may change the gateway by using LoRa WAN Gateway RAK831+Raspberry Pi 3 hardware, which can support more devices. Moreover, develop web applications or a Dash Board on a smartphone to monitor various environmental data. Finally, it will be the electrical system for the node devices by using solar cells to charge a battery, which can recharge so that the equipment can use at all times.

VI. ACKNOWLEDGEMENT

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Design and Analysis of Low Speed Multi-Blades Wind Turbine with Compressed Air Energy Storage (Part 1) – Design of Low Speed Multi-Blades Wind Turbine

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Abstract

The objective of this research is to study the electricity generation system using the low-wind speed multi-blade (30 blades) wind turbine and the system used a reciprocating compressor (piston compressor) to store the wind energy. Wind energy are the general energy sources in nature with infinite energy that can generate electricity. With the limitation of wind speed performance in Thailand (less than 6 m/s.), supplementary of air compressor has been included for electricity production using low speed wind turbine. This research study is aimed to design and fabricate an electricity generator by using the technology implementation in the country for the purpose of price reduction and less parts importation from the other countries. Then, the numerical analysis from CFD is decided to discuss on its performance adaptation for low speed wind turbine especially in the southern region of the country. Under this particular research work, a guideline is used to conserve and protect the environment and also suitably adjusted the equipment for the country.

Keywords: Design, Analysis, Low speed wind turbine, Multi-blades, CFD Analysis

1. Introduction

Since Thailand suffers from electricity energy crisis, Thailand imports all energy sources from other countries with values not less than 1,000,000 million baht per year and it tends to be increased continuously. With this reason, it causes the production capital and operational costs to increase in all regions of the country. Thailand consumes energy about 1.4 times of the growth of economy of the country. In other words, if the economy increased 5%, the energy consumption increased by 7%. It can be seen that energy consumption of Thailand is higher than the developed countries. Therefore, the production capital in The country is high-cost, also, the unstable of internal energy policy in the country had been affected on the project investment of renewable energy. However, the government has been set up the policy to support the incremental use of the renewable energy in the country such as solar energy, biomass, wind energy, and municipal waste.

Comparison between alternative energy and fuel energy, technically the use of alternative energy provides more energy, is easily moved and cost-effective for users. As for energy production, alternative energy production is cheaper than the fuel energy production including transportation and management (Kaldellis et al., 2017). Solar energy, geothermal energy, wind energy are the general energy sources in nature with infinite energy, thus they are classed as green energy that can generate electricity (Department of Alternative Energy Development and Efficiency Ministry of Energy, 2003). From the study the wind performance in Thailand, it was found that many areas of Thailand (92.6%) have average wind speeds of less than 6 m/s as shown in Table 1 which is at the very low end of wind speeds and it is not suitable for electricity production using wind turbines for high electric energy [HVDC/HVAV] (Lemofouset, 2003). With the limitation of wind speed performance in Thailand, which has low wind speed,

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the energy management processes for electricity production using low wind speed and air compressor shall supplementally be included (Palasai et al., 2010). Wind energy always changes in both amplitude and direction so a wind turbine is used to produce electricity in areas which have high-speed wind and it can result in higher electrical current (Lemofouset, 2003; JIA et al., 2004; Palasai et al., 2010). However, wind energy has the limitation in inconstant wind speeds and thus, it requires many techniques to store the energy for more benefits: especially, to respond to the user need to store daily the left-over energy.

Therefore, in this research study is aimed to design and fabricate an electricity generator using the multi-blade wind turbine (30 blades) by using the tech-

nology implemented in the country to reduce price and imports from the other countries. After design the multi-blades wind turbine prototype, CFD analysis before fabrication is decided to discuss on its performance adaptation for low speed wind velocity of the country.

II. Material and Method

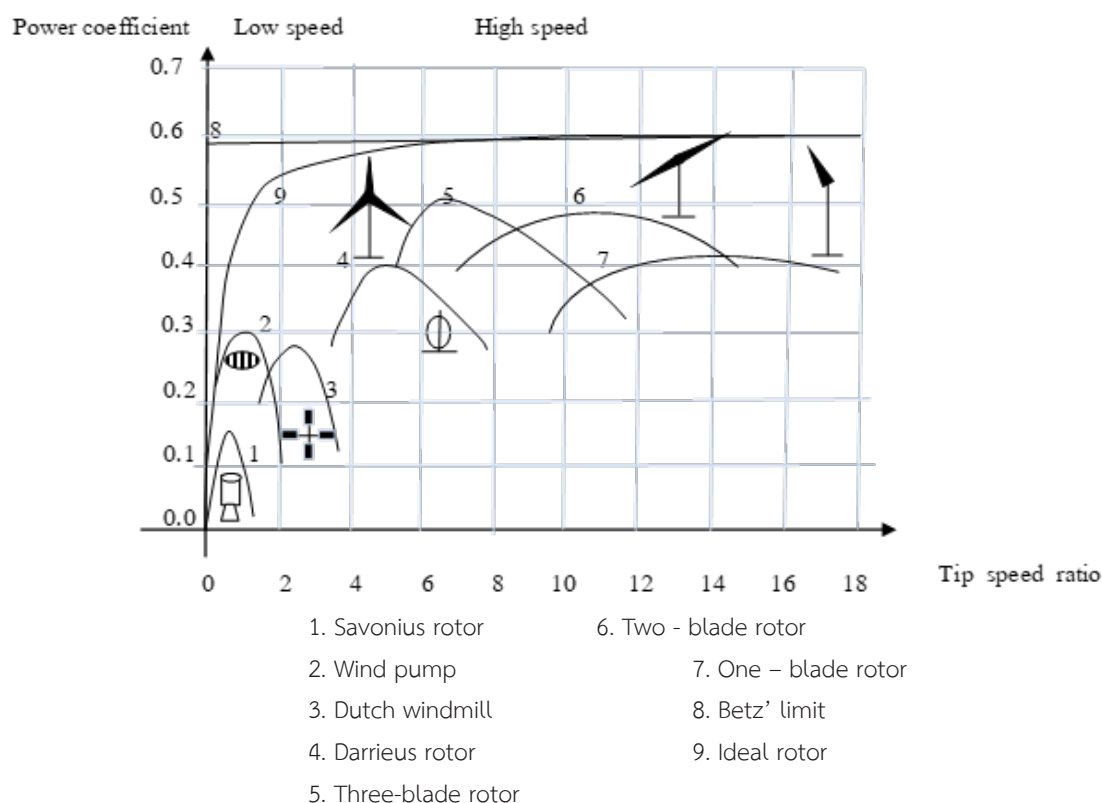
1. Design of low speed multi-blades wind turbine with compressed air energy storage

The application of the CAES is to produce electricity using a multi-blades turbine. The 30 blades turbine is chosen since it meets with the wind turbine standard for water pumping that are widely used in Thailand and it is suitable for wind-speeds less than 6 m/s.

Table 1. Wind speed in Thailand at the height of 65 m.

Average wind speed and characteristic	Poor (< 6 m/s)	Fair (6-7 m/s)	Good (7-8 m/s)	Very Good (8-9 m/s)	Excellent (>9 m/s)
Land area (sq.km)	477,157	37,337	748	13	0
% of Total land area	92.6	7.2	0.2	0	0
M W potential	N A	149,348	2,992	52	0

Table 2 Results of parameters affecting the power coefficient.



According to previous studies, it was found that the use of a multi-blades turbine can provide more torque, as shown in Table, 2 which is suitable for the low-wind speeds of Thailand. The energy storage for this compressed air is very small and provides very low compressed air. This is consistent with low wind speeds and therefore the turbine can spin continuously and constantly. The compressed air from the compressed air tank is passed to a compressed air generator to generate the electricity and connected to the power line of the Provincial Electricity Authority of Thailand (PEA). The PEA has funded and supported the compressed air energy storage using low speed multi-blade wind turbines in Thailand which is similar to this topic.

The electricity generation system using the multi-blade wind turbine has the concept as follows: it will store the compressed air while the turbine is spun. The axle of turbine is connected to a piston and it functions to pump air into the compressed air tank. Once the tank is full, the valve is opened with a suitable pres-

sure and the air is then transmitted to drive another piston in which its shaft is connected to the generator to supply the AC electricity to the distributed power line of PEA. Such systems can accumulate the wind energy for all wind speed that can drive the turbine to spin. The storage in the form of compressed air is low in the operation and maintenance costs with a long-term life time (20-30 years) which is longer than a battery life time (3-5 years). This research studies can create the prototype of the electricity storage system using a multi-blade turbine (30 blades) to compress the air in a low wind speed environment. The researchers selected the compressed air system with pressure less than 7 bar which is standard for compressed air storage and accumulate energy in the compressed air tank to produce the electricity as shown in Fig. 1. The experimental and calculated results of the performance and efficiencies of each system are compared with those in the laboratory as shown in Fig. 2.

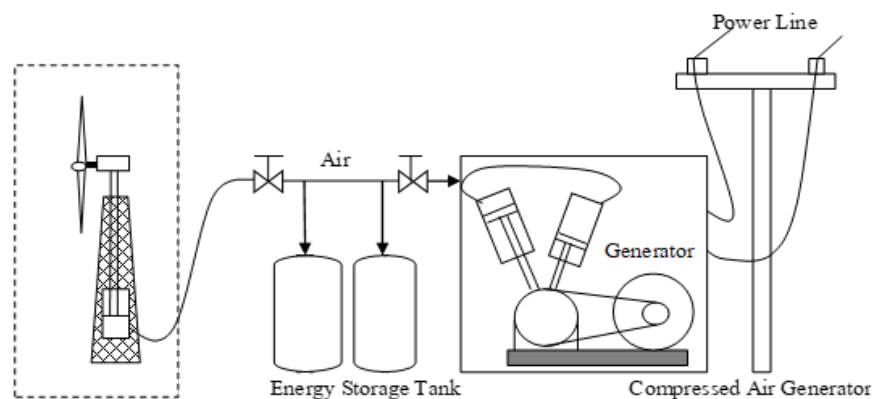


Figure 1. Electricity Generation System using Multi-blades Turbine and Compressed Air Storage

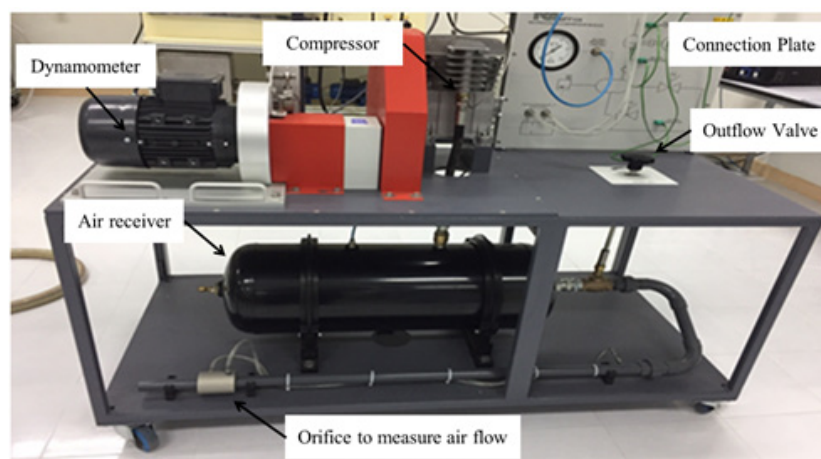


Figure 2. Laboratory test set for measuring the compressed air system using piston (The motor is used to replace the wind turbine)

2. Design and fabrication of multi-blades wind turbine prototype for compressed air

The guideline to use the wind energy at highest efficiency of this research (As shown in Fig. 3) focuses on the design of the turbine to be suitable for air compression and for areas of installation of the turbine. The wind turbine can produce energy if the wind speed is not too high or too low. Once the turbine is stopped, the rotor cannot produce energy. It is important to find the proper wind speed to obtain the maximum power.

$$\text{Power coefficient } C_P = \frac{P}{\frac{1}{2}\rho AV^3}$$

$$\text{Torque coefficient } C_Q = \frac{Q}{\frac{1}{2}\rho AV^2 R}$$

3. Analysis of low speed multi-blades wind turbine

As a results, the design before calculating by Computational Fluid Dynamics, CFD has been shown in Fig. 4.

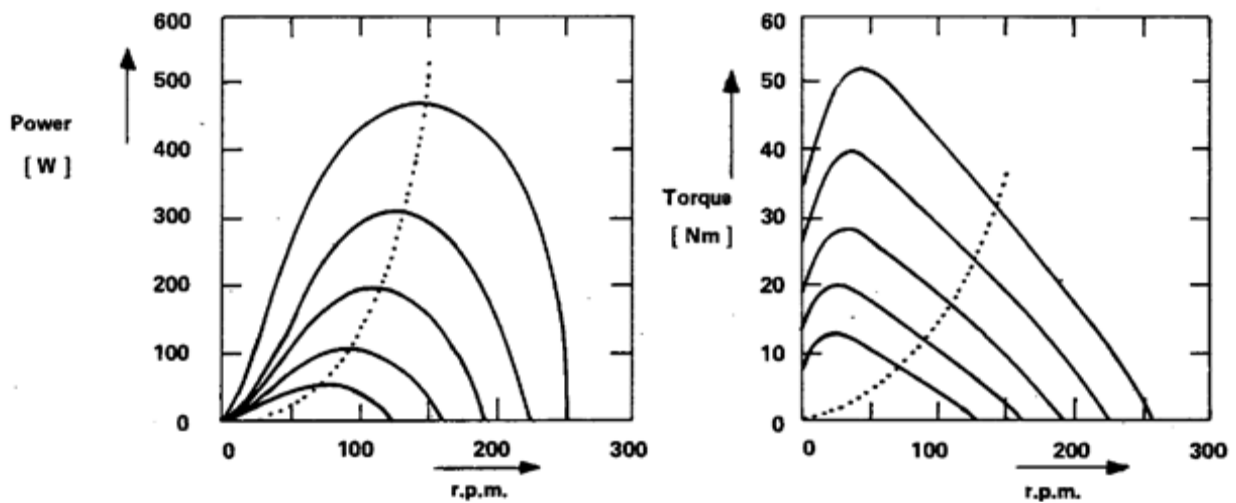


Figure 3. Relationship between the power and torque of rotor at different wind speed

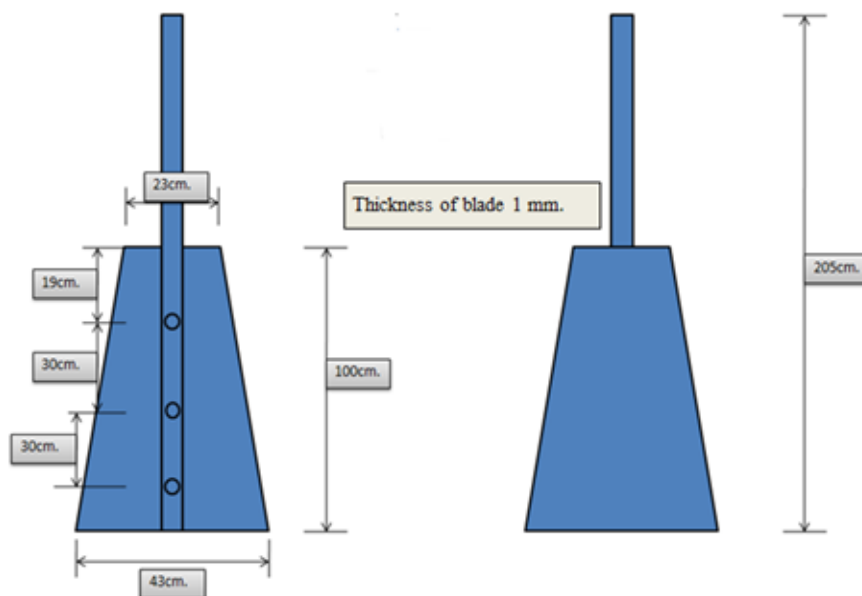


Figure 4. Shapes and dimensions of multi-blades wind turbine

The model has been designed and engineered by using the CFD including with the momentum theory verification. as follow:

Blade materials = Flat plate; Blade radius = 2.75 m. ; Number of blades = 30 ;

Wind turbine = Non twist blade ; Cut in wind speed = none ; Cut out wind speed = none

III. Result and discussion

1. Analysis simulation vector of low speed multi-blades wind turbine

Fig. 5 shows a model for numerical analysis. ANSYS FLUENT V.15 was used to study the behavior of air flow through a multi-rotor wind turbine by defining the conditions of the wind speed of 2-5 m/s. Under this particular studies, the results show the effects of power and torque and also the algorithms used in the calculation are SIMPLEC (Semi-Implicit Method for

Pressure Linked Equations-Consistent) and turbulence models $k-\epsilon$, which are commonly used in turbine flow calculations due to their less resources and high accuracy. The condition will stop at the error value below $1.0E-5$. And the inlet boundary condition is defined as the velocity inlet with uniform wind velocity across the cross-section. While the back will be the outlet of the pressure (pressure outlet). The model mesh is set to rotate around the center of rotation (Turbine Axis). The grids near the surface are optimized to increase computation accuracy. For the case of a displacement effect in the boundary layer, the $y+$ value of the turbine surface in the case of a 5 m / s wind speed is controlled to be less than 10 m/s. Then, the number of grids of the entire model become 6.5 million.

Figs. 6 and 7 show the behavior of the inlet air flow and the back of the turbine at wind speed of 2 m/s. The velocity vector shows the spinning of air as it

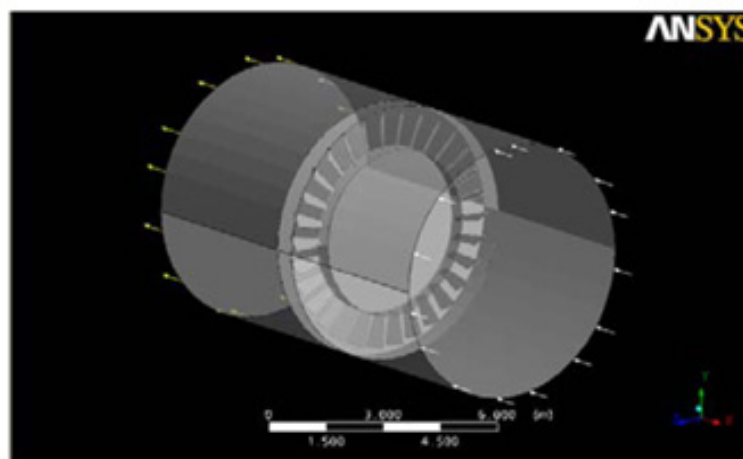


Figure 5. Simulation of multi-blades turbine in wind tunnel

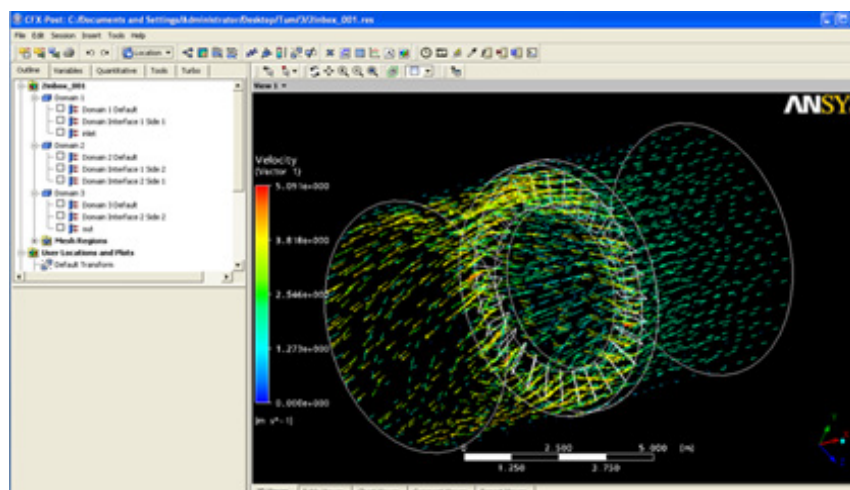


Figure 6. Vector of wind speed of 2 m/s

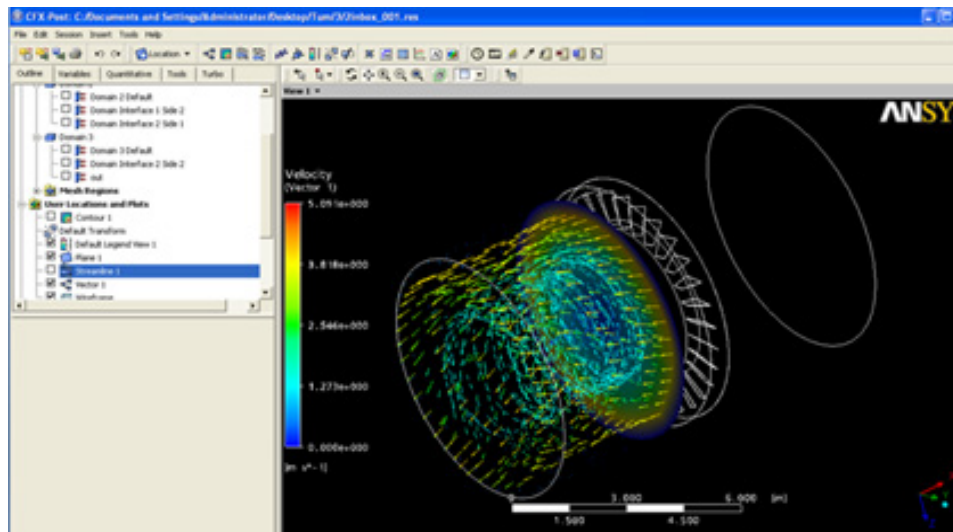


Figure 7. Vector of the back of the wind turbine at wind speed of 2 m/s



Figure 8. Installation of the multi-blade wind turbine

flows through a turbine. Then, the impact of the flow against the turbine blades affects the direction of the axial air flow sides due to the installation of the turbine blades with torsional angles. The turbulence flow will occur at the rear even after passing through the turbine. But the intensity of the turbulence is reduced, which is observed from the vector orientation that has begun to align the flow to the axis again. Then, the fabrication and installation of the multi-blades wind turbine has been done as shown in Fig. 8.

2. Analysis Results

Fig. 9 shows the relationship between torque and rotational speed of a multi-blades turbine. From the simulation with wind speed conditions in the range

of 2-5 m /s, the results of the study showed that the correlation lines in each velocity were similar. And the torque increases with the the increasing of the rotational speed within 4 rpm. And also at the rotational speed of 4 rpm, the torque is maximal in all wind speed conditions and decreases continuously with the increasing of wind speed. The decreasing rate of torque after the initial peak is higher than the range of higher rotational speed. Under this study, the rotational speed range at the maximum torque value has been corresponded to the wind speed where the maximum speed condition is 5 m /s. Then the multi-blades turbine is able to generate 3100 N.m of torque.

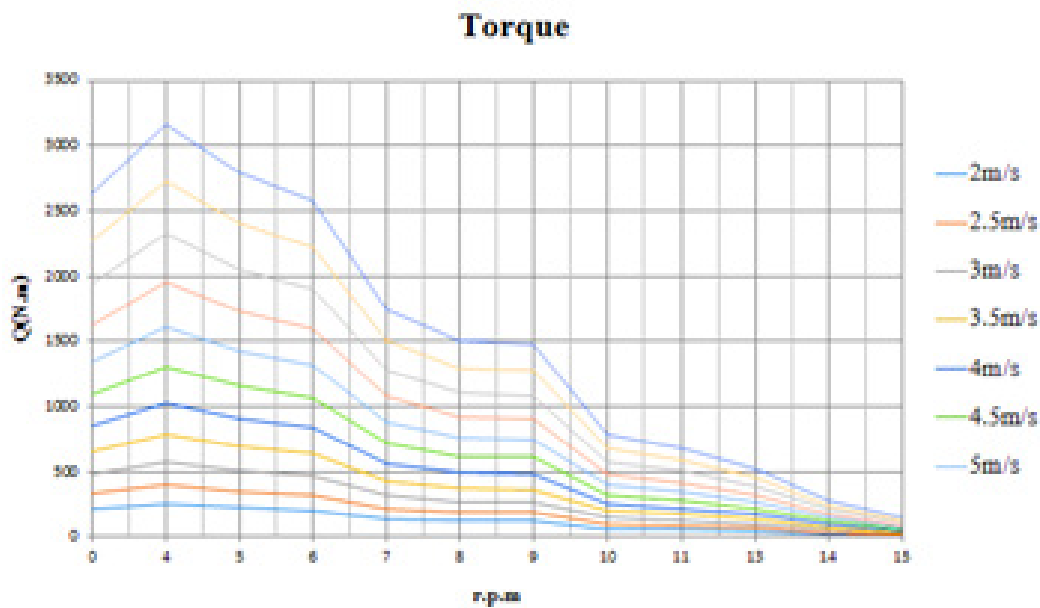


Figure 9. Torque of multi-rotor blades Turbine

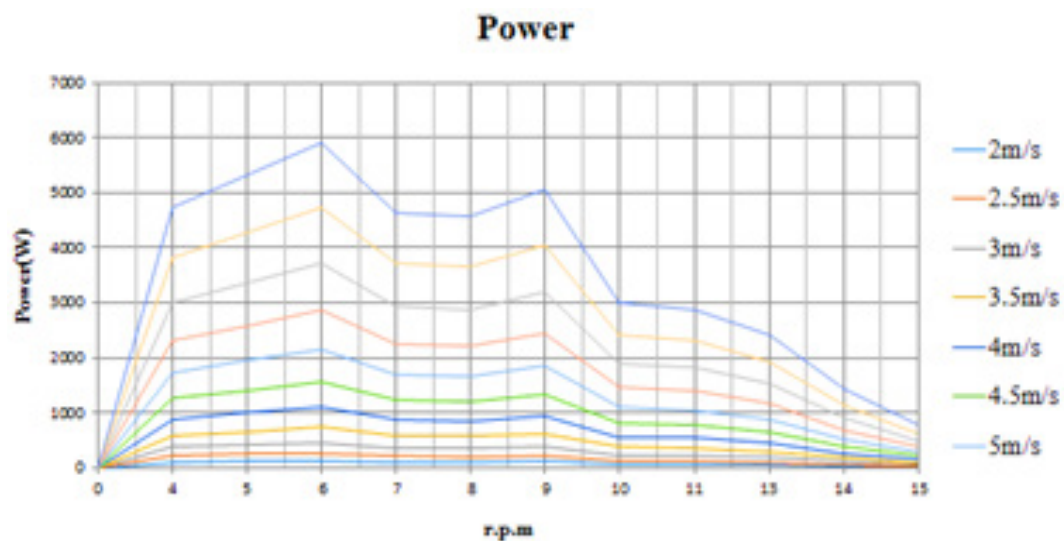


Figure 10. Power from multi-blade Turbine

Fig. 10 shows the relationship between power and speed of a multi-blades turbine in the range of 2-5 m /s wind speed. From the study, it was found that the relative speed of each speed was similar to the results of torque. But the maximum power will occur at a higher rotational speed at 6 rpm. A turbine with a higher wind speed has a greater maximum power. And the reduction rate of the power after the initial peak is less than the range of the higher rotational speed.

Fig. 11 shows the comparison between torque and turbine power at the wind speed conditions of 5 m

/s which is a condition in which the turbine has maximum torque and power. The comparison results will determine the optimal rotational speed in the multi-blades turbine applications due to the torque and power peaks occur at the different rotational speeds. The optimal turbine speed in this study was 5.2 rpm. which is in the range of the maximum torque and power of the multi-blades turbine. At this rotational speed, the torque and power of the multi-blades turbine has been reduced from the max value of xx and yy percent respectively.

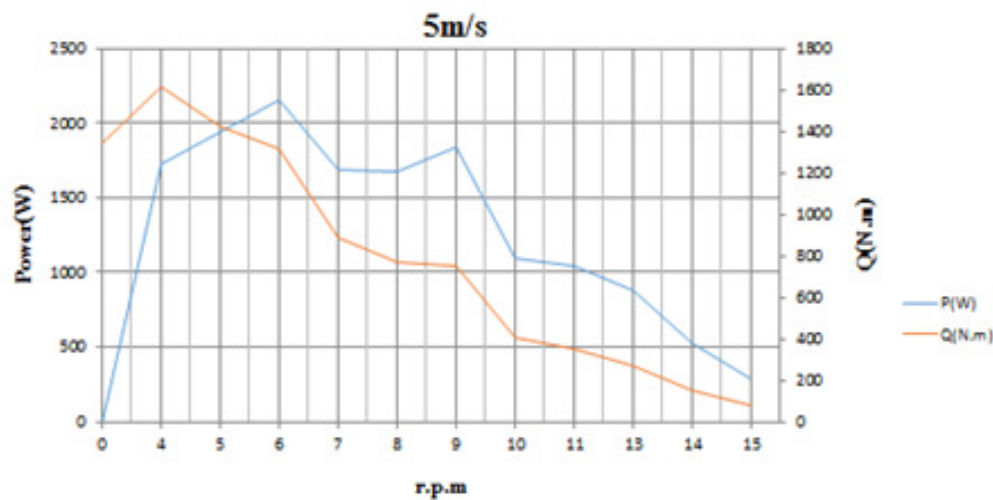


Figure 11. Simulation results at wind speed of 5m/s

IV. Conclusion

The study results of the electricity generator using the multi-blade turbine (30 blades) and air compressor to store the wind energy using a piston are shown a model for numerical analysis by defining the conditions of the wind speed of 2-5 m/s. Under this particular studies, the effects of power, torque and also the algorithms used in the calculation are SIMPLEC and turbulence models k- ϵ , which are commonly used in turbine flow calculations. The correlation lines between torque and rotational speed of a multi-blades turbine in each velocity were similar. And also the torque increases with the the increasing of the rotational speed and at the rotational speed of 4 rpm, the torque is maximal in all wind speed conditions and decreases continuously with the increasing of wind speed. For the case of the

relationship between power and speed of a multi-blade wind turbine in the range of 2-5 m/s wind speed, the maximum power will occur at a higher rotational speed at 6 rpm. And the optimal rotational speed in the multi-blades wind turbine applications in this research study was 5.2 rpm which is in the range of the maximum torque and power.

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The author wishes to express their gratitude to the staff members of Department of Mechanical Engineering, Faculty of Engineering, Princess of Naradhiwas University for fabricating implements and conducting the research experiment and to Strategic Scholarships Fellowships Frontier Research Networks (Specific for Southern region) for support the grant research.

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Development of Drying Process Combining Hot Air with Drying Cyclone for High Moisture Content Materials

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Abstract

This research presented the drying method which combined flowing hot air with drying cyclone for continuous production process development. Drying products are focused on the crushed durian peel to use as raw material in Carboxymethyl cellulose production and shredded coconut to offer alternative method instead the conventional production, which roasted by hot pan. An experimental was conducted from designed and fabricated drying process system, which employed centrifugal blower to generate air flow and electric heater as a heat source. Continuous feeding rate of fresh durian peel and coconut was maintained at 200 g/min, and 15 rounds of feeding have been tested. Air temperatures at 70°C, 80°C, and 90°C and air velocities at 25.7 m/s, 32 m/s, and 38 m/s were tested. Experimental results founded that air temperature enhancement had more influenced on the rounds feeding than those air velocity factor. For temperature at 90°C and velocity at 38 m/s, drying rate represented the highest value. All experimental results could be concluded that the proposed development method that employed hot air with drying cyclone had an ability to dry the durian peel and to roast coconut as continuous production instead the convention method.

Keywords: Carboxymethyl Cellulose, Drying durian peel, Roasted coconut production, Processed coconut, Drying

1. Introduction

One of the most impact to the world environment is a plastic pollution. Finding new raw material to reduce the plastic use is an interest solution. Organic matter, i.e. by produce from fruit product industrial seem to be a good chance, especially for southernmost of Thailand. Processing of synthetic durian peel into Carboxymethyl cellulose, CMC is promising and interesting. This is because it can be used as a raw material for many products, creating packaging for agricultural products in the Thailand's southernmost province, or OTOP products. Therefore, it is expedient to grow business opportunities or upgrade to small businesses or SMEs (Petpradub, 2018).

However, the process to create a raw material from durian peel synthesis for obtaining CMC from conventional drying process was found that the pro-

cess was costly and time-consuming. To give the process more practical to extend to industrial possibility, becoming mass product process, the study to obtain the method for preparing the drying durian peels, which have high moisture content, in sufficient product rate was important.

Phosee et al. (2013) studied the effect of the drying hot air at 55, 65 and 75 °C to the drying characteristic of mint leaves. The result shown that the temperatures at 55 °C presented the most suitable color of the mint leaves. But, at 75 °C, the minimum drying time was received, having three times lower than the temperature of 55 °C case. As a result of this study, the temperature level had a significant effect on the drying time. According to the study of Pintana et al. (2016), the study was focused on the effect of hot air to local product rice cracker drying rate. It was found that the tem-

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perature and hot air velocity were the most important parameters on drying time. The characteristic of the reducing rate of moisture content at the beginning shown that the rate was higher than that last period. The relationship between the remaining of moisture content and time corresponded to the quadratic polynomial relation. Wisaiprom et al. (2018) experimented that the effect of relative low humidity of drying air, which was maintained the range of 35-55%, to the shrimp drying process by deploying hot air at 40, 50 and 60 °C was focused. The tests shown that the hot air at 60 °C gave the lowest drying time, which was equal to 150 min. and 13.51% (d.b) of remaining moisture content.

Literature reviews as mentioned above can be concluded that drying system by employing the hot air is widely used for drying application of various products. Then, the aim of this study is to experiment the use of hot air combining with drying cyclone to introduce alternative method of the drying system. The test products are durian peel and crushed coconut to study the drying characteristic of difference initial moisture content to extend the understanding of presented drying system and to introduce the drying method that can develop to be continuous process.

II. Study procedure and data processing

2.1 Experimental set-up

Fig.1 represents vital details of the experimen-

tal set-up of drying system that conjugates hot air with cyclone. The hot air is supplied from centrifugal type blower, which is powered by a 5.5 kW DC motor. At the blower inlet, 180 mm dia. (D_1) and 900 mm long pipe with expanded entry cross section including with pack of 10 mm dia. tubes and 100 mm long insertion at the entrance region to regulate the streamline is installed to use as the velocity measurement portion. at the distance 300 mm prior the blower inlet, the uppermost portion of the pipe was drilled to allow to insert the velocity measurement tool probe. Velocity magnitudes along vertical direction with increment of 10 mm for each position were measured by employing the hot wire anemometry, Extech® model SDL350 having 0.2-25 m/s range of measurement and $\pm 5\%$ accuracy from reading value.

The 3 velocity profiles as shown in Fig.2 were adopted to calculate the average air velocity on the discharge side by estimating from equation (1) as continuous flow without leak at the blower.

$$V_{1,avg} = \frac{\sum_{i=0}^{17} V_i}{18} \quad (1)$$

Then, average air velocities at discharge side ($V_{2,avg}$), using 83 mm dia. pipe (D_2), were obtained by calculating from equation (2).

$$V_{2,avg} = V_{1,avg} (D_1^2 / D_2^2) \quad (2)$$

Then, the average velocities of 25.7 m/s, 32 m/s and 38 m/s were obtained according to the suction side

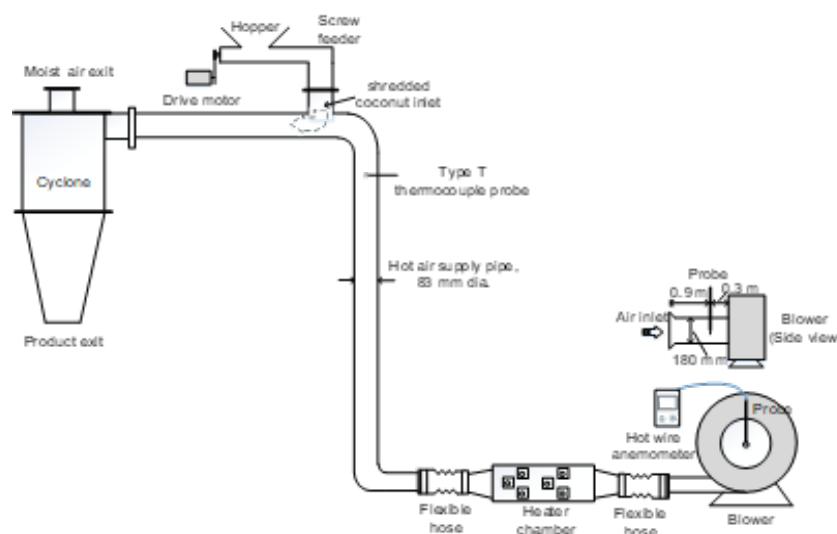


Figure 1. Experimental set-up of drying system combining hot air and drying cyclone

velocities of 4.3 m/s, 5.5 m/s and 6.8 m/s ($V_{1,avg}$), respectively. Flow conditions on both sides by representing from Reynold number, $Re = V_{1,avg} D / \nu$, base on pipe diameter D and velocity average were shown in the Table 1. Kinematic viscosity, ν , was chooses at 27°C and 80°C for suction and discharge sides, respectively. Discharged air flows through the heater chamber, having 6x1,000 W, to heat up for accelerating the moisture transfer from the product. The PID control unit with T type thermocouple was employs to measure the air temperature locates prior the exit of product, which is conveyed from screw feeder driving by adjustable speed DC motor to maintain 200 g/min feed rate. The temperature of hot air was controlled at 70°C, 80°C, and 90°C for study the effect of temperature to drying characteristics. After hot air and the product collision at exit of product, the air dragged the product by shear fore effect into the drying cyclone. Due to the geometry of the cyclone as shown in the Fig. 3, occurrence of the swirling flow induces the product to rotate along the cyclone wall while descent

to the product exit at the bottom.

2.2 Experiment

Crushed durian peel and crushed coconut as shown in the Fig. 1 for drying products was reparation as the raw product was used to study the drying characteristic when employed fabricated drying system. Drying products for 1 kg were load in a hopper that closed with the firm lid for preventing higher pressure of the hot air leaking to ambient air. Subsequently, screw feeder, which was driven by adjustable speed DC motor, was constantly fed into discharge pipe at the rate of 200 g/min. The product after interacting with hot air was dragged along hot air flow into drying cyclone by shear force of high velocity air flow. Effect of cyclone geometry led the both incoming fluid and product to be rotated movement while product decent to the product exit, which connect to the collecting product bottle. So, the hot air with moisture was forced to flow out from the exit at uppermost section of the cyclone.

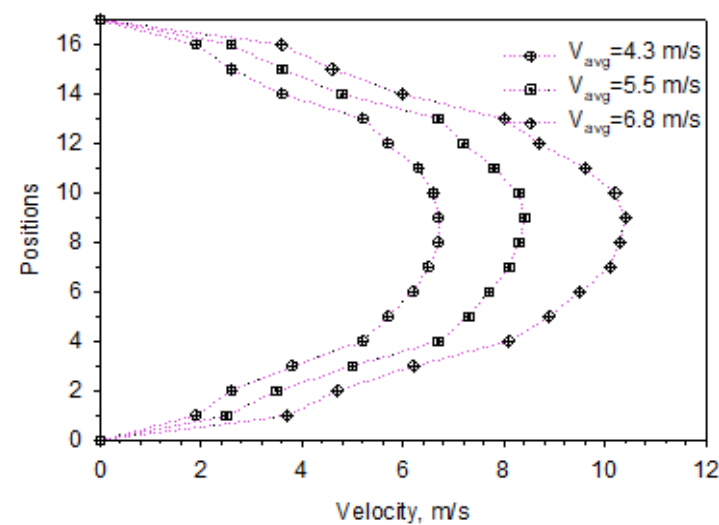


Figure 2. Velocity profiles in the suction side along tube centerline for calculating average velocity

Table 1. Reynold number base on pipe diameter and velocity average on the both sides of blower

$V_{1,avg}$	$V_{2,avg}$	R_e	
		Suction side	Discharge side
4.3	25.7	48,266	227,004
5.5	32	61,736	290,354
6.8	38	76,328	358,983

2.3 Moisture content examination

Moisture content decrease of the product after drying for each round was determined by the difference of net moisture content between pre-drying and post-drying product. Product example from the drying process with amount of 20 g of each round drying by using digital scale (SHIMADZU Model TW3202L) which has ± 0.002 g linearity was measured before making complete dry by using electric oven for 24 hours at 70°C. Then, weights of pre-drying and post-drying product were compared to examine the decrease of moisture for each round of drying. The present study limited the maximum round of drying at 15 for each product. Moisture content for bet basis can calculate according to the eq. (3).

$$\text{Moisture content} = \frac{w-d}{w} \times 100\%, \% (\text{wb}) \quad (3)$$

Where w was product wet weight before drying and d referred to the dry weight after drying with oven.

III. Results and discussion

Experimental results of the drying product of durian peel product are categorized into 3 topics; 1. effect of hot air temperature 2. effect of hot air velocity and 3. physical of dried product for each round of drying.

3.1 Effect of hot air temperature

Fig.3 shows drying characteristic of durian peel that is affected from hot air temperature. This experiment maintains air velocity at 38 m/s. Preferable air temperatures at 70°C, 80°C, and 90 °C are studied in order to avoid burning the product and still productively accelerate the moisture removal from product.

The air temperature has an important effect on the drying characteristic of durian peel. Pre-test moisture of the durian peel in the range of $82.1 \pm 1.7\%$ by weight gradually decreases after finishing for each round. Rate of drying for higher air temperature exhibits clearly faster of moisture removal than the lower especially at the beginning of the test. For first 7 rounds from start, linear relationship between moisture content and round of drying is observed. At the lower air temperature condition, moisture content presents lower drying

rate according to the tested temperature level which can notice from gradient of curves. After passing the linear section, lower drying rate is obtained from this section before reaching the constant drying rate condition. The pattern of drying rate is quite similar for all temperature levels but show difference the drying rate. As higher temperature level has better ability to remove the moisture from product, the test at 90°C reaches the constant condition at first after finishing 13 rounds of drying with residual of moisture content of 1.9 percent. After finishing 15 rounds of drying, residual of moisture contents shows that 80°C and 70°C conditions cannot reach the constant condition.

Fig.4 presents the effect of the hot air velocity with constant temperature of 90°C to drying characteristic of crushed coconut. The product has an initial moisture content of $50.2 \pm 1.3\%$. Drying characteristic at the beginning of the test shows that the drying rate has higher than the later round. Enhancement of the air temperature can accelerate the moisture removal from the product. Then, round of drying before reaching the constant moisture constant state can be reduced to compare to the lower air temperature condition. To compare with the durian peel, the results exhibit that all of 3 levels of air temperature can reduce the residual moisture content into constant state within 15 rounds of drying because the crushed coconut has a considerably lower initial moisture content. The case of 90°C is the lowest drying rounds which needs only 8 rounds of drying before going to constant state.

3.2 Effect of hot air velocity

Fig.5 shows the effect of hot air velocity to the drying characteristic of durian peel by investigating at 25.7 m/s, 32 m/s, and 38 m/s while air temperature is set at 90°C.

Decreasing rate of moisture content at the beginning of the 3 velocities obviously shows that the air velocity is also impact parameter to the moisture removal ability of the drying system. Nevertheless, in the case of velocity equal to 25.7 m/s and 32 m/s exhibit that residual moisture content after completing 15 rounds of drying cannot reach to the moisture constant condition. To compare with the case of shredded coco-

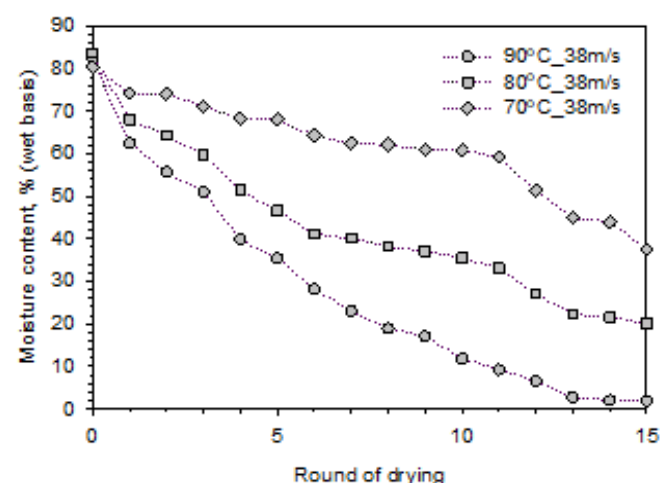


Figure 3. Effect of drying temperature, 70°C, 80°C, and 90°C, to the drying characteristic of durian peel at constant hot air velocity of 38 m/s

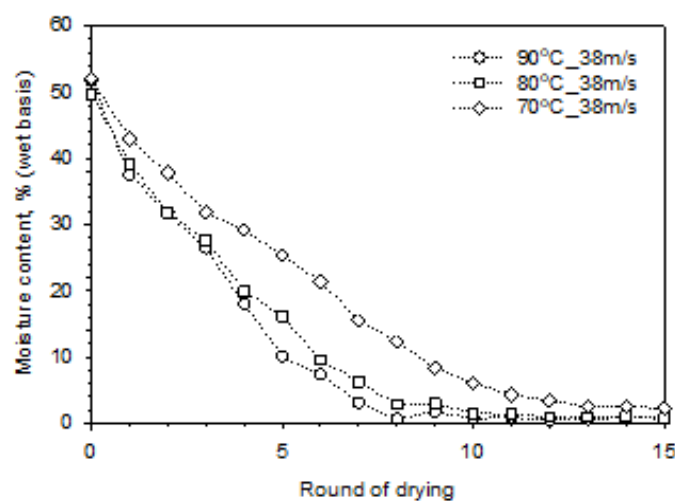


Figure 4. Effect of drying temperature, 70°C, 80°C, and 90°C, to the drying characteristic of crushed coconut at constant hot air velocity of 38 m/s

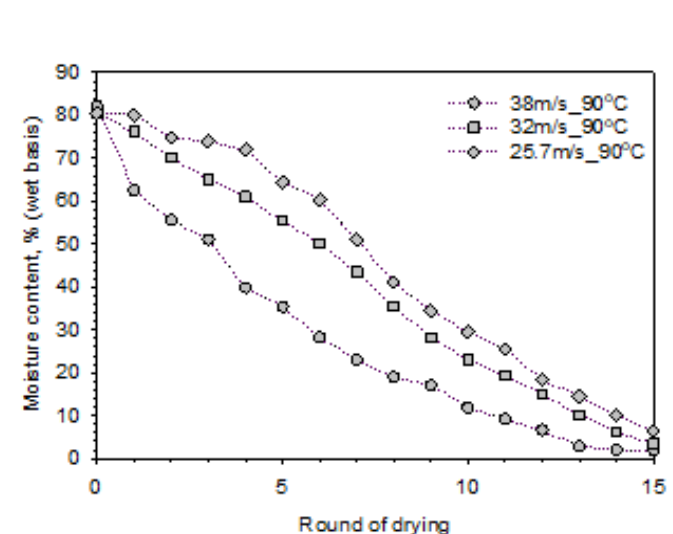


Figure 5. Effect of hot air velocities, 25.7 m/s, 32 m/s and 38 m/s, to drying characteristics of durian peel at constant hot air temperature, 90°C

nut which has less initial moisture content, the result in Fig. 6 shows that the residual moisture content at the beginning of all 3 levels of air velocity are similar. In the case of 32 m/s and 38 m/s, there is a tendency for the moisture to remain almost constant when entering the 8 and 10 cycles respectively. From the above results, it shows that the case of shredded coconut drying requires wind speed. 32 m/s can be dried to a constant humidity of less than 15 cycles, which is different from the case of durian rind that requires only 38 m/s.

IV. Physical characteristics

Fig. 7 shows that the dried durian peel examples are obtained from each round of drying. Due to relatively high of initial moisture content, the characteristics before drying characterizes as sticky material. After feeding few rounds, the durian peel starts to crumble and shows the fibers more clearly. Decreasing of the

moisture can be overserved visually. For the first three rounds, it is found that drying process has few affects to the color changing.

Fig. 8 presents dried coconut after finishing 15 rounds of drying. For hot air condition of 90°C with 25.7 m/s, 32 m/s, and 38 m/s, color intensity and grain sizing of crushed coconut are similar. Comparing to the roasted coconut from the local market, Narathiwat province, Thailand, shows that the texture is quite difference. The cause could be explained by the remaining moisture making color lighter than absent moisture product from the market. Finer grain of roasted coconut from market clearly observes because roasting in hot pan promotes the coconut movement resulting to reduce sizing of the grain by chaotic crushing from stir process while presented process utilized moisture transfer from product to moving hot air technic, leading to low crushing opportunity between grains and container wall.

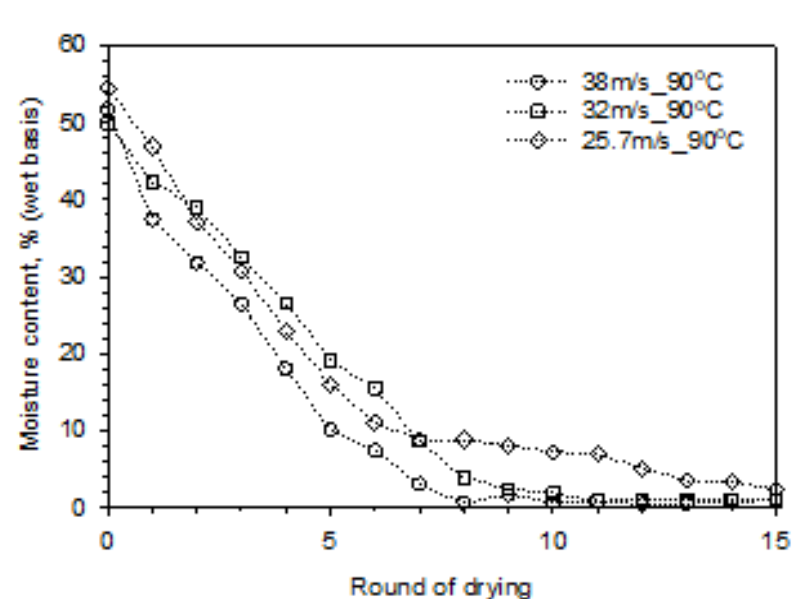


Figure 7. Effect of hot air velocities, 25.7 m/s, 32 m/s and 38 m/s, to drying characteristics of crushed coconut at constant hot air temperature, 90°C

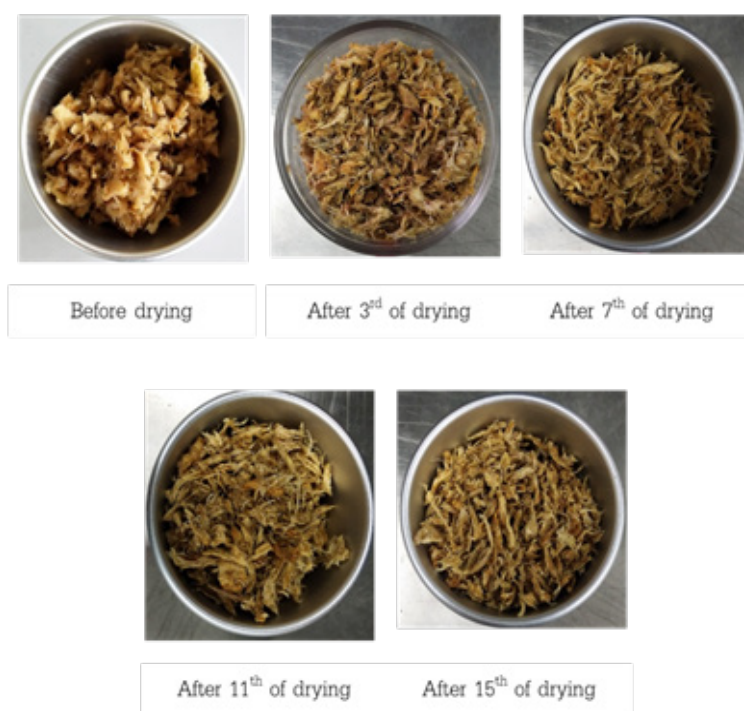


Figure 7. Physical characteristics of durian according round of drying

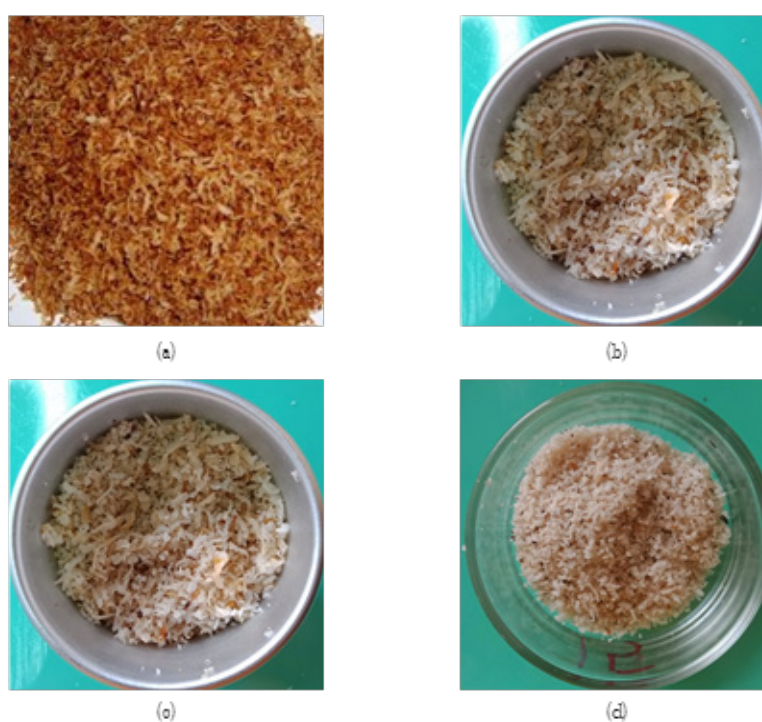


Figure 8. Comparison of the crushed coconut drying products for various velocity levels to selling product from local market in Narathiwat province; (a) product from local market (b) 25.7 m/s (c) 32 m/s and (c) 38 m/s at 90°C

V. Conclusion

The present study intended the results of hot air drying with drying cyclone for preparing of dried durian peel in the process of transforming durian peel into Carboxymethyl cellulose and drying of drying shredded coconut for developing a continuous roasted coconut production process. The results of the experiment can be summarized as follows.

1. rying system that was developed by using hot air with drying cyclone has the potential to be used for drying durian peel and shredded coconut as it can reduce the humidity until moisture content reached a constant remaining state. And it can be applied to a continuous process by connecting cyclones equal to the required number of drying cycles.

2. Durian peel drying requires a higher temperature and hot air velocity than that of coconut due to higher initial moisture content. To consider the same drying conditions, temperature and hot air velocity), round of drying of coconut is less than that of the durian peel.

Acknowledgement

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Antimicrobial Activities and Metal Chelation Ability of New Water-Soluble Chitosan Derivatives Having N-carboxymethyl Groups

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Abstract

In this article, novel aminoamine grafted chitosans containing hyperbranched-N-carboxymethyl groups are synthesized, characterized and tested for their potential usage. The synthesis is achieved by, using a commercially available chitosan with known chemical conversions. Two successive steps, Michael addition of amino groups to methyl acrylates followed by amidation with ethylenediamine, are repeated to generate hyperbranched chitosans. Subsequent connection of N-carboxymethyl groups to the synthesized hyperbranched chitosans led to the modified chitosans containing hyperbranched-N-carboxymethyl groups. These novel modified chitosans are characterized by FTIR-UATR (Fourier transform infrared-universal attenuated total reflectance) and ¹³C CP/MAS (¹³C Cross polarization/magic angle spinning). The modified chitosans show significantly improved water solubility which is a highly desirable property for some applications, compared to the original chitosan. The antimicrobial activity test showed that the modified chitosans display higher efficiency for antimicrobial activity against *Staphylococcus aureus* ATCC 29213, *Micrococcus luteus* ATCC 10240 and *Shewanella putrefaciens* ATCC 8071 compared to the original chitosan. ICP-MS (inductively coupled plasma-mass spectrometer) analyses are used to confirm that these modified chitosans have superior affinity to chelate heavy metals, compared to the unmodified starting chitosan. These modified chitosans are considered high potential utilities for human life and environmental concern.

Keywords: Antimicrobial activity, Chitosan, Hyperbranched polymer, Metal chelation

Introduction

Chitosan is a natural polymer obtained by deacetylation of chitin, the second most abundant polysaccharide exists in nature. Chitosan is the main component found in exoskeleton of crustaceans such as crab and shrimp. It was also found in the cell walls of many fungi and yeast, and in the cuticles of insects (Song et al., 2018). Chitosan consists of repeating units of anhydro-N-acetyl-D-glucosamine and anhydro-D-glucosamine; the latter has higher proportion as shown in Figure 1.

Chitosan draw a lot of attentions of many research groups because of its unique properties, especially its non-toxicity, biocompatibility, and biodegradability

(Sashiwa et al., 2003; Xing et al., 2005). Due to chitosan ability to chelate with metals using its free amine and primary and secondary hydroxyl groups, one potential application of chitosan is in water treatment (Ahmad et al., 2015; Qu et al., 2008). In addition, chitosan and its derivatives have been found to have antimicrobial activity (Goy et al., 2016; Mourya et al., 2008). However, the natural chitosan is only soluble in organic acids like acetic or formic acids which make its utilization quite limited. Fortunately, due to the presence of free active amino groups in chitosan, chemical modifications seem to be approachable means to overcome the solubility issue (Sashiwa et al., 2004; Baumann et al., 2001).

Dendrimers have attracted considerable attention due to their highly branched characteristics that

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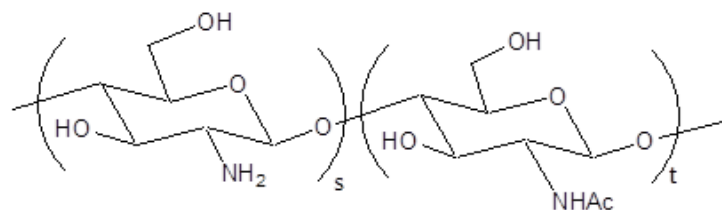


Figure1. Chitosan ($s > t$)

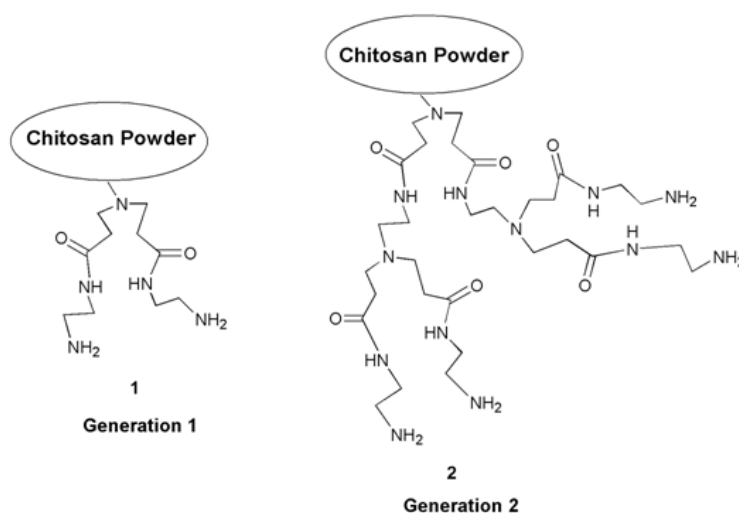


Figure2. Polyamidoamine dendrimer grafted chitosan powder.

can be modified to change their physical and electronic properties (Fréchet, 2003). As such, one could potentially modify chitosan with dendrimers to alter both dendrimer and chitosan properties. Chitosan-dendrimer hybrids were found to possess better water-soluble properties than the unmodified chitosan (Chanthatay-anonth et al., 2010; Sashiwa et al., 2002). Polyamidoamine dendrimer can be successfully grafted on chitosan powder (Tsubokawa et al., 2000). (Figure 2)

In this work, we report an uncomplicated method for synthesizing aminoamine grafted chitosan containing hyperbranched-N-carboxymethyl groups with improved water solubility (Figure 3). The antimicrobial activity of these new modified chitosan and metal chelation ability were investigated, compared to the unmodified chitosan.

Experimental procedure

All chemicals, purchased from Fluka Chemical and Sigma-Aldrich companies were used as received. Low molecular weight chitosan was obtained from Flu-

ka Chemical (degree of deacetylation = 72%, M_n = 150 kD) and Sigma-Aldrich (degree of deacetylation = > 85%, M_n = 50 kD) companies. Compounds 1 and 2 were prepared following the method described in the literature (Tsubokawa et al., 2000). All reactions were performed under a dry nitrogen atmosphere.

FTIR-UATR spectra were recorded on a Perkin Elmer System 2000FT-IR spectrometer. Samples for IR were examined using a universal attenuated total reflectance (UATR) with a diamond crystal. ^{13}C CP/MAS NMR spectra were recorded on a Bruker DPX-300 spectrometer. ICP-MS is a method for the determination of cadmium, nickel, or copper in samples. to cadmium(II) than to nickel(II) and copper(II).

Synthesis and characterization of generation one (G-1) (A, M_n = 150 kD), (B, M_n = 150 kD, further partial hydrolysis), (C, M_n = 50 kD), and (D, M_n = 50 kD, further partial hydrolysis) and generation two dendrimer (G-2) (E, M_n = 150 kD), (F, M_n = 150 kD, further partial hydrolysis), (G, M_n = 50 kD) and (H, M_n = 50 kD, further partial hydrolysis)

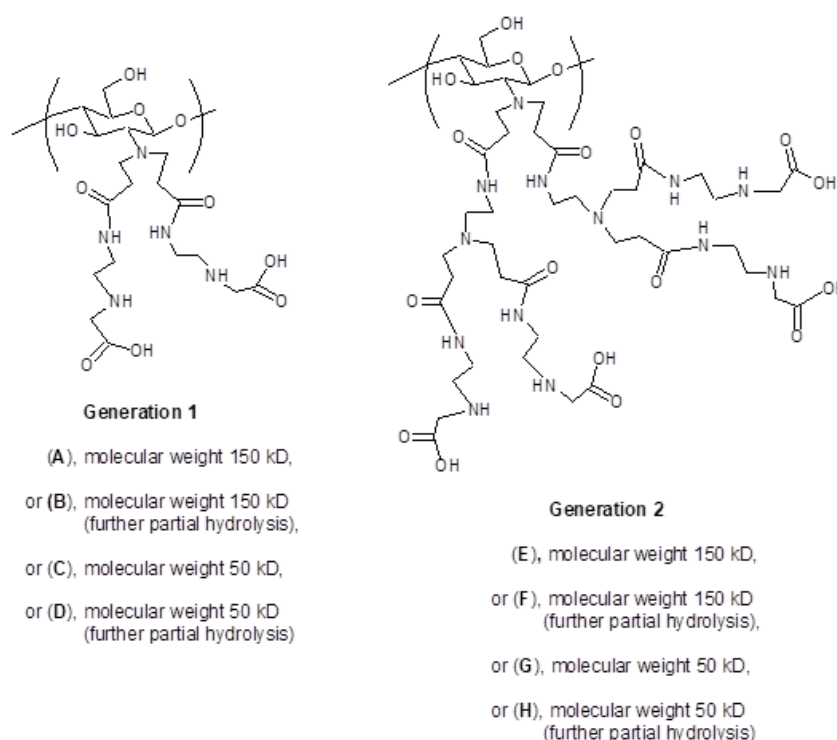


Figure 3. Chitosan derivatives containing hyperbranched-N-carboxymethyl groups.

A modified literature procedure was used (Colo et al., 2004). Either compound 1 or 2 (0.5 g) is dissolved in an aqueous 0.7% (v/v) acetic acid solution (50 mL). Any insoluble materials are filtered off before glyoxylic acid (10 mL) is added to the solution at room temperature. The mixture is then stirred further at that temperature for 2 hours before 1 M NaOH is added drop by drop until the pH value reaches 4.5. After that the mixture is stirred for an additional 1 hour. Then, sodium cyanoborohydride aqueous solution is added dropwise. The mixture is stirred further at room temperature for 1 hour after the addition is complete. Ethanol was slowly added to precipitate a pale- yellow powder, which was filtered, washed with ethanol several times, and dried to afford generation one dendrimer (G-1) or generation two dendrimer (G-2).

Generation one dendrimer (G-1) (A) (0.6 g) IR (cm^{-1}) 3285, 2931, 1630, 1571, 1370, 1017; ^{13}C CP/MAS NMR δ (ppm) 174.9, 164.5, 104.9, 85.0, 75.2, 62.0, 41.7, 23.5.

Generation one dendrimer (G-1) (B) (0.6 g) IR (cm^{-1}) 3281, 2919, 1622, 1572, 1377, 1019; ^{13}C CP/MAS NMR δ (ppm) 175.5, 164.7, 105.4, 84.1, 75.6, 60.3, 39.4.

Generation one dendrimer (G-1) (C) (0.6 g) IR (cm^{-1}) 3279, 2875, 1624, 1570, 1376, 1024; ^{13}C CP/MAS

NMR δ (ppm) 174.2, 164.7, 105.5, 84.0, 75.2, 61.5, 48.7, 38.2, 24.1.

Generation one dendrimer (G-1) (D) (0.6 g) IR (cm^{-1}) 3276, 2860, 1623, 1566, 1436, 1023; ^{13}C CP/MAS NMR δ (ppm) 175.1, 164.8, 105.6, 83.7, 75.3, 60.8, 47.9, 38.4.

Generation two dendrimer (G-2) (E) (0.6 g) IR (cm^{-1}) 3280, 2872, 1630, 1571, 1374, 1027; ^{13}C CP/MAS NMR δ (ppm) 174.9, 164.5, 104.9, 85.0, 75.2, 62.0, 41.7, 23.5.

Generation two dendrimer (G-2) (F) (0.6 g) IR (cm^{-1}) 3288, 2867, 1635, 1563, 1376, 1021; ^{13}C CP/MAS NMR δ (ppm) 174.3, 164.8, 105.6, 75.0, 61.6, 48.7, 38.7.

Generation two dendrimer (G-2) (G) (0.6 g) IR (cm^{-1}) 3276, 2870, 1623, 1566, 1436, 1023; ^{13}C CP/MAS NMR δ (ppm) 174.0, 164.5, 104.8, 84.6, 75.1, 62.4, 37.8, 23.6.

Generation two dendrimer (G-2) (H) (0.6 g) IR (cm^{-1}) 3280, 2872, 1622, 1575, 1373, 1027; ^{13}C CP/MAS NMR δ (ppm) 174.6, 164.7, 104.5, 75.2, 60.7, 40.4.

General procedure for determination of water solubility

The procedure described in the literatures was used (Chanthatayanonth et al., 2010). The derivatives or starting chitosan (30 mg) were distributed in water

(10 mL) for 48 hours. Solutions of 0.1 M HCl and 0.1 M NaOH were used to adjust the pH of the suspensions. The water solubility was determined at pH 5, 6, 7, 8, and 9. The weight of the dry remaining undissolved derivatives and starting chitosan was determined. The weight of dissolved derivatives and dissolved starting chitosan was determined as well after evaporation of the aqueous solution under reduced pressure. To minimize the measurement error, at least four measurements were averaged for each sample.

Antimicrobial activity

The antimicrobial activity of the derivatives and starting chitosan was evaluated against *Staphylococcus aureus* (S. aureus) ATCC 29213, *Micrococcus luteus* (M. luteus) ATCC 10240 and *Shewanella putrefaciens* (S. putrefaciens) ATCC 8071, obtained from the Faculty of Medical Technology, Mahidol University, Thailand, using agar dilution method. S. aureus, a Gram-positive bacterium, is a powerful pathogen in human disease (Shelburne et al., 2011). M. luteus, a Gram-positive bacterium, can cause meningitis and endocarditis (Gupta et al., 2019). S. putrefaciens, a Gram-negative bacterium, can cause bacteremia and cellulitis (Vignier et al., 2013).

The tested compounds were individually mixed with Muller Hinton Broth (MHB), a medium containing beef infusion, casamino acids or peptone, and starch, to obtain a final volume of 2 mL. The microorganisms were cultured in MHB at 37 °C for 24 h and diluted with 0.9% normal saline solution to adjust the cell density of 10⁸ CFU/mL compared with 0.5 McFarland. The microorganisms were further incubated at 37 °C for 24-48 h. For agar dilution, the solutions with defined numbers of bacterial cell are spotted directly onto the nutrient plates that have incorporated different antimicrobial and antibacterial agent concentrations. The following concentrations of chitosan derivatives were used 2500, 1250, and 625 µg/mL at pH 5.75 MHB (Muller Hinton Broth). All the plates were incubated at 37 °C for 24-48 hours.

The tested solution was transferred to the Muller Hinton Agar (MHA) by two-fold dilution to obtain the concentrations ranging of 625, 1250, and 2500 µg/

mL. After incubation, the presence of bacterial colonies on the plates indicates the growth of the organism. The antimicrobial activity of tested compounds was evaluated by observing the growth of microorganisms on MHA at pH 5.75 and grading 4+ (100%), 3+ (75%), 2+ (50%), 1+ (25%), and no growth 0 (0%).

General procedure for adsorption of metals at pH 7

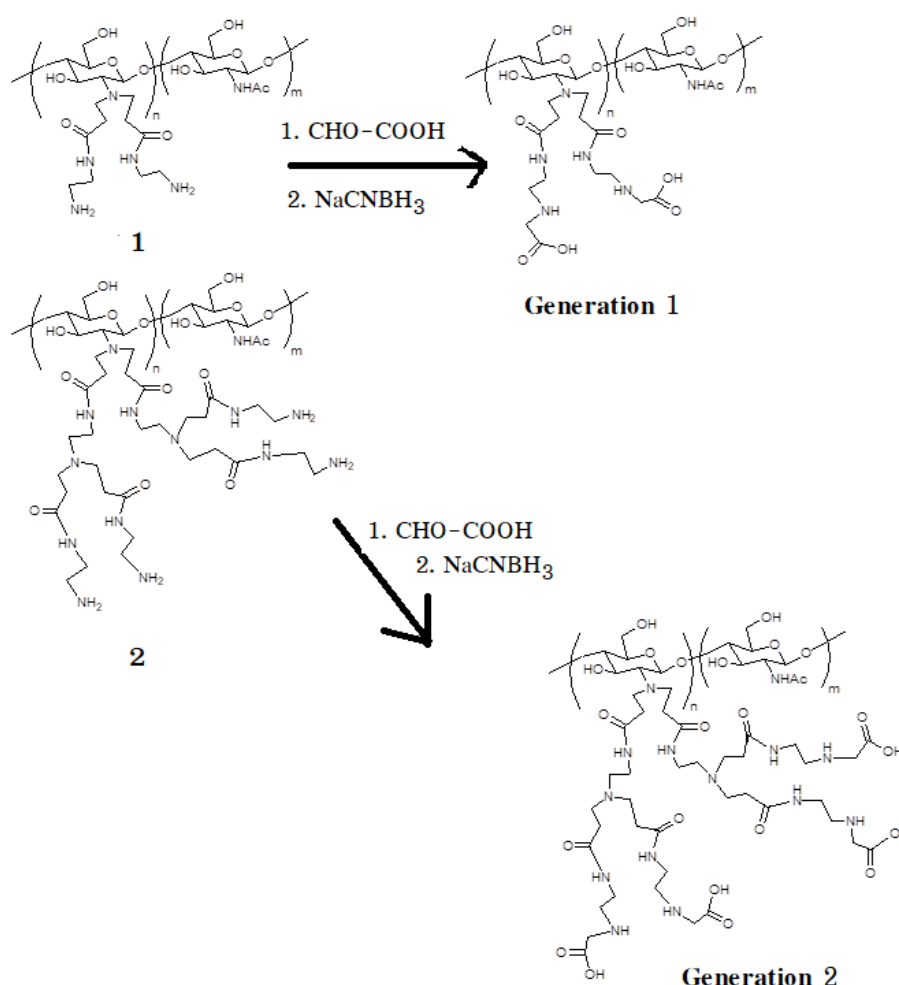
The procedure described in the literatures was used (Chanthatayanonth et al., 2010). Copper, cadmium, or nickel sulphate solutions (0.02 M, 10 mL) were passed slowly through the columns [glass tubing (ø = 0.6 cm), which were packed with chitosan or chitosan derivatives (100 mg)]. The adsorption of metals by chitosan and chitosan derivatives was determined by ICP analysis.

RESULTS AND DISCUSSION

Synthesis and characterization of generation one (G-1) (A, Mn = 150 kD), (B, Mn = 150 kD, further partial hydrolysis), (C, Mn = 50 kD), and (D, Mn = 50 kD, further partial hydrolysis) and generation two dendrimer (G-2) (E, Mn = 150 kD), (F, Mn = 150 kD, further partial hydrolysis), (G, Mn = 50 kD) and (H, Mn = 50 kD, further partial hydrolysis)

Compounds 1, 2, and partial hydrolysis of chitosan were synthesized according to the procedure described in the literatures (Baumann et al., 2001; Tsubokawa et al., 2000). Generation one dendrimer (G-1) (A), (B), (C) or (D) and generation two dendrimer (G-2) (E), (F), (G) or (H) were prepared by the analogous procedure reported in the publication (Colo et al., 2004), as illustrated in Scheme 1.

The identity of the modified chitosans is confirmed by FTIR-UATR. The characteristic absorption peaks of glyoxylic acid grafted dendritic hyperbranched chitosan presents two broad peaks at 3285 cm⁻¹ (in the range 2400-3700 cm⁻¹) which attributed to O-H bond of carboxylic acid and at 1630 cm⁻¹ (in the range 1600 and 1700 cm⁻¹) which attributed to C=O bond of carboxylic acid. Also, 13C CP/MAS NMR shows chemical shift at 164 ppm which represents the C=O moiety.



Scheme 1. Preparation of chitosan containing hyperbranched-N-carboxymethyl groups (G-1) and (G-2).

Water solubility

The water solubility of chitosan and new chitosan derivatives is shown in Table 1. It was found that chitosan derivatives containing hyperbranched-N-carboxymethyl groups had significantly higher water solubility compared to the starting material. This increase in water solubility was due to the hyper branched-N-carboxymethyl group that put on. It was also found that G-1 and G-2 had similar water-soluble properties to the chitosan derivatives. This might be due to the fact that the polarity of G-2 was decreased by extended chain length, although the numbers of carboxyl groups in G-2 is higher than G-1. Attempting to enhance water solubility by further partial hydrolysis of chitosan derivatives was carried out without success. There was no noticeable higher level of water solubility observed (A and B, C and D, E and F, and G and H). Quite possibly, the partial hydrolysis failed to produce any significant change in

the degree of deacetylation. As expected, the solubility of lower molecular weight chitosan (50 kD) and its derivatives in water, at the same pH, is slightly higher than that of higher molecular weight chitosan (150 kD) and its derivatives.

Antimicrobial activity

Growth inhibition of bacteria in the presence of chitosan derivatives was observed compared with starting chitosan (Tables 2 and 3). The results indicated that both starting chitosans with concentration ranging from 625-2500 $\mu\text{g/ml}$ have no antimicrobial activity against *M. luteus*, *S. aureus* and *S. putrefaciens* while the new chitosan derivatives containing hyperbranched-N-carboxymethyl groups show improved activity against these species with a minimum concentration 625 $\mu\text{g/ml}$. The chitosan derivatives have better antimicrobial activities than the starting chitosan. This is likely the contribution of their improved solubility in water.

Table 1. The water solubility of chitosan and new derivatives at various pHs^a

Entry	Compound	Water solubility (%)				
		pH 5	pH 6	pH 7	pH 8	pH 9
1	Starting Chitosan (Mn = 150 kD)	19	19	11	12	12
2	Starting Chitosan (Mn = 50 kD)	21	21	21	24	22
3	A (G-1)	84	87	88	90	90
4	B (G-1)	86	83	89	87	89
5	C (G-1)	80	83	82	83	84
6	D (G-1)	84	90	87	84	75
7	E(G-2)	90	98	85	84	96
8	F (G-2)	74	76	84	90	90
9	G (G-2)	81	85	95	81	88
10	H (G-2)	70	75	78	75	79

^a Samples (30 mg) were dispersed in water (10 mL) for 48 h and the pH of the suspensions were adjusted with 0.1 M HCl or 0.1 M NaOH.

Table 2. Antimicrobial activity of chitosan (Mn = 50 kD) and its derivatives

Entry	Compound	M. luteus	S. aureus	S. putrefaciens
1	Chitosan			
	625 µg/mL	4+	4+	4+
	1250 µg/mL	4+	4+	4+
	2500 µg/mL	4+	4+	4+
2	C (G-1)			
	625 µg/mL	1+	2+	2+
	1250 µg/mL	0	1+	1+
	2500 µg/mL	- ^a	0	0
3	G (G-2)			
	625 µg/mL	2+	1+	1+
	1250 µg/mL	1+	0	1+
	2500 µg/mL	0	- ^a	0

^a Antimicrobial activity was not tested.

Grading the growth of microorganisms, 4+ (100%), 3+ (75%), 2+ (50%), 1+ (25%), and no growth 0 (0%).

Table 3. Antimicrobial activity of chitosan (Mn = 150 kD) and its derivatives

Entry	Compound	M. luteus	S. aureus	S. putrefaciens
1	Chitosan			
	625 µg/mL	4+	4+	4+
	1250 µg/mL	4+	4+	4+
	2500 µg/mL	4+	4+	4+
2	A (G-1)			
	625 µg/mL	0	2+	0
	1250 µg/mL	- ^a	2+	- ^a
	2500 µg/mL	- ^a	1+	- ^a
3	E (G-2)			
	625 µg/mL	0	1+	1+
	1250 µg/mL	0	1+	0
	2500 µg/mL	- ^a	0	- ^a

^a Antimicrobial activity was not tested.

Grading the growth of microorganisms, 4+ (100%), 3+ (75%), 2+ (50%), 1+ (25%), and no growth 0 (0%).

Table 4. Adsorption of metals by chitosan (Mn = 150 kD) and its derivatives at pH 7^a

Entry	Compound	Cd (%) ^b	Cu (%) ^b	Ni (%) ^b
1	Chitosan	10.0	9.5	8.1
2	A (G-1)	15.1	11.3	10.3
3	B (G-1)	13.5	10.8	11.3
4	E (G-2)	16.0	11.6	9.7
5	F (G-2)	14.5	12.1	11.2

^a Copper, cadmium, and nickel sulphate solutions were passed slowly through the columns [glass tubings (ø = 0.6 cm), which were packed with samples (100 mg)].

^b Determined by inductively-coupled plasma (ICP) analysis.

Adsorption of metals

The adsorption/chelation of metals by chitosan and chitosan derivatives was investigated at pH 7 (Tables 4 and 5). Sulphate solution was used in this study since it has been reported that the metal uptake was higher from sulphate solution than solutions of chloride and nitrate, when nickel(II) and cadmium(II) are offered separately (Qin et al., 2004). In addition, sulphate anion

differs from chloride and nitrate by its higher charge so it may be more effective in ionic binding. It was found that the new chitosan derivatives show good coordination ability to metals and have higher affinity to cadmium(II) than to nickel(II) and copper(II). The chelating behavior, with heavy metals, of lower molecular weight chitosan (50 kD) is slightly better than that of higher molecular weight chitosan (150 kD) and its derivatives.

Table 5. Adsorption of metals by chitosan (Mn = 50 kD) and its derivatives at pH 7^a

Entry	Compound	Cd (%) ^b	Cu (%) ^b	Ni (%) ^b
1	Chitosan	11.2	10.8	9.4
2	C (G-1)	17.0	12.1	11.2
3	D (G-1)	19.4	14.0	11.7
4	G (G-2)	15.0	14.0	12.3
5	H (G-2)	15.6	14.5	11.1

^a Copper, cadmium, and nickel sulphate solutions were passed slowly through the columns [glass tubings (\varnothing = 0.6 cm), which were packed with samples (100 mg)].

^b Determined by inductively-coupled plasma (ICP) analysis and thermo gravimetric analysis (TGA).

Conclusions

In this study, we present the successful preparation of the new chitosan derivatives containing hyperbranched-N-carboxymethyl groups by a robust method. Their higher water solubility and antimicrobial activities compared to the original chitosan at neutral pH range were demonstrated. These properties lead to varieties of potential usages for human safety against bacterial contamination. The new chitosan derivatives displayed improved chelation properties compared to the starting chitosan. They can be therefore applied for discarding heavy metal waste in the environment.

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The Development of Alternative Test Innovation for Learning Assessment

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Abstract

This research has developed a concept map as a tool for learning evaluation intended to analyze the size of the variance in each element, compare the coefficient of reference summary, compare the exactness when the pattern and number of examiners are different while developing training courses to apply concept mapping techniques for learning assessment and evaluation of training results. The sample in this study is divided into 2 groups: 4 examiners, and 48 students from Rajabhat Rajanagarindra University. The research tool used is an activity plan for the use of concept maps for learning outcome assessment, concept mapping evaluation form, quizzes, training assessment. The research results indicate that;

When the examination pattern is different even though the number of inspectors is the same, the Generalizability Coefficient then is statistically different with a significant level of 0.05. When the examination pattern is the same but the number of assessor is different, then the Generalizability Coefficient is statistically different at a significant level of 0.05. The score in all conditions has a high Concurrent Validity and statistically significant difference at 0.05. Training courses in applying the concept mapping techniques for learning measurement and evaluation are the most appropriate for all items. Evaluation results of training courses in applying concept mapping for measuring and evaluating learning outcomes are at a high level for all items except for the knowledge on the topic prior to training which is at a moderate level.

Keywords: concept mapping, generalizability coefficient, evaluation of a learning achievement

Introduction

The measurement and evaluation of the study is a psychological assessment where items to be measured are quite abstract, and there are extraneous variables involved. The operator therefore may not have full control over those variables. As a result, there is a potential error that may occur at any time. Therefore, for each test, the obtained score will be the sum of two points: the true score and the error score. The tolerance score can be either positive or negative. And the discrepancy that occurs may be due to many reasons, for example, poor quality measurement tool, operator lacking expertise, the variation of the examinees, discrepancy in sampling the content, behaviors, etc.

Due to the aforementioned reasons, it can be

seen that the tools used in the measurement are important parameters that the assessor must pay attention to and care for. Ruiz-Primo, Schultz, and Shavelson (1996) sought to find out how to measure and evaluate results in science. They wanted to investigate what the students know and what they can do. In this study, they used the concept mapping to measure and evaluate the results. West, Pomeroy, Park, Gerstenberger, and Sandoval (2000) studied the application of concept mapping to assess the critical thinking of medical students. And Srinivasan, McElvany, Shay, Shavelson, and West (2008) studied the implementation of conceptual mapping in measuring and evaluating medical students. This can be seen that in foreign countries, there are people interested in applying conceptual maps to

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measure and evaluate learners' learning outcomes or even to assess critical thinking, which is an advanced thinking. For Thailand, the use of concept mapping to measure and evaluate still receives very little attention from people interested.

Concept mapping is not a newly emerging technique or method. It was developed and has been used in education for over 30 years (Buldu & Buldu, 2010). Novak & Gowin (1972) pioneered and developed this concept based on Ausubel's Theory of Meaningful Learning (1968). Ausubel believes that learning is a result of assimilation, knowledge, and stories that have been newly acquired combined with the existing concept the learners already possess and it is the expansion of knowledge by the learners themselves. Ausubel also pointed out that teaching methods to achieve meaningful learning depend on three conditions as follows:

- 1) New knowledge must contain logical meaning as resulted from the learners' prior knowledge.
- 2) The structure of the prior knowledge must be related to the new knowledge.
- 3) The learner must understand and have the determination to learn meaningfully, otherwise, the first two conditions will result in memorization learning. Novak visualized Ausubel's ideas into concrete charts and continuously pioneered the research since 1972.

Measurement and evaluation using concept mapping is an important and challenging process since there are several sources of variability. This is consistent with the concept of McClure, Sonak, and Suen (1999) who studied using concept mapping as a tool and found that the quality of the concept mapping may have multiple sources of variation, such as scoring methods, discrepancies from students' knowledge, and discrepancies from the assessor, etc. Such of these discrepancies affect the efficiency of the concept mapping. Ruiz-Primo and Shavelson (1996) stated that analyzing the quality of concept mapping by using traditional test theories such as retesting is not suitable for determining the quality of mind mapping. Instead, the importance of the assessor should be considered. This is consistent with Chaiyapruet Serirak et. al (2540) who stated that in the analysis of the validity of continuous measurement

for student's performance, the traditional validity theory like splitting the Cronbach's alpha coefficient test into two halves would not be suitable. Because these theories have an agreement that the test must measure the same thing in parallel and must perform the exam once. But the assessment using concept mapping is of different characteristics. Thus, the theory of validity approximation or the so-called Generalizability Theory is, therefore, a suitable theory to analyze the validity of the assessment using concept mapping.

From the above document and research, the application of concept mapping for measurement and evaluation in Thailand receives a little attention. But in contrast, in foreign countries, they are widely studied. In 2013, in the educational research course, the researcher developed the concept map scoring criteria, analyzed the size of the variance in each of the scoring components, compared the Generalizability Coefficient of the scoring criteria when the scoring criteria and the number of assessors are different. In the study, the researcher found the problem that during the examination, students periodically raised their hands in question indicating a lack of understanding in the implementation of concept mapping for measurement and evaluation. Therefore, in this study, the researchers develop a concept mapping for the course of the Principles of Education Measurement and Evaluation in the topic of the Instrument for measuring learning behavior and analyzing the size of variance in each component of the concept mapping, compare the Generalizability Coefficient of the concept mapping in case the pattern of examination and number of assessor are different and when the Concurrent Validity of the concept mappingscores are already compared. And the researcher developed a training course for the application of mind mapping techniques for measurement and evaluation and evaluated the training course. The researchers wanted to disseminate the knowledge gained from this research to teachers/assessors in the educational area of Chachoengsao Province in order to learn the alternative assessment pattern for use in the actual scenario and to bring the results of the assessment to effectively improve and develop the learners.

Research Objectives

1. To compare the Generalizability Coefficient of the concept mapping when the pattern of examination and the number of examiners are different
2. To compare the validity of the concept mapping scores when the pattern of examination and the number of examiners are different
3. To develop a training course on applying concept mapping techniques for learning measurement and evaluation.
4. To evaluate the training course on applying concept mapping techniques to measure and evaluate learning achievement.

Scope of the Study

For responding to the objectives 1 and 2

1. Target groups include 4 teachers in the teaching professional group and teacher students enrolled for a course of the Principles of Education Measurement and Evaluation in the first semester of the academic year 2018 of 48 students from Rajabhat Rajanagarindra University

2. Research variables

2.1 There are 2 independent variables, namely;

2.1.1 Three patterns of scoring including:

2.1.1.1 The assessor inspects every concept map of every student.

2.1.1.2 The assessor inspects every concept map of some students.

2.1.1.3 The assessor inspects some concept maps of all students.

2.1.2 The number of inspectors is classified into 3 levels, namely;

2.1.2.1 2 persons

2.1.2.2 3 persons

2.1.2.1 4 persons

2.2 There are 2 dependent variables, namely

2.2.1 Generalizability Coefficient

2.2.2 Concurrent Validity

For responding to objectives 3 and 4

1. Target groups include 48 teacher students who enrolled for a course of the Principles of Education Measurement and Evaluation in the first semester of the academic year 2018 from Rajabhat Rajanagarindra University

2. Research Variables

2.1 There are 2 independent variables, namely;

2.1.1 Training courses on applying the concept mapping techniques to measure and evaluate learning achievement.

2.1.2 Students

2.2 There are 2 dependent variables, namely

2.2.1 Course Quality

2.2.2 Satisfaction of the training participants

3. The period of study is the first semester of the academic year 2018.

4. Content used in the development of this concept mapping is the content of the course of the Principles of Education Measurement and Evaluation.

Research hypothesis

1. The Generalizability Coefficient of concept mapping with the examination pattern where the assessors inspect every concept map of all students will provide higher value than in other patterns of all assessors.

2. The Generalizability Coefficient of concept mapping with a higher number of assessors will provide a higher value of the Generalizability Coefficient than those with a smaller number of assessors.

3. The Concurrent Validity of concept mapping with the examination pattern that the assessors inspect every concept mapping of all students will provide higher value than those of other patterns in every number of assessor.

4. The Concurrent Validity of concept mapping with the higher number of assessors will be higher than those with less number of assessors in all patterns of examination.

Research Methodology

The research tools consisted of activity plans in the implementation of concept mapping for learning evaluation. The concept map evaluation form for assessing learning achievement in 12 topics. The researcher collected data by themselves in the Semester 1/2018 in the course Principles of Education Measurement and Evaluation from 48 persons of the sample group. Researchers organized teaching and learning activities each time and allow students to complete the concept map assessment form in 12 topics. After that, all concept map forms are photocopied into 4 copies, given to 4 assessors with the researchers explained the examination methods and scoring criteria created by the researchers and have the assessors to inspect every student's concept map along with taking notes and then bringing the results of the examination to prepare and analyze the information as follows

1. Compare the Generalizability Coefficient of concept mapping when the pattern and number of assessors are different using Woodruff and Feldt's UX1 formula (1986, p. 393-413) (for responding to purpose 1).

2. Compare the Concurrent Validity of the concept mapping score when the pattern and number of assessors are different using the Pearson Product Moment Correlation coefficient analysis for scores obtained from different test patterns and different numbers of assessor with the final exam scores on the course of the Principles of Measurement and Evaluation of education. And compare the Concurrent Validity of the scores when the pattern and number of assessors are different. The correlation coefficient will be converted into Fisher's standard Z score and then tested for the parallel difference of the correlation coefficient by using Chi-Square statistics (for responding to objectives 2)

3. Consider the suitability of the training plan by using mean and standard deviation values (for responding to the objective 3)

4. Evaluate the results of training on the course of the application of concept mapping for measuring and evaluating learning results by calculating the mean and standard deviation values (for answering to objec-

tives 4)

Research Results

Comparing the Generalizability Coefficient of mind map scores when the pattern and number of assessor are different and testing for the difference of the Generalizability Coefficient when the examination pattern is different but the number of assessors is the same, the results reveal that all conditions are statistically significantly different at a level of 0.05 indicating that at least 1 pair of Generalizability Coefficient for each condition is different. When testing the parallel difference of the Generalizability Coefficient where the test pattern is different but the numbers of assessors are the same, it showed a statistically significant difference at 0.05 level. And when considering the assumptions set out in Clause 1 that "the Generalizability Coefficient of the mind map score with the examination pattern where the assessors inspect of every mind map of all students would have a higher value than other scoring patterns in all numbers of assessor". It can be seen that this is consistent with all the assumptions defined. When the pattern is the same but the number of assessors is different, it is found that all conditions have a statistically significant difference at a level of 0.05, indicating that at least 1 pair of the Generalizability Coefficient for each condition was different. When testing the parallel difference of the Generalizability Coefficient values when the test pattern is the same but the number of assessors is different, it is found a statistically significant difference at the 0.05 level for all pairs. And when considering the assumptions set out in Clause 2 that "the Generalizability Coefficient of the concept mapping score with a higher number of assessors, will provide the higher value than the Generalizability Coefficient with a lesser number of assessors". This can be seen that all hypotheses are true.

Comparing the Generalizability Coefficient of the concept map score when the pattern and number of assessor are different, the results in comparing the Generalizability Coefficient of the concept map scores when the pattern is different but the number of assessors is the same, it shows statistically significant differ-

ence at the 0.05 level following the hypothesis 3 stating that “the Generalizability Coefficient in the concept map scores in the course of the Academic Research with the examination pattern where the assessors inspect every concept map of all students will have a higher value than in other patterns in every number of assessors”. This indicates that the scores obtained from the different examination patterns but the same numbers of assessors will have different values of Generalizability Coefficient. The results in comparing the Generalizability Coefficient with the same the test patterns but the different numbers of the assessor, it shows statistically significant difference at the 0.05 level following the hypothesis 4 which states that “Generalizability Coefficient of concept map score in the course of the Academic Research in education with a higher number of assessors will provide higher value than those with lesser number of assessors in all patterns of examination”. This indicates that the scores obtained from the same examination pattern but different numbers of assessors will have different values of Generalizability Coefficient.

The results in developing the training course in applying the concept map techniques for measuring and evaluating learning outcomes (responding to Objective 3), all 3 experts considered the suitability of the curriculum, objectives, procedures for organizing activities and documents related to organizing the activities, the application of concept mapping for assessing the learning outcomes on the basic knowledge of mind map and the utilization of mind map for learning evaluation, and found that they are appropriate in the highest level indicating that the curriculum developed is appropriate.

Results in evaluating the training course in applying concept mapping for measuring and evaluating learning outcomes (responding to objective 4), the result found that among 48 respondents, 39 are female students, accounting for 81.25 percent, and 9 males, accounting for 18.75 percent. All respondents agree that the time to attend the training is reasonable, accounted for 100.00 percent. Most of the respondents have a high level of overall opinion about the suitability of the course with a mean value of 4.11. When sorting the mean value in descending, it is found that the content

is useful at a high level with the mean value of 4.41, followed by the opinion that the knowledge gained can be used in practice at a high level with the mean of 4.26. And the lowest mean belongs to the opinion that the availability of audiovisual equipment is at a high level with the mean of 3.58. Most respondents have opinions about training materials with a total mean of 3.90. When sorted the mean values in descending, it is found that the knowledge gained can be utilized for practice to a large extent with the mean of 4.39. The suitability of the content of the training is at a high level with the mean of 4.38 and the lowest mean fell to the opinion that the knowledge of this topic before attending the training was at the medium level with the mean of 2.61. Respondents are satisfied with the training course with a total mean of 4.21. When sorted the mean in descending, it is found that participants are very satisfied with the registration process at a high level with a mean of 4.31, followed by the satisfaction with snack food with the mean of 4.30 and the least mean falls to the location/training room with the mean of 4.05.

Discussion

1. The results in comparing the Generalizability Coefficient of concept map scores when the test pattern and the number of assessors are different, it is found that all conditions have a statistically significant difference at a level of 0.05, which is consistent with the assumption 1 stating that “the Generalizability Coefficient of the concept map score with the pattern that assessors inspect all the concept map of all students have a higher value than those of other scoring patterns. This may be due to the score obtained from the examination pattern that assessors inspect every concept map of all students is obtained by bringing the examination results from 2, 3, and 4 assessors to be averaged as the scores of each student which is the ideal form of scoring (Sudweeks et al., 2005).

When the examination patterns are the same but the numbers of assessor are different, it is found that all conditions have a statistically significant difference at the 0.05 level, which is consistent with the hypothesis set out in Article 2 stating that “Generalizabil-

ity Coefficient of the mind map score with the higher number of assessors will be higher the value than those the Generalizability Coefficient with a lesser number of assessors". This is consistent with Sirichai Kanjanawasi (2007) stating that whatever pattern of examination, multiple assessors should be used in scoring each test maker and then the average or total scores should be provided instead of the test maker's ability. This will help reduce the variance due to the assessors and the remaining discrepancies which will help increase the validity.

2. Comparing the concurrent validity of concept map score when the pattern and number of examiners are different, it is found that each condition, examination pattern, and number of assessors that differ will have a statistically significant difference at a level of 0.05, indicating that scores obtained from all conditions of the number of assessor and examination patterns have different values of concurrent validity. This is consistent with the assumption that "the Concurrent Validity of the concept mapping score with the examination pattern where the assessors inspect every concept map of all students have a higher value than those of other patterns in every number of assessors" and "the Concurrent Validity of mind map score with a higher number of assessors will have a higher value than those of lesser number of assessors in all patterns of examination". This may be due to the researchers explained the method of checking the mind map in detail to the assessors, thus allowing the assessors to understand and create the concept mapping through careful consideration of experts in every step. Thus, this enables students to fully understand and express their knowledge and ideas, resulting in the Concurrent Validity.

3. Experts commented on the arrangement of activities to apply the concept mapping for learning evaluation, the introduction, and the application of concept mapping for learning evaluation saying that they were the most appropriate. This indicated that the developed activity plans are appropriate for the implementation of the concept mapping for learning evaluation. This is because the researchers conducted a

detailed synthesis of course content, therefore, making the results of the expert's assessment the most appropriate.

4. Most respondents have a high overall opinion about the suitability of the course at a high level averagely and the lowest mean falls to the availability of audio-visual equipment. This is because the researcher may not be ready in the preparation of the conference room for training. And the results of this evaluation will be considered for the next training.

Most respondents have overall opinions about training materials with the mean value at a high level, and the lowest average mean value fell to knowledge on this topic before training, which is consistent with the concept of Novak (1983).

The respondents are satisfied with the overall training at a high average level. When sorting the mean in descending, it is found the lower average level in the matter of the location/training room. This is because the researchers may not be ready in the location/training room, and the results of this evaluation will be considered for the next training.

Recommendations

1. Recommendations in applying the research results

For scholars and educators interested in implementing the concept map, the pattern of examination where the assessors inspect every concept map of all students should be used. This is due to there are higher levels of Generalizability Coefficient and Concurrent Validity than other patterns of scoring. And the greater number of assessors should be used since the Generalizability Coefficient and Concurrent Validity are higher than those with lesser number of assessors.

2. Suggestions for the next research

2.1 Study in the feasibility of scoring the concept mapping using a computer or other scoring tools should be conducted.

2.2 Study in the implementation of the concept mapping should be conducted to assess students' learning outcomes using research methodology and development and to apply to other courses.

2.3 Study in the application of concept mapping for learning evaluation by using other techniques such as filling words in the map, creating the mind map, creating words in lines so as to expand the knowledge in a broader range.

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Study on Growth Rate Performance of Sheep Fed with Super Napier Grass Silage Treated with *Lactobacillus buchneri* and *Lactobacillus plantarum*

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Abstract

This research was aimed to study the growth rate performance of sheep fed with super Napier grass silage treated with *Lactobacillus buchneri* and *Lactobacillus plantarum*. Thirty (30) growing sheep were randomly distributed to three treatments with ten sheep serving as replications per treatment. The treatments were as follows:

Treatment 1–super Napier grass silage without inoculants (control).

Treatment 2– super Napier grass silage with *L. buchneri*.

Treatment 3 – super Napier grass silage with *L. plantarum*.

The effect on the growth rate performance of sheep were measured and analyzed by using analysis of variance in a completely randomized design (CRD).

The results revealed that super Napier grass (SNG) silages treated with inoculants had a higher levels of crude protein, crude fiber, crude fat, ash and nutrient detergent fiber compared with the untreated SNG silages. The DM fraction of the SNG treated silages was increased in contrast to the untreated where the moisture content increased. The experiment trial indicated that SNG silage treated with *Lactobacillus buchneri* and *Lactobacillus plantarum* (T2 and T3) influenced. In terms of the growth parameters, significant ($P < 0.01$) differences were noted on body weight, weight gained, average daily gain (ADG) feed consumption and feed efficiency (FCR). The feeding trial indicated that SNG silage treated with *Lactobacillus buchneri* and *Lactobacillus plantarum* (T2 and T3) influenced sheep growth rate performance, weight gain, feed intake and days to market. Thus, addition of beneficial microbes improve the nutritional quality of silage and increased nutrients levels resulting to higher growth of sheep.

Keywords: Growth rate performance, Super Napier grass silage, *Lactobacillus buchneri* and *Lactobacillus plantarum*

INTRODUCTION

Feed resources for ruminant livestock production in the country (Philippines and Thailand) normally are natural forage crops, natural pastures and natural plants but almost are low in quality of grasses which are limited in supply during the dry season. Today, ruminant animals are now fed with fermented or preserve feeds and has been very popular especially with dairy and beef cattle that require high level of nutrition in order to achieve high milk and beef production. Nowadays, the use of corn silage and others fodder crops as green

forage in ruminant feeding has increased rapidly due to its high yielding properties, relatively high content of energy, palatability and easy incorporation in total mixed ration. Scarcity of feed for ruminants is one of the important problems for rearing livestock during summer especially in the country and other tropical countries (Jamsawat et al., 2017). However, livestock raisers can conserve feed resources by producing silages when feed resources are abundant during rainy season. Since silage is an alternative for ruminants especially in production situations that require consistent nutrition on a daily

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basis, condition of silage has a significant impact on its quality for reasons that forage often contains many detrimental types of bacteria. In fact, the primary goal of making silage is to maximize the preservation of original nutritional value of the forage crop at the highest value possible during storage for feeding at a later date. The traditional method of fermentation in the silo however, is a much uncontrolled process usually leading to less than optimal preservation of nutrients.

Feed shortage and low quality of forage crops in the country are the major constraints to the development of ruminant industry. To overcome these problems, feeding of ruminants with conserved forages which is becoming popular among enterprising livestock raisers in the country is an important feeding strategy to ensure the success of ruminant production in the country. (Khaini et al., 2015). Small ruminant production is a very significant component of livestock production throughout the world and more specifically in the developing countries. Small ruminants has the ability not only to survive different environmental conditions but also able to utilize poor quality feed.

In recent times, the use of corn silage and others fodder crops silage as green forage in ruminant feeding has increased rapidly due to its high yielding properties, relatively high content of energy, palatability and easy incorporation in total mixed ration. The concept of adding a microbial inoculant to silage was to add fast-growing homo fermentative lactic acid bacteria (LAB) in order to dominate the fermentation resulting in a higher quality silage, (Kung & Ranjit, 2001). *Lactobacillus buchneri* and *Lactobacillus plantarum* are some of the most common LAB inoculants in the fermentation of silage. Poorly preserved silages have poor fermentation quality; they are unpalatable to stock and reduced feed intake. These silages are also likely to have suffered extensive degradation of protein, resulting in poor utilization of the silage nitrogen by animals. In order to assist in the fermentation process, various silage additives have been used to improve the nutrient and energy recovery in silage, and when fed to livestock it will subsequently improve animal performances. The different species of lactobacillus were tested to find out the

effectiveness of the lactobacillus species as additives in ensiling “super Napier” known as “Pakchong 1” which was developed and produced in Thailand. The “Super Napier Grass” (SNG) is a cross of ordinary Napier grass (*Pennisetum purpureum*) and Pearl Millet (*Pennisetum glaucum*) can yields more crude protein of about 16 to 18 percent (Kiyothong, 2014). This grass requires lower inputs and easier to establish compared to corn and can be a good alternative, especially in production situations that require consistent nutrition on a daily basis. It is for this reason that two silage additives were tested to find out the effectiveness of preserving the quality of super Napier grass and its effect on the growth rate performance of sheep.

METHODOLOGY

Silaging and Evaluation

The *L. buchneri* and *L. plantarum* additives that were used in this experiment were purchased in Korean Culture Collection of Microorganism. Cultures that were cultivated anaerobically in De Man, Rogosa and Sharpe (MRS) agar medium in 250 ml flasks incubated at 30°C for 2 day in an orbital shaker (Thermo Scientific Max Q 2000, USA) at 100 rpm. Cultures were diluted in demineralized water before use. Inoculant wadded at a theoretical rate 1.0x10⁵cfu/g. prior to inoculation, inoculant will be diluted with distilled water to achieve the required concentration and keep for silage production.

Super Napier grass were sourced out from Isabella State University, Enchague, Isabella farm. The SNG were manually harvested at the maturing stage approximately 80 to 90 day of regrowth and were chopped into 2-3 centimeters.

Fifteen plastic drum silos with a capacity of 20 L were randomly assigned to three treatments by four factor experiment. The SNG were ensiled into 20-L drum silo and stored in dark and ambient temperature (5°C - 10 °C) for 0, 7, 15 and 30 days. The treatments were the following:

Treatment 1 – super Napier grass without inoculants (control).

Treatment 2 – super Napier grass treated with *Lactobacillus buchneri*.

Treatment 3 – super Napier grass treated 30°C with *Lactobacillus plantarum*.

Ensiling Procedure for Super Napier Grass

Fifteen kilogram of SNG grass each replication were inoculated with or without 3% (w/v) of *L. buchneri* or *L. plantarum* through spray method followed by thorough mixing. The samples were ensiled into 20-L drum silo and stored in dark and ambient temperature for 0, 7, 15, and 30 days. Triplicate silos were opened and the upper part 1/5 of silages were discarded before sampling of approximately 100 g. after each incubation period. Silage extracts will be prepared immediately by macerating a 50 g. silage samples with a 300 ml. of distilled water. These were collected through double cheesecloth and used to determine pH value and concentrations of volatile fatty acids (VFA) and volatile basic nitrogen and ethanol. Dry matter (DM) content of grass and silages were determined by a vacuum freeze-drying method (Uchida et al., 1986). The dried samples were grinded and then the crude protein was determined by the Kjeldahl method. NDF, ADF, and ADL were measured by the method of Goering & Van Soest (1970). Water soluble extracts was prepared by macerating 40 g of fresh silage sample in 400ml distilled water. The pH of the extracts were measured by using electric pH meter (PH71/PH72 personal pH / ORP meter, Yokogawa Electric Corporation, Japan). Fermentation products, pH and ammonia were determined in silage extracts, prepared by adding 270g demineralized water to 30g silage and homogenizing for 5min in a laboratory blender. Volatile fatty acids were analyzed using an HPLC device (Agilent Technologies 1200 series).

Data Gathered and Statistical Analysis

The chemical analysis of SNG and the chemical analysis of super Napier grass silage were determined, recorded and served as basis of evaluating the quality of silages as affected by the different additives/inoculants. All data gathered were tabulated and analyzed using analysis of variance in Completely Randomized Design (CRD). Significant differences among treatments were also analyzed using the Least Significant Difference (LSD).

Growth Rate Performance of Sheep

A total of thirty (30) heads of growing sheep were acquired from a commercial farm in Bulacan and Nueva Ecija, Philippines. The animals were randomly distributed into three (3) treatments. There were ten (10) animals assigned for each treatment each serves as replication. The experiment was laid out using the Completely Randomized Design (CRD) with the following treatments:

Treatment 1– super Napier grass silage without inoculants (control).

Treatment 2– super Napier grass silage with *L. buchneri*.

Treatment 3– super Napier grass silage with *L. plantarum*.

Feeding and Management of Experimental Animals.

The sheep were gradually introduce to their respective diet over two week's period and were fed ad libitum before the feeding trial officially began. Each experimental sheep were given the assigned diet throughout the feeding period. The amount of silage offered daily is computed approximately 4-5 % of body weight on a dry matter basis. The total amount of daily feed required were divided into morning (8:00) and afternoon (17:00) feeding. All animals were given free access to fresh drinking water and trace mineral salts throughout the experiment. The experimental sheep were permitted to adapt to the diets for two weeks prior to the actual feeding trial. Initial weights of the animals were measured after the acclimatization period. Clean and fresh drinking water were given at all times. The water was changed two times a day, morning and afternoon or as needed. Identical care and management were provided to the sheep throughout the feeding trial.

Weighing of Experimental Animals.

The initial weight were recorded. Bi-weekly weighing were done during the entire observation period in the morning before feeding every times. The final body weights were determined and blood samples were collected at the end of the feeding trial. The experimental animals were weighed before feeding in the morning. All data gathered on the growth rate perfor-

mance parameters of sheep were recorded, evaluated and analyzed using analysis of variance in Completely Randomized Design (CRD). Significant differences among treatments were also analyzed using the Least Significant Difference (LSD).

RESULTS AND DISCUSSION

Chemical Analysis of Super Napier Grass.

The chemical analysis of SNG was shown in Table 1. Results of the chemical analysis of super Napier grass as fresh and as dry matter bases were analyzed. The basis analysis were as follows: crude protein content was 1.21 %, crude fiber, 5.37%, crude fat, 10.12%, moisture, 85.09 %, ash, 1.01% and neutral detergent fiber, 10.20 percent. Likewise, the analysis as dry matter basis were as follows: crude protein content, 8.12%, crude fiber, 36.02%, crude fat, 67.87%, ash, 6.87% and neutral detergent fiber, 68.41%.

The chemical analysis used in this study is below the findings of percent (Kiyothong 2014) with a CP. concentration of 16–18 percent of a 45 days cutting interval. The low CP. concentrations of Napier grass was attributed to the high structural cell wall carbohydrates that increase rapidly with maturity causing decline in CP. concentration and digestibility (Van Soest 1994). Likewise, studies of (Cuomo et al., 1996), also demonstrated the effects of cutting interval on yield and quality vary with cultivars management practices and environmental conditions. Therefore, appropriate cutting management is essential for high production and quality of this species (Tessema et al., 2010).

Chemical Analysis of Untreated and Treated Super Napier Grass Silage.

The chemical analysis (composition) of SNG treated and untreated (DM basis) was shown in Table 2. Results of the analysis of the different silages treated and untreated varied among the treatments. After 7 days of fermentation, it was observed that the level of crude protein content of silage treated with inoculants had increased by 20% in T2 and 16% in T3, while those silage treated with plain water, (T1) had a reduction of 19.17 percent. Similar observation of improvement with silages treated with inoculant was noted on crude fiber, ash and neutral detergent fiber. The pH level prior to ensiling ranged from 6.5 to 7.0 and at the end of 30 days fermentation, the pH level drop due to lactic acid production with pH ranged from 4 to 4.5. The variation on the pH levels was probably due to the different inoculants used. It is worthy to mention that at the end of the 30th day of fermentation nutrient levels was improved. There was a noticeable improvement of ash and crude fiber content in all treatments, treated or untreated. Although there was a slight reduction on the crude protein content of SNG in all treatments from the start, the crude protein content of the treated silages were higher than the untreated ones. On the other hand, there was a substantial increase of crude fat in the untreated silages compared to the treated silages; however, at the end of 30 days of fermentation, there was a marked increase in the level of crude fat in treated silages higher than the untreated silages.

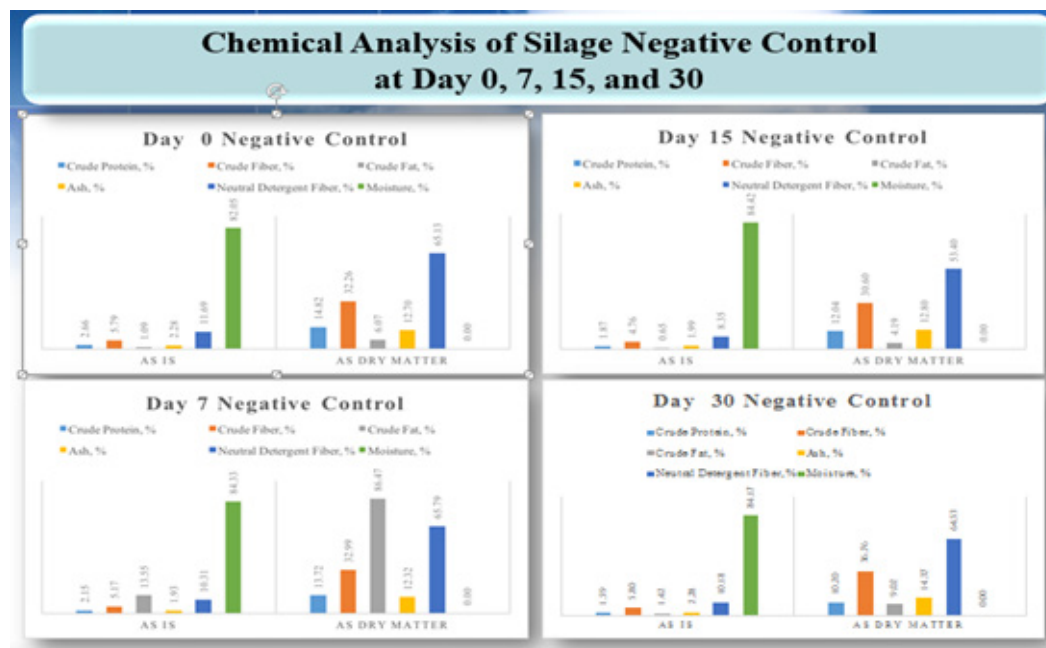
The result of the study conforms to the main objective of manufacturing silages which is to maximize

Table 1. Chemical analysis of super Napier grass.

PARAMETERS	FRESH	DRY MATTER
Crude Protein, %	1.21	8.12
Crude Fiber, %	5.37	36.02
Crude Fat, %	10.12	67.87
Moisture, %	85.09	-
Ash, %	1.01	6.77
Neutral Detergent Fiber, %	10.20	68.41

Table 2. Chemical composition of untreated and treated SNG silage with bacterial inoculant at DM basis.

PARAMETERS	T1 – w/o inoculant		T2 - <i>Lacto. buchneri</i>		T3 - <i>Lacto. Plantarum</i>	
	Day 0	Day 7	Day 0	Day 7	Day 0	Day 7
Crude Protein, %	2.66	2.15	1.72	2.07	2.24	2.59
Crude Fiber, %	5.79	5.17	5.23	6.00	5.17	6.92
Crude Fat, %	1.09	13.55	2.47	1.39	8.88	1.29
Ash, %	2.28	1.93	1.93	2.21	1.51	2.09
NDF, %	11.69	10.31	11.96	13.06	10.84	12.56
Dry Matter, %	82.05	84.33	83.17	81.08	83.93	80.90

**Figure 1.** Graphical Presentation of Super Napier Grass Silage Treated with Plain Water (control) from day 0 to day 30 of Fermentation.

the preservation of original nutrients in the forage crop for feeding at a later date. The result likewise confirmed reports that fermentation is really an uncontrolled process usually leading to less than optimal preservation of nutrients. The used of inoculants is therefore necessary to assist in the fermentation process. Silage additives have been used to improve the nutrient and energy recovery in silage, and when fed to livestock it will subsequently improve animal performances. In conclusion, these studies confirmed that the applying of molasses improved fermentative quality, feed intake and digestibility of Napier grass (Bureenok et al., 2012).

The graphical presentation of the untreated and treated super Napier grass is illustrated in figure 1,

2 and 3. The moisture content in T1- control increases as fermentation progresses then dropped starting on the 15th day to 30th day of fermentation. Whereas, the treated silages decreases consistently from day 7 to day 30 of fermentation. It is interesting to note that there were clear differences on the nutrient levels among the different treatments with higher levels in the treated silages. The illustration is a clear indication that nutrient levels in silaging is improved and preserved as manifested by the absence of mold. The result of this study is supported by Driehuis & Wikselaar (2000) in corn silage treated with *L. buchneri* was more stable than untreated silage. They suggest that improved aerobic stability was due to the ability of *L. buchneri* to ferment lactic

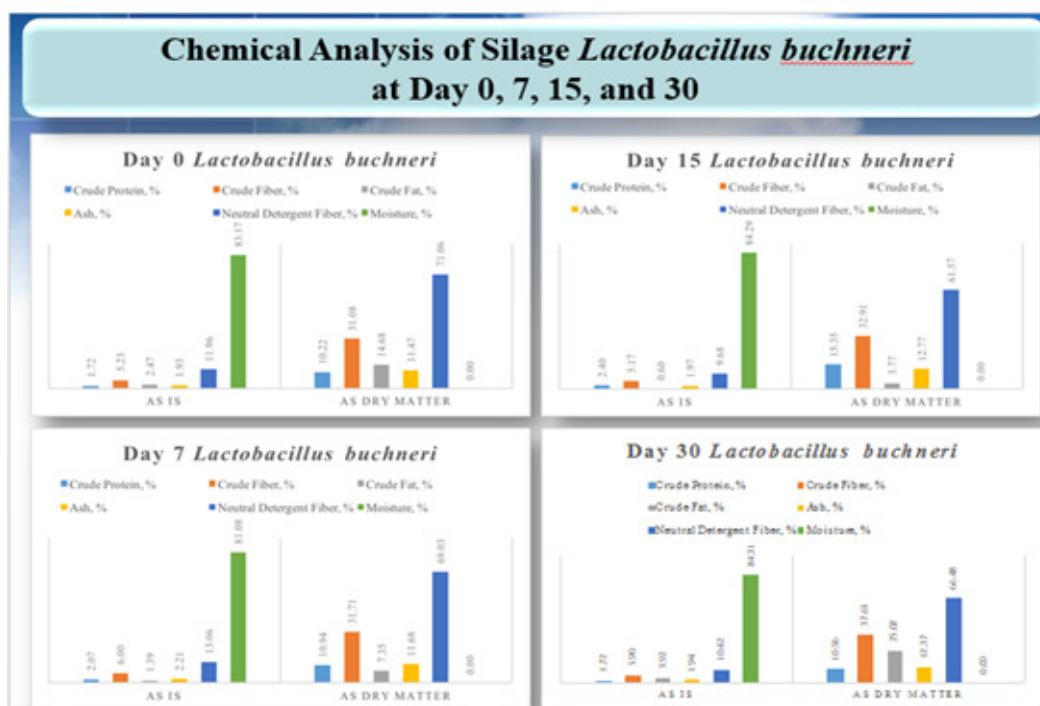


Figure 2. Graphical Presentation of Super Napier Grass Silage Treated with *L. buchneri* from day 0 to day 30 of Fermentation.

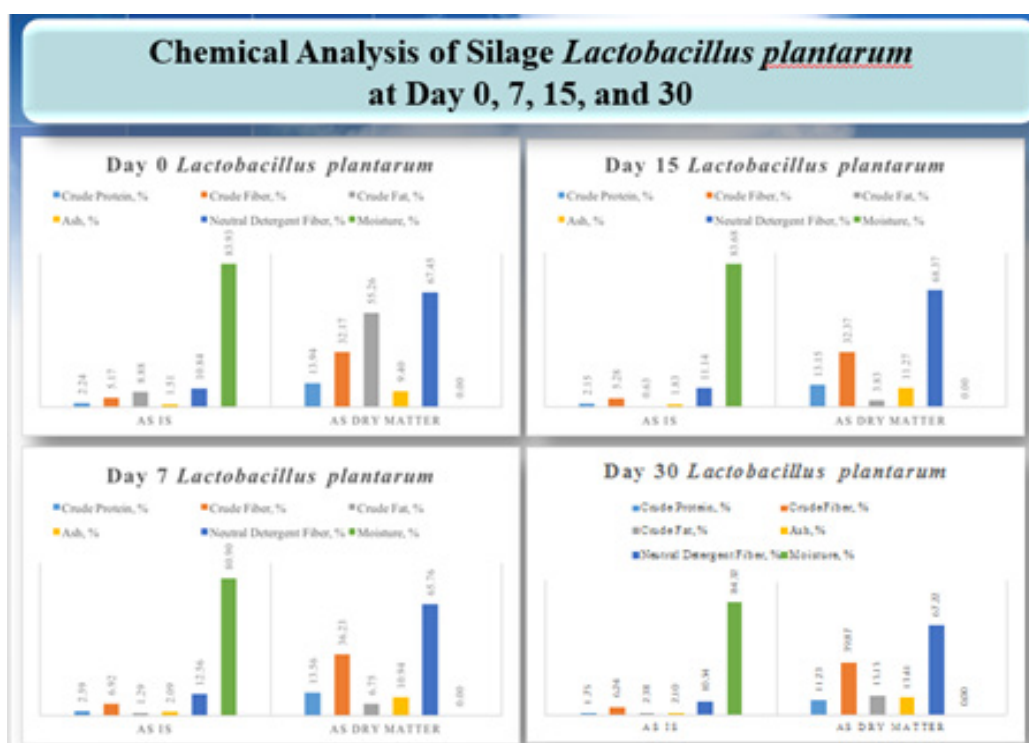
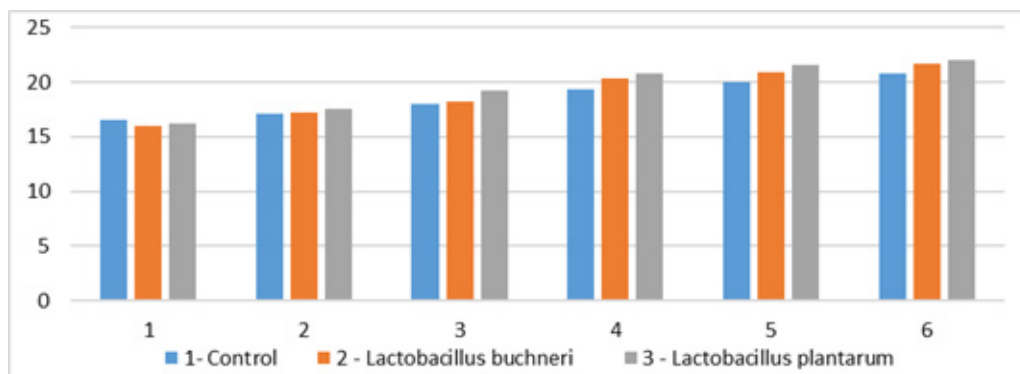


Figure 3. Graphical Presentation of Super Napier Grass Silage Treated with *L. Plantarum* from day 0 to day 30 of Fermentation.

Table 3. Initial Body Weight and Bi-Weekly Body Weight of Sheep Fed with Silage.

TREATMENTS	Ave. Bi-weekly Body Weight (BW), kg.					
	Initial	0-14	15-28	29-42	43-56	57-70
1- Control	16.50	17.05	17.95	19.30b	20.05b	20.75b
2 - <i>Lactobacillus buchneri</i>	16.00	17.20	18.25	20.35a	20.85b	21.70b
3 - <i>Lactobacillus plantarum</i>	16.25	17.50	19.20	20.75a	21.55a	22.05a
Result	ns	ns	ns	*	*	*
% C.V.	6.09	5.67	5.23	4.02	3.83	3.51

Means with common letter are not significantly different with each other using LSD

**Figure 4.** Graphical Presentation on Bi-weekly Body Weight of Sheep Fed with Super Napier Grass Silage.

acid to acetic acid and 1, 2 propanediol.

Although the result are encouraging, it should be noted that other literature reports varied markedly among due to environmental factors. The variability in results from this experiments involving silage fermentation indicates that further evaluations are necessary to broaden the database of additives for the ensilage of super Napier grass.

Growth Rate Performance of Sheep

The health and vigor of the experimental sheep were generally normal throughout the duration of the feeding trial. No apparent signs or symptoms of diseases were observed.

Body Weight.

Significant differences were noted on the body weight of the experimental sheep (Table 3 and figure 4). At the end of the 42nd day of feeding, significant differences ($P < 0.05$) was noted among the different treat-

ments. Treatment 2 and 3 significantly had a higher BW over Treatment 1 (control) but no significant difference was observed between Treatment 2 and 3. Though similar growth pattern was observed, the result at the end of the 56th day of feeding revealed that Treatment 3 obtained the heaviest BW that is significantly heavier than T2 and T1 (control).

At the end (70th day) of the feeding trial, Treatment 3 with *Lactobacillus buchneri* was observed to be significantly heavier ($P < 0.05$) than Treatment 2 with *Lactobacillus plantarum* and 1 (control without additives). Although Treatment 2 and 1 were statistically the same, there is a clear indication that sheep fed SNG treated silage (T2) is numerically higher than the sheep fed with untreated silage (T1). The higher BW of sheep fed with SNG treated silage might be due to the additives that could have improved digestibility resulted to higher nutrient intake as the result to rapid rate of fermentation

occurring in the rumen This observation is supported by the findings of Kung & Ranjit (2001) that animals respond positively to microbial inoculants for ensiling in terms of intake, gain, and milk production.

Result of the study showed that feeding of super Napier grass silage was higher than the sheep fed with untreated silage as similar with the studies conducted by Khaini et al., (2015) in cattle reported that feeding of silage influenced steer growth rate. The result of the study on the feeding of silage to sheep was supported by the studies of Kung & Ranjit (2001) with corn silage as the main source of feed for cattle but also as a combination with other forages including pasture grass. Studies on the effect of lactic acid bacteria (LAB) on animal performance indicated that feeding cattle with silages treated with LABs improve ruminant performance. Likewise, in several trials conducted by Muck (1993) reported that inoculants exhibited substantial effect on performance on live weight gain, milk production, increase in intake and feed efficiency. This suggest the ensiling of SNG with microbial inoculants to improve the nutritional quality of SNG especially when there is abundant supply of grasses and feeding them to sheep during summer time when there is scarcity of roughages.

Feed Consumption.

The average bi-weekly DM intake of silage of the experimental animals is shown in Table 4 and graph-

ically presented in Figure 5. Non-significant result was observed on the DM intake of silage on the early stages(14th to 28th) of the experiment but results showed significant variation ($P<0.05$) as noted on the 29th to 42th day of feeding period but from 56th to 70th day of feeding, significant differences ($P<0.01$) were noted among the experimental animals. The cumulative feed consumption likewise showed significant ($P<0.01$) differences among the treatments.

Based on the result of the feeding trial, the DMI increased linearly with the silage containing inoculants. This could be due to the higher palatability and good fermentation characteristics of feeds which attracted the sheep to consume more amount of SNG silage. Another reason for the increased in the DM intake of the feed might be due to the chemical composition of the SNG silage and probably due to higher amount of fermentable carbohydrate and energy which increases the digestibility of the SNG silage with inoculants. Likewise, the DM intake differences may be attributed to rapid rate of fermentation occurring in the rumen. In a study conducted by Wiese et al., (2013) on the growth and carcass characteristics of prime lambs fed diets containing urea, lupines or canola meal as a crude protein source, he reported that higher DMI was due to a better availability of nutrients which are readily been degraded by rumen microbes.

Table 4. Average Bi-weekly and Total Dry Matter Intake of experimental animals (kg.)

TREATMENTS	Ave. Bi-weekly Body Weight (BW), kg.					
	0-14	15-28	29-42	43-56	57-70	Total
1- Control	8.51	9.05	9.70b	10.05bc	10.40b	47.71b
2 - <i>Lactobacillus buchneri</i>	8.70	9.65	10.15b	10.70ab	11.15a	50.35b
3 - <i>Lactobacillus plantarum</i>	8.80	10.00	10.35a	10.80a	11.25a	51.20a
Result	ns	ns	*	**	**	*
% C.V.	6.18	6.18	4.12	3.43	6.09	3.98

Means with common letter are not significantly different with each other using LSD

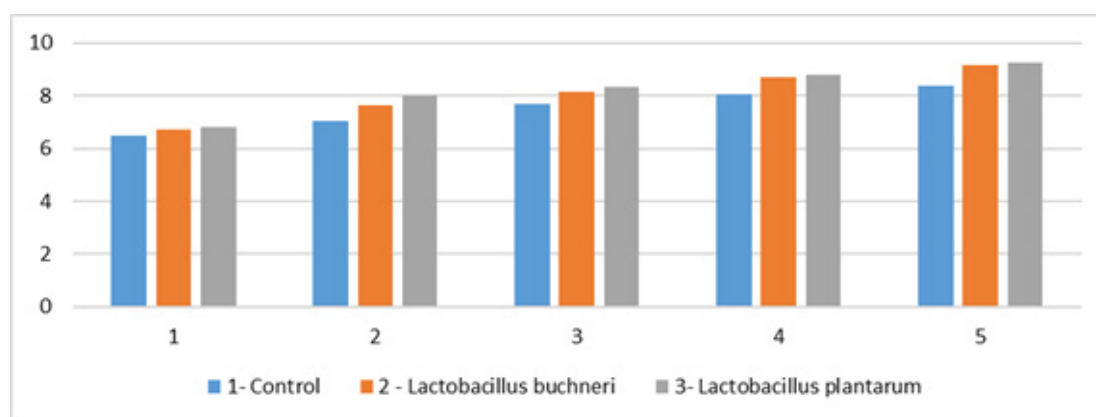


Figure 5. Graphical Presentation on Bi-weekly Feed Consumption (DM) of Sheep Fed with Super Napier Grass Silage

Table 5. Average Body Weight Gain (ABW), Average Daily Gain (ADG), Dry Matter (DM) intake, and Feed Conversion Rate (FCR) of sheep fed with SNG silage.

TREATMENTS	Ave. Bi-weekly Body Weight (BW), kg.				
	Body Wt. Gain (Kg.)	ADG, Grams	DM intake (Kg.)	FCR (DM)	57-70
1- Control	4.25b	60.72b	47.71b	8.94b	10.40b
2 - <i>Lactobacillus buchneri</i>	5.60a	80.00a	50.35b	7.26ab	11.15a
3 - <i>Lactobacillus plantarum</i>	5.80a	82.85a	51.20a	7.21a	11.25a
Result	**	**	*	**	**
% C.V.	3.98	6.50	5.79	10.24	6.09

Means with common letter are not significantly different with each other using LSD

Body Weight Gain, Average Daily Gain, DM Intake and Feed Conversion Ratio.

Table 5 present the total body weight (BW) gain, average daily gain, dry matter intake and feed conversion ratio of sheep fed silage diet during the 70 days of feeding trial. Significant differences ($P < 0.01$) were observed among treatments on the total BW gain of sheep fed with SNG Silage treated with additives. The average daily gain (ADG) as a measure for growth also revealed significant ($P < 0.01$) differences among the treatments. The positive improvement of Treatment 2 and 3 was the result of higher nutritive values of silages with additives as compared to the silages without additives. This implies that *Lactobacillus buchneri* and *Lactobacillus plantarum* (T2 and T3) additives can improve quality of silages that can provide higher nutritive value and therefore influence growth rate of sheep.

Sheep fed with SNG silage diet treated with *Lactobacillus plantarum* additives (T3) was the most efficient feed converter and this could be due to higher levels of nutrients as reflected in the chemical composition of silages at 7 days of treatment.

The result of the study on the feeding of silage to sheep was also supported by the studies of Kung & Shaver (2001) with corn silage as the main source of feed for cattle but also as a combination with other forages including pasture grass. Weinberg (2013) described the effect of lactic acid bacteria (LAB) on animal performance that feeding cattle with silages treated with LABs improve ruminant performance. Likewise, in several trials conducted by Spoelstra (1992) and Muck (1993) reported that inoculants exhibited substantial effect on performance on live weight gain, milk production, increase in intake and feed efficiency. Result of the study

was similar with the studies conducted by Khani et al., (2015) in cattle that feeding of silage influenced steer growth rate. This suggest the ensiling of SNG with microbial inoculants to improve the nutritional quality of SNG especially when there is abundant supply of grasses and feeding them to sheep during summer time when there is scarcity of roughages. In conclusion, these studies confirmed that the applying of inoculants improved fermentative quality, feed intake and digestibility of Napier grass (Bureenok et al., 2012).

CONCLUSION AND RECOMMENDATION

The trial revealed that there is a great potential for improvement with the addition of beneficial

microbes such *Lactobacillus buchneri* and *Lactobacillus plantarum* as it improves nutritional quality of SNG silage thus influenced ruminant animals (sheep) growth rate performance, average daily gain (ADG), DM feed intake and feed efficiency.

It is recommended that more research is needed to broaden the database of additives for the ensilage of SNG and to determine the nutrient digestibility and the combination of grasses to silage to reduce feed costs. Likewise, there is a need to find out if there is a deleterious effect to the end product's taste, tenderness, palatability and overall acceptability of mutton. However more research is needed to elucidate the mode of action of SNG treated silages.

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Natural rubber-based mechanical modifiers for poly (lactic acid)Wasan Tissanan¹ and Pranee Phinyocheep^{1*}

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Abstract

Poly(lactic acid) (PLA), a compostable and biodegradable polymer, is a high-brittle polymeric material. Therefore, mechanical property improvement of the PLA is challenging by utilization of natural rubber (NR), a green elastomeric and renewable materials. In this study, NR and chemically modified NR to epoxidized NR (ENR) are explored as impact modifiers for the PLA. The as-prepared ENR with 30 mol% epoxide content (E30NR) and NR are melt-blended with PLA at various rubber contents (1 to 5 wt.%). The result illustrates the concurrent increment in elongation ability and impact performance of PLA, approximately elevenfold and twofold, respectively, with adding 5 wt.% E30NR compared with those of NR/PLA blends with the same rubber content. In addition, the 5 wt.% E30NR is an efficient impact modifier for PLA as the elongation at break and the impact strength is increased approximately fifteen and four times, respectively, compared to the PLA. The E30NR/PLA blends launch superior modulus and strength when compared to NR/PLA blends. Furthermore, E30NR/PLA films transparency demonstrated from transmittance percentage shows higher transparency than NR/PLA blend films. Consequently, NR-based utilization as a mechanical modifier could be considered a sustainable and alternative way for the value-added of NR and increment of PLA's applications.

Keywords: Impact modifier; Natural rubber; Poly(lactic acid); Sustainable development

Introduction

Natural rubber (NR) is a bio-based and renewable material received from the *Hevea brasiliensis* tree, consisting mainly of cis-1,4 isoprene units (Toki et al., 2002). NR has a number of outstanding aspects, for instance, high flexibility and high tensile strength, as well as biodegradability (Smitthipong et al., 2016). Therefore, it has been utilized as a raw material in several products, ranging from personal protective equipment and medical devices to car and aircraft tires (Thomas & Mathew, 2011). The rubber plantations of Thailand are distributed across all regions of the country. It is one of the agricultural products with mass production in Thailand, the world's largest natural rubber producer (Pyay et al., 2019). Over the years, the high rubber production rate has severely unbalanced the demand and supply gap resulting in a dramatic drop in natural rubber prices. In addition, the unsaturated hydrocarbon structure of NR causes some drawback properties such as low heat and

thermal resistance, and low oil resistance. Therefore, modification of NR structure has been widely studied to improve these disadvantages, and widen its area of applications. For instance, hydrogenation and epoxidation are chemical modification techniques to increase the heat resistance and oil resistance of the rubber (Saengdee et al., 2020). Furthermore, the development of NR for the additive in plastic is an emerging and interesting challenge. This concept of NR's utilization is considered for the value-added of rubber and the increasing plastic applications.

Poly(lactic acid) (PLA), a compostable and biodegradable polymer, is obtained from natural feedstocks, such as rice, corn, and wheat with clean-productive manufacturing (Hamad et al., 2015). Nowadays, we are facing plastic waste problem from petroleum-based plastic as it is not compostable and required several years for partial degradation. Therefore, the PLA has been increasingly demanding for various plastic prod-

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ucts. However, the PLA is a high-brittle plastic because of high glass transition temperature (T_g) approximately 55-60 °C, limiting its applications (Becker et al., 2010). Blending of an elastomeric material with the PLA is one of the techniques to improve the performance of PLA. NR which is a bio-based and renewable material mentioned earlier, is a good candidate to toughen the PLA. However, the effectiveness of NR for toughening PLA is still insufficient due to the poor interfacial interaction coming from the difference in the polarity between NR and PLA phases (Bitinis et al., 2011). Consequently, several researchers have dedicated to modifying NR-based products to improve the mechanical performance of PLA. Many types of the as-prepared rubbers by the escalating polarity of rubber, such as NR grafted with poly(butyl acrylate) (Zhang et al., 2011), NR grafted with glycidyl methacrylate (Juntuek et al., 2012), hydroxyl epoxidized NR (Phetphaisit et al., 2019), and epoxidized hydrogenated NR (Tessanan et al., 2020), have deliberately been utilized for blending PLA. Nowadays, many attempts to improve PLA's mechanical properties using NR and its derivatives have been paid to increase the value-added NR and widespread applications of PLA. This concept may be regarded as a sustainable way for practical development.

In this work, epoxidized NR was prepared via epoxidation reaction under the latex medium, and it is considered a green process (Tessanan et al., 2020). The idea for attaching epoxide groups is to increase the polarity of rubber. Epoxidized NR containing 30 mol% epoxide content (E30NR) is prepared, and the chemical structure of as-synthesized E30NR is asserted using Four-

rier-transform infrared spectroscopy (FTIR) and proton Nuclear Magnetic Resonance ($^1\text{H-NMR}$) spectroscopy. Afterward, the E30NR is physically melt-blended with PLA by various rubber contents (i.e., 1, 3, and 5 wt.%) using an internal mixer. Mechanical properties (tensile and impact performances) of polymer blends system are investigated. Moreover, the film transparency of ENR/PLA blends is conducted to ensure the mechanical improvement of PLA. Unmodified NR/PLA blends are also prepared in the same weight ratios to compare their performance with the E30NR/PLA blends system.

Experimental procedure

Materials

PLA (2003D) produced from NatureWorks Co. Ltd., USA with melt flow index (MFI) of 6.0 g/10 min (190 °C/2.16 kg). High ammonia natural rubber (HANR) latex was received from Thai Rubber Latex Co. Ltd., Thailand. Hydrogen peroxide (35%w/w) was supplied by QRec, New Zealand. Formic acid was purchased from Carlo Erba Reagent, USA.

Preparation of epoxidized NR

Epoxidized NR was prepared in the latex stage, a green process, with a condition following Tessanan and co-workers (Tessanan et al., 2020). Briefly, 0.15 mol formic acid and 0.62 mol hydrogen peroxide were simultaneously added into 600 mL NR latex (20%DRC) at 60 °C for 20 h. At the end of reaction, epoxidized NR was received and coagulated by methanol followed by several times of washing by water. The schematic preparation of epoxidized NR is shown in Figure 1.

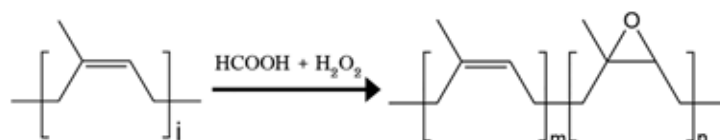


Figure 1. Schematic preparation of epoxidized NR in latex stage

Rubber/PLA blends

PLA and rubbers (NR and E30NR) were dried in a vacuum oven at 50 °C for 48 h to remove humidity. PLA pellets were melt-blended with various amounts of rubber content ranged from 1 to 5 wt.% using an internal mixer (HAAKE™ Rheomix 90). The mixing condition was operated at 170 °C with a 50rpm rotor speed for 15 min. The blend compositions are summarized in Table 1. After the end of mixing, the blends were taken out and cooled to ambient temperature before grinding by a grinder machine. All granulated rubber/PLA blends were dried in a vacuum oven at 40 °C for 48 h and kept in the desiccator.

Characterizations

Chemical structure of NR and E30NR was analyzed by FT-IR analysis (Perkin Elmer-2000). An attenuated total reflectance infrared (ATR-IR) mode was operated in the range of wavenumber between 4000-400 cm^{-1} with 32 scans and a resolution of 4 cm^{-1} . $^1\text{H-NMR}$ analysis (AM 400 spectroscopy 300 MHz) was utilized to assert the chemical structure of modified NR. 10 mg of sample was dissolved in deuterated chloroform (CDCl_3) for measurement. The percentage of epoxidation of E30NR was calculated from the integrated peak areas from $^1\text{H-NMR}$ spectrum following equation (1).

$$\% \text{ Epoxidation content} = \left[\frac{A_{2.70}}{A_{2.70} + A_{5.10}} \right] \times 100 \quad (1)$$

$A_{2.70}$ and $A_{5.10}$ are the integrated peak areas of methine protons adjacent to the epoxide and methine protons of the double bond units.

Thermal decomposition of rubber was measured by a thermal gravimetric analyzer (Mettler, Q500/TA Instrument). Approximately 10 mg of rubber was performed with heating from 40 °C to 600 °C using a heating rate of 10 °C/min under nitrogen atmosphere.

Thermal transition relaxation of samples was investigated by using a differential scanning calorimeter (Perkin Elmer DSC 7). Rubbers were carried out from 40 °C to 600 °C by a heat-cool-heat cycle with a heating rate of 10 °C/min.

Uniaxial tensile behavior of PLA blends was operated following ASTM D882 using a universal testing machine (Instron 5566). Twelve rectangular sheets with dimensions 10×90×0.5 mm^3 were measured at 50 mm/min crosshead speed with static load cell of 1 kN under room temperature (25 ± 2 °C).

Impact performance was carried out following ASTM D256 by impact tester (Zwick 5102 Pendulum). Six specimens were notched and operated under the Izod mode test at room temperature (25 ± 2 °C).

Transparency of PLA blend films was determined by a UV-Vis spectrophotometer (JASCO V-530, Perkin Elmer) with the 400 to 700 nm scanning wavelength. The 100- μm film thickness was prepared by compression molding at 170 °C for 2 min under the 105 bars pressure.

Table 1. Rubber/PLA blend compositions.

Samples	PLA (wt.%)	NR (wt.%)	E30NR (wt.%)
Neat PLA	100	-	-
NR/PLA (1/99)	99	1	-
NR/PLA (3/97)	97	3	-
NR/PLA (5/95)	95	5	-
E30NR/PLA (1/99)	99	-	1
E30NR/PLA (3/97)	97	-	3
E30NR/PLA (5/95)	95	-	5

Results and discussion

Chemical structure and thermal properties of epoxidized NR

FTIR spectra of NR and E30NR are illustrated in Figure 2. NR spectrum demonstrates the specific absorption peaks at 1664 and 836 cm^{-1} , belonging to $\text{C}=\text{C}$ stretching and $\text{C}=\text{C}-\text{H}$ out-of-plane bending vibrations, respectively (Fig. 2a). After the epoxidation reaction, the epoxidized NR spectrum still shows NR's characteristic peaks, and, moreover, it provides the new peaks at 1245 and 875 cm^{-1} , attributing to symmetric and asymmetric $\text{C}-\text{O}-\text{C}$ stretching vibrations, respectively. Moreover, there is a slight decline in the intensity variation of carbon-carbon-double bond peaks observed at 1664 cm^{-1} , compared to the absorption peak at 1375 cm^{-1} (CH_3 bending vibration) of the epoxidized NR spectrum. It can

illustrate the change in unsaturation units into epoxide units of rubber after epoxidation reaction. Figure 3 shows $^1\text{H-NMR}$ spectra of NR and E30NR. As a result, NR reveals the unique signals at 5.10 ppm (a), 2.03 ppm (a'), and 1.67 ppm (a''), belonging to methine protons nearby isoprene unit, methylene protons, and methyl protons, respectively. Meanwhile, epoxidized NR still shows the characteristic signal of the virgin NR and observed the two-new peaks at 1.30 ppm (c), and 2.70 ppm (d), assigning to methyl protons and methine protons of the epoxide ring, respectively (Phinyocheep et al., 2005; Samran et al., 2005). In addition, as calculated epoxide content following equation (1), the epoxidized NR consists of 29.63 mol\% epoxide content and is defined as E30NR.

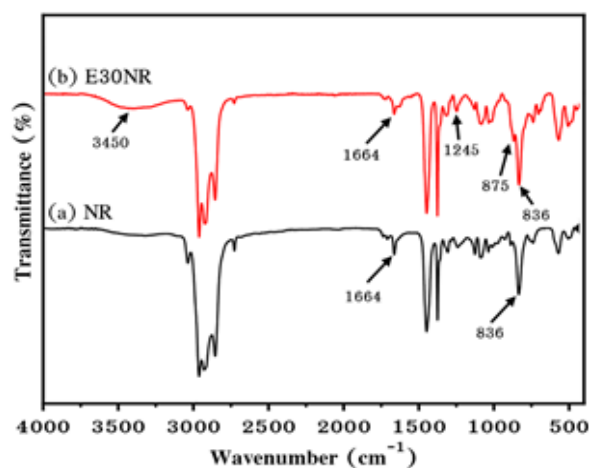


Figure 2. FT-IR spectra of (a) NR and (b) E30NR.

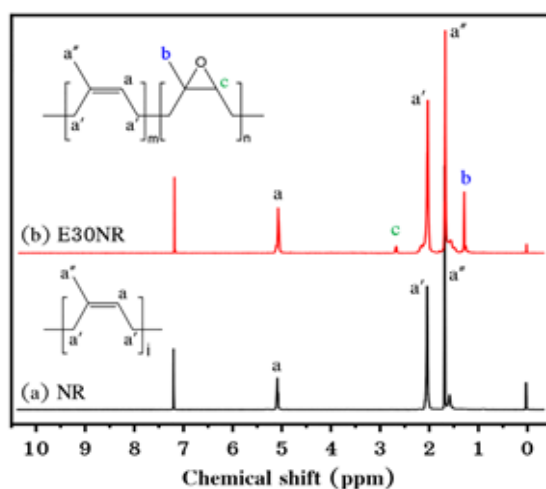


Figure 3. $^1\text{H-NMR}$ spectra of (a) NR and (b) E30NR.

Thermal resistance of rubbers was evaluated by TGA analysis, as presented in Figure 4. The decomposition temperature, including onset decomposition temperature (T_o), fastest decomposition temperature (T_f), and final decomposition temperature (T_n) of rubbers, were measured. The results show that NR begins to decompose at approximately 290 °C and undergoes the fastest decomposition rate at about 348 °C before it completes at approximately 425 °C. The thermal resistance of E30NR is demonstrated at approximately 312 °C (T_o), 364 °C (T_f), and 442 °C (T_n). The attaching epoxide groups along the NR backbone provides higher thermal-resistant material. This result may be due to the characteristic nature of epoxide-based material, having high chemical and thermal resistance (Sun et al., 2018).

Furthermore, the thermal relaxation behavior of rubbers (NR and E30NR) was conducted using DSC analysis, as shown in Figure 5. The T_g of NR appeared at approximately -65 °C. After the epoxidation reaction, the T_g of NR shifts from -65 °C towards the high-temperature zone at -34 °C (E30NR). This phenomenon can be described to the attaching rigid-epoxide ring onto NR molecular chains, resulting in the restriction of the segmental-chain motion (Hamzah et al., 2016).

Mechanical properties

Tensile properties (Young's modulus, Tensile strength, elongation at break) of rubber/PLA blends system are demonstrated in Figure 6-8. Young's modulus and tensile strength of neat PLA are 2.00 GPa and 62.4 MPa, respectively, with only 6.18% elongation at

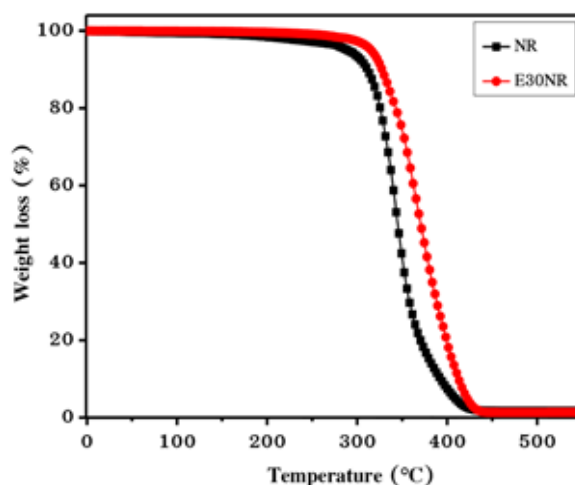


Figure 4. Thermal decomposition of (a) NR and (b) E30NR.

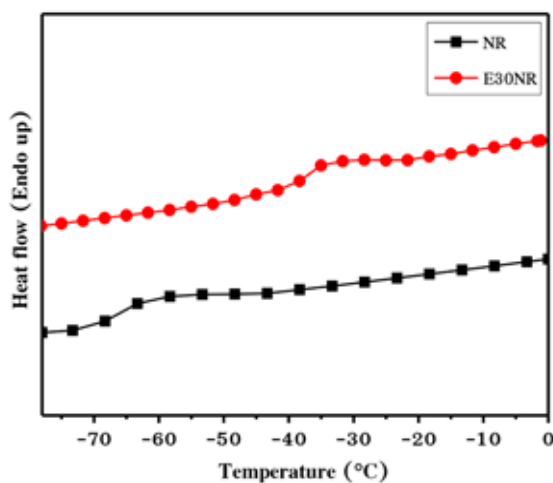


Figure 5. DSC thermograms of (a) NR and (b) E30NR.

break. The addition of rubber reduces the modulus of PLA in the blends with increasing rubber contents. The moduli values tend to reduce from 2.00 GPa (neat PLA) into 1.61 GPa (NR/PLA blend) and 1.75 GPa (E30NR/PLA blend) containing 5 wt.% rubber (Figure 6). The E30NR/PLA blends at different rubber content have higher moduli than the NR/PLA blends at the same rubber content. Figure 7 illustrates the gradual reduction of the uniaxial tensile strength by adding rubber contents. The strength values decline from 62.4 MPa (neat PLA) down to 34.65 MPa (NR/PLA blend) and 40.60 MPa (E30NR/PLA blend), consisting of 5 wt.% rubber. The E30NR/PLA blends provide higher values of strength compared to that of NR/PLA blends, followed by PLA. This result could be explained due to the addition of elastomeric material into the hard-brittle polymer, leading to the

decrement in stiffness and strength (Bitinis et al., 2011; Zhang et al., 2011). The improving polarity of rubber in E30NR can escalate the interfacial interaction between rubber and PLA phases, resulting in the improving modulus and strength compared to NR/PLA blends (Rosli et al., 2016). Considered on elongation ability as displayed in Figure 8, NR/PLA blends increase slightly from 6.18% (neat PLA) to 8.49% (5 wt.% NR). Meanwhile, E30NR/PLA blends upsurge to 89.38% (5 wt.% E30NR). At 5 wt.% rubber content, the elongation ability of E30NR/PLA blend is elevenfold and fifteenfold when compared to NR/PLA blend and neat PLA, respectively. As a result, it can attribute that the improving polarity of NR with epoxide groups could enhance the compatibility between rubber and PLA matrix.

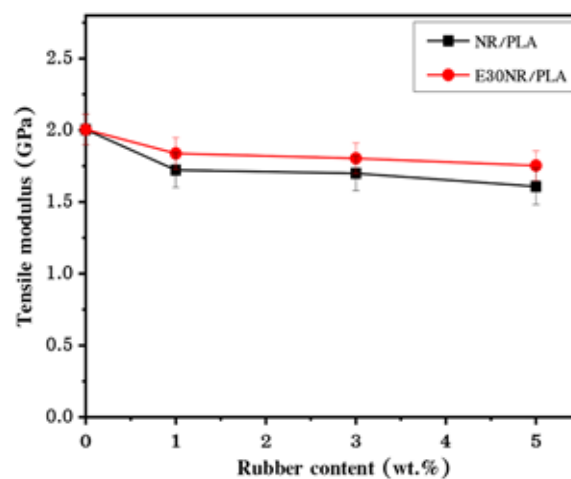


Figure 6. Tensile modulus of rubber/PLA blends at various rubber contents (0 to 5 wt.%).

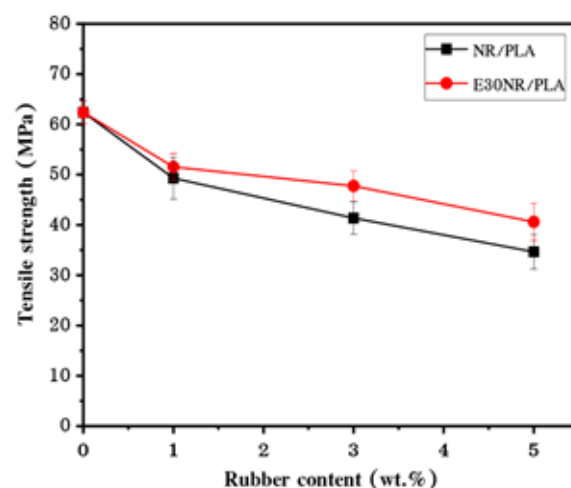


Figure 7. Tensile strength of rubber/PLA blends at various rubber contents (0 to 5 wt.%).

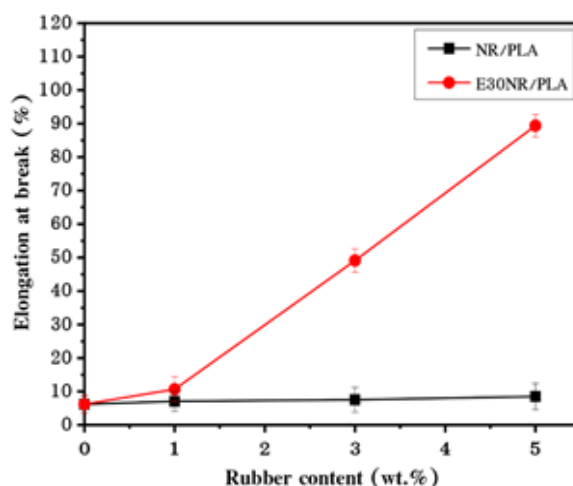


Figure 8. Elongation at break of rubber/PLA blends at various rubber contents (0 to 5 wt.%).

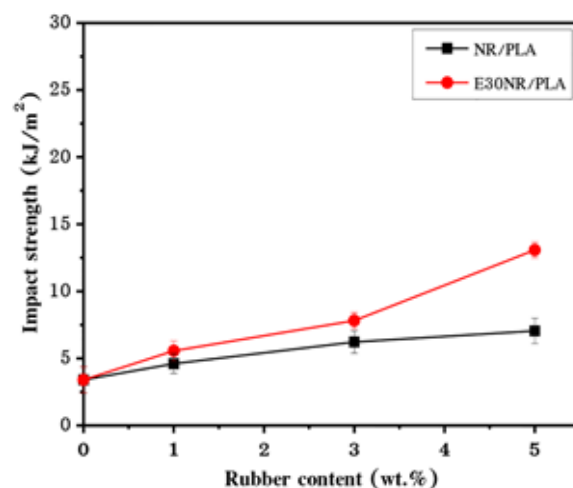


Figure 9. Impact properties of rubber/PLA blends at various rubber contents (0 to 5 wt.%).

The brittleness of the plastic is normally considered by the impact property. The PLA has low impact strength which limit its application. The addition of a soft material should improve its impact strength. Figure 9 shows the impact strength of the rubber/PLA blends system. The addition of rubbers (NR and E30NR) can escalate the toughness of PLA because the elastomeric nature of rubber can act as a stress concentrator for dissipating energy obtained from an external force (Bitinis et al., 2011; Rosli et al., 2016). NR/PLA blends with NR contents (1 to 5 wt.%) reveal the slight increment in the impact strength from 3.40 kJ/m² (neat PLA) towards 7.05 kJ/m² (5 wt.% NR content). In terms of E30NR/PLA blends, the impact strength values boost to the maximum value at 13.08 kJ/m² by adding E30NR contents up to 5 wt.%. The impact performance of E30NR/

PLA (5/95) increases about twofold compared to NR/PLA (5/95) blends and fourfold compared to the neat PLA. This significant enhancement can ascribe to a decrement in interfacial tension and an increment of segmental interaction between the modified rubber and the PLA matrix (Tessanan et al., 2020).

Optical properties

Transparency of plastic sheet is defined as the transmission of visible light in the short range of 540-560 nm, according to ASTM-D1746-03 (Mathlouthi, 1994). The 550-nm wavelength had been chosen to investigate the transmittance percentage of neat PLA and rubber/PLA blend films, as presented in Figure 10. The light transmittance of neat PLA was found at 91.30%, typically high transparent material. The light transmittance of films is reduced with the addition of rubbers (1

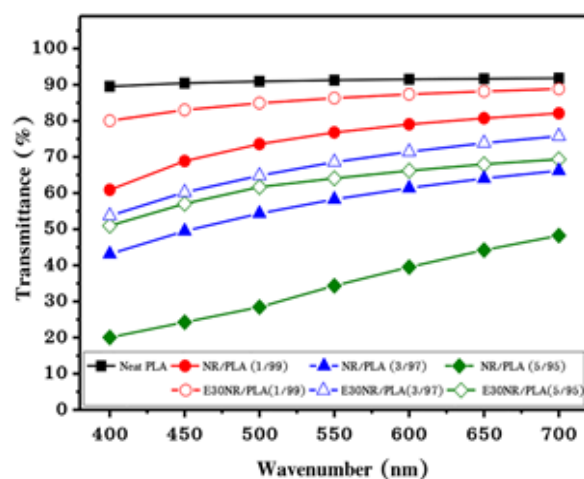


Figure 10. Transmittance percentage of rubber/PLA blend films at various rubber contents (0 to 5 wt.%)

to 5 wt.%). NR/PLA blend films provide light transmittance ranging between 34.34% (5 wt.% NR) to 76.79% (1 wt.% NR). Meanwhile, E30NR/PLA blend films reveal between 64.08% (5 wt.% E30NR) to 86.30% (1 wt.% E30NR). It could be explained that the incompatibility of NR and PLA results in the film's heterogeneity, leading to a decrement of the light transmittance. However, the enhancing polarity of NR to E30NR can escalate the partial compatibility between rubber and PLA, resulting in improved film transparency.

Conclusions

The enhancing potential and effectiveness of NR and modified NR, as mechanical modifiers, for the brittle PLA is still an interesting challenge. In this work, the NR and as-synthesized E30NR were utilized for improving the mechanical properties of PLA. The result reveals the dramatic enhancement in elongation ability and impact performance with the addition of E30NR when compared to NR. The NR could increase slightly

the mechanical properties of the PLA while the E30NR is an efficient impact modifier for PLA. In particular, the 5 wt.% E30NR/PLA could enhance the elongation at break and the impact strength, approximately fifteen and four times, respectively, compared to the neat PLA. Furthermore, the film transparency is improved for E30NR/PLA blends compared to NR/PLA blends. This development was performed to reach the way for high value-added and new potential application of NR as well as PLA, supporting the sustainability concept for saving the Earth.

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