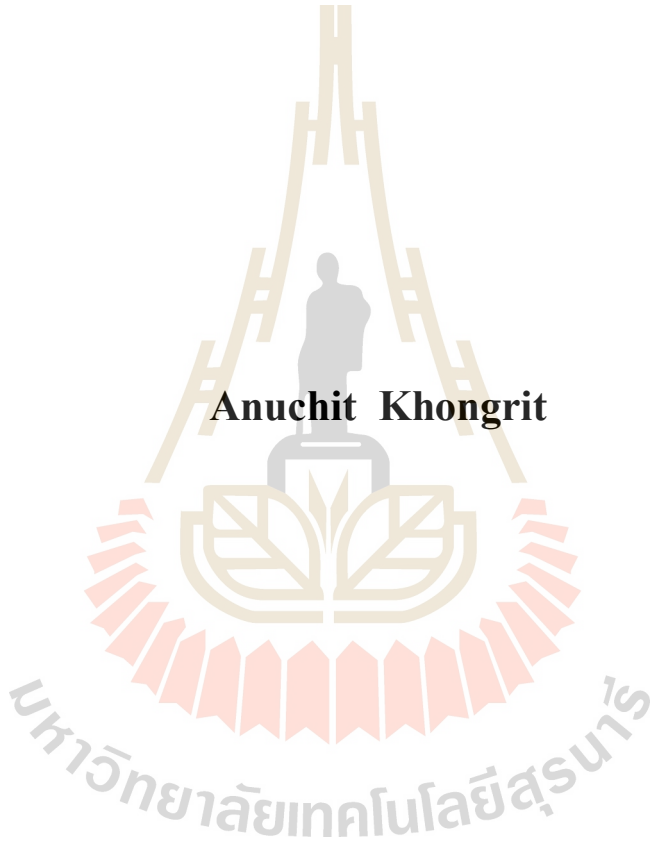
WOOD COMPOSITE BASED ON CROSSLINKED POLYPROPYLENE

Anuchit Khongrit



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ไม้ประดิษฐ์เชิงประกอบจากพอลิโพรพิลีนระบบร่างแห

นายอนุชิต คงฤทธิ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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WOOD COMPOSITE BASED ON CROSSLINKED POLYPROPYLENE

Suranaree University of Technology has approved this thesis submitted in partial fulfillments of the requirement for a Master's Degree.

Thesis Examining Committee

Nitinat Suppakarn

(Asst. Prof. Dr. Nitinat Suppakarn)

Chairperson

(Asst. Prof. Dr. Utai Meekum)

Member (Thesis Advisor)

(Asst. Prof. Dr. Wimonlak Sutapun)

Member

(Prof. Dr. Sukit Limpijumnong)

Vice Rector for Academic Affairs

(Assoc. Prof. Flt. Lt. Dr. Kontorn Chamniprasart)

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อนุชิต คงฤทธิ์ : ไม้ประดิษฐ์เชิงประกอบจากพอลิโพรพิลีนระบบร่างแห (WOOD COMPOSITE BASED ON CROSSLINKED POLYPROPYLENE) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.อุทัย มีคำ, 178 หน้า.

การศึกษาสูตรการผลิตไม้ประดิษฐ์เชิงประกอบที่มีพอลีโพรพิลีนโครงสร้างร่างแหเป็นเมทริกซ์ โดยวิธีการเชิงสถิติแบบการทดลองแบบพหุคูณ (2^k) พบว่าจะต้องใช้ปริมาณของไวนิลไซเลนและผงไม้ที่ระดับสูง และใช้ปริมาณผงทาล์คัมที่ระดับต่ำ ผลของการเติมพอลีเอทธิลีนที่มีค่าน้ำหนักโมเลกุลสูงยิ่งยวด (UHMWPE) และส่วนผสมระหว่างพอลีเอทิลีนที่มีค่าน้ำหนักโมเลกุลสูงยิ่งยวด และ ยางสังเคราะห์เอทธิลีนโพรพิลีนไดเมอร์ (EPDM) ลงในสูตรไม้ประดิษฐ์เชิงประกอบ พบว่าการเติมพอลีเอทิลีนที่มีค่าน้ำหนักโมเลกุลสูงยิ่งยวดในปริมาณที่สูง มีผลทำให้ความเหนียวของชิ้นงานลดลง เนื่องจากเม็ดผงพอลีเอทิลีนที่มีค่าน้ำหนักโมเลกุลสูงยิ่งยวดเกิดเกาะเป็นกลุ่มขนาดใหญ่ ปริมาณการใช้พอลีเอทิลีนที่มีค่าน้ำหนักโมเลกุลสูงยิ่งยวดที่เหมาะสมเท่ากับ 10 ส่วนโดยน้ำหนัก การเติมยางสังเคราะห์เอทธิลีนโพรพิลีนไดเมอร์เพื่อเพิ่มความเหนียวของชิ้นงานไม้ประดิษฐ์เชิงประกอบ ทำให้ค่าแรงต้านการตกกระแทกเพิ่มขึ้น แต่จะทำให้อุณหภูมิการบิดงอมีค่าลดลง ดังนั้นจากผลการทดลองจึงแนะนำให้ใช้ปริมาณของยางสังเคราะห์ไม่เกิน 10 ส่วนโดยน้ำหนัก

ผลของปริมาณไดคิวมิลเปอร์ออกไซด์ที่ใช้เป็นตัวริเริ่มปฏิกิริยาอนุมูลอิสระ สำหรับปฏิกิริยาการเกิดโครงสร้างร่างแหของพอลีโพรพิลีนในวัสดุเชิงประกอบ พบว่าการเพิ่มปริมาณไดคิวมิลเปอร์ออกไซด์ทำให้คุณสมบัติเชิงกลและคุณสมบัติเชิงความร้อนลดลง นอกจากนั้นผลการศึกษาปริมาณของไวนิลไซเลนก็แสดงให้เห็นว่าค่าความแข็งแกร่งเชิงกลและคุณสมบัติเชิงความร้อน เพิ่มมากขึ้นตามปริมาณการใช้สารไวนิลไซเลนที่เพิ่มมากขึ้น และความสามารถในการเกิดโครงสร้างร่างแหก็มีค่าเพิ่มขึ้นตามปริมาณของสารคู่ควบไวนิลไซเลนด้วย สูตรการเตรียมไม้ประดิษฐ์เชิงประกอบจากพอลิโพรพิลีนโครงสร้างร่างแห่โดยใช้ปริมาณสารไวนิลไซเลน 15 ส่วน และ ไดคิวมิลเปอร์ออกไซด์ในปริมาณ 0.1 ส่วน โดยน้ำหนัก เป็นระบบสารก่อร่างแห จะทำให้ได้คุณสมบัติของไม้ประดิษฐ์โดยรวมที่ดี การใช้พอลิโพรพิลีนชนิดโคพอลิเมอร์ ผสมกับ โฮโมพอลิโพรพิลีน ในลักษณะของพอลิเมอร์ผสม เพื่อเพิ่มค่าความเหนียวของไม้ประดิษฐ์เชิงประกอบ พบว่ามีเพียงค่าคุณสมบัติความแข็งแกร่งต้านแรงกระแทกเท่านั้นที่มีค่าเพิ่มขึ้น ดังนั้น สัดส่วนที่แนะนำของพอลิโพรพิลีนโคพอลิเมอร์ใน

พอลิเมอร์ผสม เท่ากับร้อยละ 80 โดยน้ำหนัก วัสดุเชิงประกอบไม้ประดิษฐ์จากพอลิโพรพิลีนโซ่ร่างแหที่เตรียมได้มีคุณสมบัติความทนทานต่อการกัดกินของปลวกเทียบเท่ากับกับไม้สัก

สาขาวิชา วิศวกรรมพอลิเมอร์ ลายมือชื่อนักศึกษา 04ธ์ก

ปีการศึกษา 2554 ลายมือชื่ออาจารย์ที่ปรึกษา

ANUCHIT KHONGRIT : WOOD COMPOSITE BASED ON CROSSLINKED POLYPROPYLENE. THESIS ADVISOR : ASST. PROF. UTAI MEEKUM, Ph.D, 187 PP.

DESIGN OF EXPERIMENT/CROSSLINKED PP/FRACTURE TOUGHENER/ SILANE, DCP CROSSLINK SYSTEM AND SAUNA TREATMENT.

The study of composite material based on crosslinked PP by mean of the 2^k DOE approach found that the high level of silane, wood flour and lower talc contents must be followed. Adding UHMWPE and UHMWPE/EPDM were studied. It was found that agglomeration of UHMWPE at high contents were responsible for the lower in the toughness of the sample. The optimal dose of UHMWPE suggested from the study was at 10 phr. EPDM rubber as fracture toughener indicated that the more EPDM concentration the more improvement in impact strengths but vastly lower in the HDT. Only 10 phr of EPDM was recommended.

Effect of DCP as free radical initiator in the crosslinked PP based WPC was resolved. It was found that increasing DCP contents had lowered the mechanical and thermal properties. The further studied on the influence of VTMS reviewed that improvement of the mechanical strength and HDT of WPC was directly correlated with the silane addition. The increasing in the degree of crosslinking with increasing the coupling agent was adopted to explain. VTMS at 15 phr and 0.1 phr of DCP crosslink system was advised. Toughness enhancement of WPC by using PP copolymer blended with homo PP was attempted. It was found that only impact strength was achieved. PP copolymer fraction at 80% by weight was endorsed. WPC

derived from crosslinked PPs manifested as good as durability behavior in compare with the excellent termite resistivity teak wood.

School of Polymer Enginering

Student's Signature Anvchit

Academic Year 2011

Advisor's Signature

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SYMBOLS AND ABBREVIATIONS

%	=	Percent
^{o}C	=	Degree Celsius
µm	=	Micrometer
g	=	Gram
g/cc	=	Grams per centimetre cubed
g/cm^3	=	Gram per cubic centimeter
GPa	=	Gigapascal
hr	=	Hour
J	=	Joule
J/m	=	Joule per mater
keV	=	Kilo electron volt
kg	=	Kilogram
kGy	=	Kilogray
kJ	=	Kilojoule
kJ/m^2	=	Kilojoule pers quaremeter
kN	=	Kilonewton
Krad	=	Kiloradiation
mm	=	Milliliter
mm/min	=	Milliliter per Minute
min	=	Minute
m^2/g	=	Square meter per gram

SYMBOLS AND ABBREVIATIONS (Continued)

MPa	=	Megapascal
phr	=	Part per hundred resin
rpm	=	Revolution per minute
w/w	=	Weight by weight
wt%	=	Percent by weight

CHAPTER I

INTRODUCTION

1.1 General Introduction

Engineered lumber, also known as composite wood or man-made wood, consists of a range of derivative wood products that are manufactured by pressing or laminating together the strands, particles, fibers, or veneers of wood with binding agent to form a composite material (Kubba 2010). Engineered wood products are defined as products manufactured from various forms of wood fiber bonded together with water-resistant adhesives. Engineered wood products are intended for structural applications and include such products as structural plywood, oriented strand board (OSB), glued laminated timber, laminated veneer lumber (LVL), and wood I-joists. These products are also known as wood composites (Steven 2001).

Nicole, Zhiyong, and Charles (2010) described about engineered wood, Wood-based composites encompass a range of products, from fiberboard to laminated beams. Wood-based composites are used for a number of nonstructural and structural applications in product lines ranging from panels for interior covering purposes to panels for exterior uses and in furniture and support structures in buildings. The classification in Table 1.1 reflects the latest product developments.

Table 1.1 Classification of wood composites.

Veneer-based material	Plywood Laminated veneer lumber (LVL) Parallel strand lumber (PSL)
Laminates	Glue-laminated timbers Overlayed materials laminated wood Multiwood composites (COM-PLY)
Composite material	Fiberboard (low-, medium-, or high-density) Cellulosic fiberboard Hardboard Particleboard, Wafer board, Flake board Oriented strand board (OSB) Laminated strand lumber (LSL) Oriented strand lumber (OSL)
Wood–non wood composites	Wood fiber-polymer composites Inorganic-bonded composites

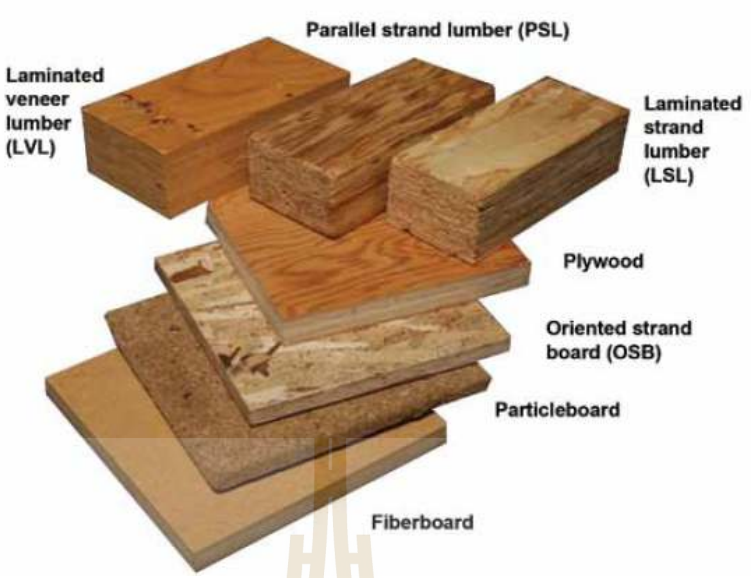

Figure 1.1 Examples of various composite products. (From top left, clockwise; LVL, PSL, LSL, plywood, OSB, particleboard, and fiberboard) (Nicole, Zhiyong, and Charles 2010).

1.1.1 Plywood

Plywood is a panel product built up wholly or primarily of sheets of veneer called plies. It is constructed with an odd number of layers with the grain direction of adjacent layers oriented perpendicular to one another. A layer can consist of a single ply or of two or more plies laminated with their grain direction parallel. Two classes of plywood are commonly available, covered by separate standards: (a) construction and industrial plywood and (b) hardwood and decorative plywood. Plywood is also used as a component in other engineered wood products and systems in applications such as prefabricated I-joists, box beams, stressed-skin panels, and panelized roofs (Nicole, Zhiyong, and Charles 2010).

1.1.2 Glulam Timber

Structural glued-laminated timber (glulam) is one of the oldest glued engineered wood products. Glulam is defined as a material that is made from suitably selected and prepared pieces of wood either in a straight or curved form, with the grain of all pieces essentially parallel to the longitudinal axis of the member. Glued laminated timber (glulam) is an engineered wood product, which can bring the natural beauty of the source wood into full play during construction. Glulam is made from sawn lumber lamina, arranged in horizontal layers, using glue; various lengths can be joined together, using scarf or finger joints, to achieve the desired length (Te-Hsin, Song-Yung, Cheng-Jung, and Ming-Jer 2008).

1.1.3 Particleboard

Particleboard is produced by mechanically reducing the wood raw material into small particles, applying adhesive to the particles, and consolidating a loose mat of the particles with heat and pressure into a panel product. Particleboard is typically made in layers, the faces of particleboard usually consist of fine wood particles and the core is made of coarser material. Particleboard is usually bonded with a Urea formaldehyde resin, although Phenol formaldehyde resins and melamine resin resins are sometimes used for applications requiring more moisture resistance. Particleboard is a wood panel product used widely in the manufacture of furniture, floor underlayment, home constructions, cabinets, stair treads, shelving, table tops, vanities, speakers, sliding doors, lock blocks, interior signs, displays, table tennis, pool tables, electronic game consoles, paneling, kitchen worktops, and work surfaces in offices, educational establishments, laboratories, and other industrial product applications (Gokay, and Ibrahim 2006).

1.1.4 Fiberboard

The term fiberboard includes hardboard, medium-density fiberboard (MDF), and cellulosic fiberboard. Several things differentiate fiberboard from particleboard, most notably the physical configuration of the wood element. Because wood is fibrous by nature, fiberboard exploits the inherent strength of wood to a greater extent than does particleboard. Fiberboard is normally classified by density and can be made by either dry or wet processes. A fiberboard with specific gravity between 0.50 and 0.80 (density between 31 and 50 lb/ft^3) is classified as medium density fiberboard (MDF) and a fiberboard with specific gravity greater than 0.80(density greater than 50 lb/ft^3) is classified as hardboard (Philip, Monlin, Al, and Deland 2007). Medium density fiberboard (MDF) is one of the main wood products used for various types of constructions. The main advantages of MDF are: (a) fewer defects such as knots and the inherent cracks usually found in solid wood, (b) high durability, and (c) easy processing (Hiroshi 2010).

1.1.5 Laminated Strand Lumber and Oriented Strand Lumber

Laminated strand lumber (LSL) and oriented strand lumber (OSL) products are an extension of the technology used to produce oriented strandboard (OSB) structural panels. The main difference is that the aspect ratio of strands used in LSL is higher than for OSL. Waterproof adhesives are used in the manufacture of LSL. One type of product uses an isocyanate type of adhesive that is sprayed on the strands and cured by steam injection. Laminated strand lumber (LSL) aim to replace some larger dimension solid sawn timber products sung underutilized commercial species. The final product concept utilizes strands from fast growing hardwood species such as aspen poplar by bonding them together with Isocyanate as

diphenylmethance di-isocyanate (MDI) adhesive under heat and pressure to form the LSL (Sven, Hans, and Larsen 2003). Oriented strand lumber (OSL) is produced from oriented flakes, in much the same way as the faces and core of OSB. In this case, though, all strands are oriented in one direction. OSL differs from LSL in that its flakes are shorter. These products have a ready market in architectural windows and doors, furniture parts, and other specialty application (Jim, Rubin, and John 2007).

1.1.6 Wood Thermoplastic Composite Materials

Wood thermoplastic composites have become a widely recognized commercial product in construction, automotive, furniture, and other consumer applications. Wood thermoplastic composites are of two main types. In the first type, the wood element serves as a reinforcing filler in a continuous thermoplastic matrix. In the second type, the thermoplastic serves as a binder to the wood elements much like conventional wood-based composites. Thermoplastics are attractive compared to traditional materials, such as steel, aluminum and thermoset composites for these applications, due to their high specific strength, corrosion resistance, superior impact resistance, high toughness and ease of shaping and recycling. The matrix in thermoplastic composites is generally comprised of polypropylene (PP), polyethylene (PE), polyamide (PA) or other polymers (Haibin, Selvum, and Uday 2009).

Wood Plastic composites or wood polymer composites (WPC) are an important and growing segment of the forest products industry. It is the combination between commercial polymers such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and wood fiber or wood flour. The common flour is obtained from sawdust of the woods, for example cedar, jack pine, black spruce, trembling aspen. WPC market is going strongly around the world. It is used as

substitute or alternative for the natural wood. Most applications are as the building and industrial materials, outdoor deck floors. It is also used for fences, landscaping timbers, park benches, window and doorframes, and indoor furniture as shown in Figure 1.2.

The business article from Plasteurope.com, presented about demand of Wood plastic composites in landscape and outdoor products, fencing and other applications will be promoted by increasing consumer recognition of the performance properties of materials'. Demand for wood plastic composite lumber will record more rapid gains than that for plastic lumber up to 2015, increasing by over 16% annually to USD 2.5 billions. Gains will be driven by ongoing consumer interest in composite lumber as a substitute for natural wood products in applications such as decking and fencing. Moreover, because wood plastic composite lumber incorporates recycled materials, it is seen as an environmentally friendly building material (Plasteurope, www, 2012).

Figure1.2 Outdoor application of WPC (wpc.blogspot, www, 2011).

Polypropylene (PP) as the thermoplastic used in a wide variety of applications, including packaging, textiles (e.g. ropes, and carpets). It also shows good fatigue resistance that makes it widely use in living applications. PP has more rigid than other polyolefin's. Polypropylene has a low cost thermoplastic, low melting temperature, good in chemical resistance. Therefore, it is commonly used as matrix in wood plastic composites. The limitations of this polymer are low impact toughness and resistance to UV degradation. Hence, mechanical properties improvement of WPC derived from this material such as impact, tensile, flexural are normally focused. Higher in the thermal properties by mean of heat deflection temperature (HDT) can benefit the wood plastic composites in term of wider the higher thermal performance applications. Thermal performance includes the thermal comfort of occupants, the capacity of heating, ventilation and air conditioning equipment and the energy used by that equipment.

The main techniques used for modification virgin polymers include grafting, cross linking, blending, and reinforced with fibres. Grafting process is known as tailoring the polymer chains. Crosslink reaction into macro chain is normally introduced for improving the properties of polymers. In some case such as PE, it can also improve the environmental resistance. Blending is the most common routine to combine outstanding properties of the two or more polymers together. In this research work dual schemes, fibre reinforcement and cross linked matrix was performed. It is known as cross linked structure makes polymer more resistant to heat and light that give rise to high degree of dimensional stability, mechanical strength.

1.2 Research objectives

The main objectives of this research study include:

(i) To investigate the optimal of the composite constituents of crosslinked polypropylene wood composites.

(ii) To improve the mechanical and thermal properties of crosslinked polypropylene wood composites.

1.3 Scope and limitations of the study

In this study, polymer matrix based on injection molding grade polypropylene homopolymer, PP700J, that is commercially available and used as composite matrix. Ultrahigh molecular weight polyethylene (UHMWPE), ethylene propylene diene terpolymer (EPDM) and polypropylene block-copolymer (PP740J) were employed as toughener for wood composite (WPC). Wood flour from saw dust with average particle size less than 1.0 mm, by mean of hammer mill sieve size, was used as reinforcement on composites. Talc as filler was employed in this study. The vinyl trimethoxyl silane (VTMS) combined with dicumyl peroxide (DCP) as free radical generator were added as crosslink agents. Sauna crosslink process was achieved by incubating the specimen in moisture saturated oven at 105^{o}C for 12 hr. It was used to accelerate the final silane condensation crosslink reaction. Impact, flexural and heat deflection temperature testing were conducted. Morphological of composite was observed by scanning electron microscopy (SEM).

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CHAPTER II

LITERATURE REVIEW

2.1 Composites from Natural Fibres

Thermoplastic/wood composites have been known for many years. Historically, most of these used wood flour to produce filled plastics. The wood flour decreased the cost, but was not usually intended to improve the performance in any substantial way. More recently, the use of natural fibres to provide a reinforcing mechanism in thermoplastics has been of substantial interest. In fact, several companies now manufacture wood fibre/thermoplastic materials for use as synthetic lumber in applications such as decking and window frames. Composites containing recycled plastics and wood fibre offer an interesting combination of properties, as well as lower cost than competitive materials, especially those based on synthetic fibres. By permitting use of moderately contaminated recycled plastics rather than requiring the use of virgin resin, these materials provide an additional market for recycled plastics, thereby helping to reduce waste disposal burdens. Composites can also be fabricated using recycled wood fibre, such as recovered paper fibre, providing an additional market outlet for recovered paper and thus further waste diversion benefits. Wood fibre/polyolefin composites are often unable to take full advantage of the potential of the fibre reinforcement, due to poor adhesion between the polymer

matrix and the fibre. Use of additives to improve adhesion between the fibres and matrix can significantly improve performance (Susan, and Indrek 2004).

Alireza (2008) review about developments in the area of wood–plastic composites (WPCs) and their applications in automotives industries using plant-based fibres. Wood–plastic composite (WPC) is a very promising and sustainable green material to achieve durability without using toxic chemicals. The term WPCs refers to any composites that contain plant fibre and thermosets or thermoplastics. In comparison to other fibrous materials, plant fibres are in general suiTable to reinforce plastics due to relative high strength and stiffness, low cost, low density, low CO_2 emission, biodegradability and annually renewable. Plant fibres as fillers and reinforcements for polymers are currently the fastest growing type of polymer additives. Since automakers are aiming to make every part either recyclable or biodegradable, there still seems to be some scope for green-composites based on biodegradable polymers and plant fibres. From a technical point of view, these bio-based composites will enhance mechanical strength and acoustic performance, reduce material weight and fuel consumption, lower production cost, improve passenger safety and shatterproof performance under extreme temperature changes, and improve biodegradability for the auto interior part.

The natural fibre reinforced polymer composites are growing in both industrial applications and fundamental research. The fibres are renewable, inexpensive, completely or partially recyclable and biodegradable. In the composite materials, natural fibres are used as reinforcing component. Properties of natural fibre are diverted from their structure and chemical compositions. The plant fibres are characterized by cellular structure, each cell unit containing crystalline cellulose

regions, which are interconnected via lignin and hemicelluloses fragments. The most commonly used natural reinforcing fibres and composite matrix are shown in Figure 1.1 (Frederick, and Norman 2004). Wood fibre is extracted from hardwood trees or softwood trees and cellulosic elements that are extracted from trees, straw, bamboo, cotton seed, hemp, sugarcane and other. As global warming awareness concern, there are two main research schemes regarding to the polymer composites reinforced with natural fibre. There are wood composites and biocomposites. The directions of the wood composite studies were as follow.

2.2 Wood Plastic Composites (WPC)

2.2.1 Polypropylene based WPC

Nicole, and Robert (2003) studied about wood flour/polypropylene (PP) composites made with various sizes of wood flour particles on the mechanical properties of composites. Wood flour particles (35, 70, 120, and 235 mesh) were compounded at 40% by weight with polypropylene. The result show increases in tensile and flexural strength and modulus of the wood flour composites were found to correspond with increases in aspect ratio. Notched impact energy increased with increasing particle size. The performance of wood fibre reinforced PP composites was compared with that of PP composites filled with wood flour contents were 20% and 40% by weight. At the 40% filler level, wood fibre also improved tensile and flexural modulus more than 20% weight wood flour composites.

Beg, and Pickerin (2008) investigated the influence of fibre length, fibre beating and hygrothermal ageing on tensile strength, young's modulus, and failure strain and impact strength of Kraft fibre reinforced polypropylene (PP)

composites. Considering effects of fibre length on properties was found to decrease whilst failure strain increased with decreasing average fibre length in composites.

Zaini, Fuad, Ismail, Mansor, and Mustafah (1996) studied the effect of filler content and size on the mechanical properties of a new type of wood based filler, oil palm wood flour (OPWF), in polypropylene (PP) was investigated. Four sizes of OPWF filler at different filler loadings were compounded using a twin screw compounder. All sizes of filler showed a similar trend of declining mechanical properties with increasing filler content. In terms of size, the composites filled with larger-sized filler showed higher modulus, tensile and impact strengths, particularly at high filler loadings.

Febrianto, Setyawati, Karina, Bakar, and Hadi (2006) studied mechanical properties of composites of wood flour (WF) and recycle polypropylene (RPP) prepared under various WF content, WF size. WF from mixed-soft wood, the composites composed of 0-70% WF, 0-70% polypropylene various size of WF (60-80;80-100 and <120 mesh). The mechanical properties of composites were greatly affected by WF content, WF size. The greater the WF loading resulted in the greater was the reduction of tensile strength and breaking elongation values and the same time the greater was the increasing of Young' modulus value. The smaller the WF size resulted in the greater the tensile strength of composites.

Mubarak, Johannes, and Hans-P (2009) investigated hybrid composites was made with jute and Cordenka man-made cellulose. The matrix material was a polypropylene/ethylene block copolymer (PP). Pultrusion technique was applied with a conventional extruder equipped. Standard test specimens were prepared with these granulates using an injection molding machine. Result of the heat distortion

temperatures (HDT-A) of the composites as a function of the jute fibre fraction. The most beneficial effect of jute incorporation into the composites is found here. The HDT value is shifted above 100°C already for 25% added jute fibre. Heat distortion temperatures (HDT) increase with increasing jute portion.

Beg, and Pickerin (2008) investigated mechanical properties of Kraft fibre reinforced polypropylene (PP) composites. This suggests that the interfacial bonding between the fibre and the matrix is poor. This can be supported by SEM, where fibre pull-out and debonding predominate at the fracture surface. The Tensile strength increased with addition MAPP, which appeared to be due to better interfacial bonding between the fibre and the matrix and thus resulted in fibre breakage.

Arbelaiz, Fernandez, Cantero, Llano-P, Valea, and Mondragon. (2005) investigated the effect of fibre treatments and matrix modification on mechanical properties of flax fibre bundle/polypropylene composites. Fracture surfaces were investigated by scanning electron microscopy. Results suggest that matrix modification led to better mechanical performance than fibre surface modification.

2.2.2 Polyethylene based WPC

Hassine, Ahmed, Patrick, and Alain (2009) investigated the effects of fibre size and fibre content. Five types of wood sawdust were investigated in their study, eastern white cedar, with sapwood and heartwood sawdust, jack pine sawdust, bark shavings; and black spruce sawdust. Fibre sizes were 24, 42 and 65 mesh and the fibre content were 25, 35, and 45% by weight. High density polyethylene (HDPE) and fibres were compounded by twin screw extrusion and then injection molding into specimen. The results showed a significantly affected from the fibre origin. Higher fibre size produces higher strength and elasticity but lower energy to break and

elongation. Increasing fibre load improves the strength and stiffness of the composite but decreases elongation and energy to break.

Fei, Qinglin, Yong, and Yanjun (2008) studied composite panels using virgin and recycled high-density polyethylene (VHDPE and RHDPE) and five types of natural fibres including four rice straw components (i.e., rice husk, rice straw leaf, rice straw stem, and whole rice straw) and wood fibre as control were made by melt compounding and compression molding. For both VHDPE and RHDPE, rice straw fibre systems had comparable mechanical properties with those of wood composites. Increase in fibre loading led to increased modulus and decreased tensile and impact strength but their impact strength was comparable or better than that of other straw fibres.

Norma, and Marcelo (2003) studied composites made from LLDPE reinforced with wood flour. Composite were mixed by counter-rotating twins crew extruder and then hot pressing. Result show effects of the wood flour concentration, the modulus increases with the wood flour content and decrease of the impact strength with the wood flour content.

Arup, and Basudam (2007) investigated LDPE-LLDPE blend and its use as jute fibre composite. Jute fibre composite mixed by single screw extruder. The result show tensile strength and flexural strength of virgin LDPE-LLDPE/jute fibre composites increased with increase in fibre content from 10 to 30%, whereas for recycled LDPE-LLDPE/jute fibre and recycled-virgin LDPE-LLDPE/jute fibre composites, tensile and flexural strength linearly increased from 10 to 20% fibre loading, followed by a decrease at 30% fibre loading.

Liu, Wua, Han, Yao, Kojima, and Suzuki (2008) studied SEM graphs of impact fractured surfaces of HDPE/Bamboo fibre composites. Without addition of any modifiers, fibre bundles with smooth and clean surfaces were devoid of HDPE matrix, indicative of indeed poor interfacial adhesion between the filler and the matrix also, some traces can be visible where BF was pulled-out. With the addition of modifiers, the broken fibres were seen to be embedded in the matrix without evident gap in the interfacial area. This was evidence of good interface bonding.

Munir, Hasan, and Gerald (2009) studied composite from wood fibre and low density polyethylene (LDPE) mixing with twin screw extruder. Results show improvements in elastic modules, hardness and HDT when wood was incorporated into the polymer matrix, however there was also a deterioration of the toughness of the composites. SEM patterns of the fractured surfaces of the composites also show the random distribution of fibres in the matrix.

2.2.3 Polyvinylchloride based WPC

Narongrit, Kantima, Chakarin, and Sirinthorn (2003) used sawdust as filler in poly vinyl chloride (PVC) the effects of sawdust content on mechanical properties being of main interest. The concentration of sawdust particles in the PVC compounds was varied from 0-40 per cent weight fraction (wt%). Generally, it was found that increasing the sawdust content resulted in a very similar trend of decrease in all mechanical properties. The results of flexural modulus and strength of the composites. It can be seen that the flexural modulus decreased with increasing wood fibre content, and then increased with sawdust content.

Gajender, Rashmi, Veena, and Narula (2010) described the effect of filler (obtained from bark of Acacia bamboo) content and its particle size (ranging

from 100 to 150 μm and <50 μm) on the properties of poly vinyl chloride (PVC) composites. A two-roll mill was used for mixing varying amounts of bark flour with PVC formulation. Samples for testing were prepared by compression molding. Tensile strength and percentage of elongation at break decreased, whereas modulus increased with an increasing amount of bark flour. Improvement in properties was significant in the presence of filler, having a particle size <50 μm as compared to filler, having a particle size ranging from 100 to 150 μm.

Ge, Li, and Meng (2004) studied Composites of unplasticized poly vinyl chloride (PVC) blended with bamboo flour and pine flour, respectively, were prepared in a batch mixer followed by compression molding. Tensile tests showed that pine flour–filled composites exhibited better mechanical properties than those filled with bamboo flour with the same particle size at the same loading level.

Rocha, Kazlauciunas, Gil, Gonalves, and Guthrie (2009) studied wood flour/poly vinyl chloride (PVC) composites. The raw materials were mixed on a two-roll mill. The final composites were obtained by controlled press molding. Result show increasing the wood flour content leads to a lower tensile strength and elongation at the yield point and a lower elongation at break. Walnut flour creates a material with better tensile properties than those provided by the bubinga flour. Thermal analyses show that the presence of wood flour leads to an increase in the degradation temperature of the main matrix.

Yu-T, De-R, Dong-S, and Jiu-J (2007) studied The SEM micrographs of a fractured surface of the treated bagasse fibre/PVC composites and the untreated BF/PVC composite. The untreated BF was pulled out of the PVC matrix with smooth and clean surfaces because of the poor interfacial adhesion. However, the treated BF

with benzoic acid was pulled out of the PVC matrix with little rough surfaces because the interfacial adhesion was better. It is evident that treated BF is more compatible with PVC rather than untreated BF.

2.2.4 Biodegradable polymer composites

Sanjeev, and Mohanty (2007) studied on wood fibre reinforced Polyhydroxy butyrate-co-valerate (PHBV) with fabricate maple composites via extrusion–injection molding process. The fabricated PHBV based bio-composites contained 10–40 wt% of the maple wood fibre. Wood fibre embodied in PHBV matrix gave an appreciable rise in tensile and flexural modulus. The storage modulus was also improved with wood fibre addition in to PHBV. Notch impact strength of PHBV was uniformly reduced with the fibre reinforcement. The major contribution to the improved Heat deflection temperature HDT with enhanced fibre content is due to fibre reinforcement which has higher HDT than the matrix. The increased HDT can also be attributed to an increase in the degree of crystallinity in PHBV due to addition of wood fibres.

Benjamin, and Jorg (2008) investigated PLA (polylactic acid) reinforced with Cordenka rayon fibres and flax fibres. The samples were produced using injection molding. Result show the highest impact strength and tensile strength were found for Cordenka reinforced PLA at a fibre-mass proportion of 30%. The highest Young's modulus was found for the composite made of PLA and flax.

Morreale, Scaffaro, Maio, and Lamantia (2008) study of the properties of biodegradable polyester/wood flour composites. The materials were prepared by changing five process variables (filler content, filler aspect ratio, pre-treatment, mixing speed, mixing temperature). Heat deflection temperature is a useful parameter

to evaluate the overall thermo mechanical resistance of a material. Result from experiment exhibit filler content and the filler aspect ratio have a statistically significant weight, since their main effects are significantly. High wood filler content will improve HDT and high level of aspect ratio will decrease HDT in this case.

Bhavesh, Susan, Michael, and Patricia. (2008) studied composites of polylactide (PLA, 100-60 wt%) and wood flour (0-40 wt%). Addition of wood flour significantly increased the flexural modulus and the storage modulus of PLA-wood flour composite. But the strength properties were not improved by adding wood. The SEM study provided evidence that there was sufficient interfacial adhesion between the PLA matrix and the wood filler to cause the composite to fail mostly through fibre breakage, rather than fibre pullout. This was likely a result of mechanical interlocking between the wood fibres and PLA matrix, and the observed filling of the wood lumens by PLA.

2.3 Toughening Wood Plastic Composites

Applications of WPC as a structural material predominantly exist in decking, railing, automotive interiors and housing. Polyethylene (PE include HDPE LDPE LLDPE), polyvinylchloride (PVC) and polypropylene (PP) hold a major share of resins used in WPC. Several kinds of WPC using wood fibre and conventional polymers have been developed and researched (Sanjeev et al. 2007). Fracture toughness and impact resistance are among the most important properties of polymers and their modified systems. A main goal in the development of modified thermoplastics is practically always to achieve process able material of high stiffness combined with sufficient impact resistance. To overcome its deficiencies various

modifying means were used through blending with other thermoplastics and rubbers through fibre-reinforcing or through filling with inorganic particles (Hristov, Lach, and Grellmann 2004).

2.3.1 Toughening via polyolefin matrix blend

Polymer blends were studied extensively with a view improving the properties of the homo-polymers involved. The benefits claimed include, for example, improvement in impact strength, tensile strength, environmental stress cracking, low temperature impact properties and so on. A study on blends of polypropylene with conventional polyolefins is of continued interest, and much of the research paid attention to the PP/PE blend. These included PP/LDPE, PP/LLDPE, PP/HDPE, and PP/HDPE/Poly (ethylene-co-propylene) (Xiaodong, Riguang, and Hangquan 1995).

Jang-O, Bong-K, Chang-S, Ki-W, Jin-K, and Won-J (1993) studied mechanical properties of binary blends such PP/LDPE and PP/HDPE. The composition of binary blends was 100/0, 80/20, 60/40, 40/60, 20/80. Blends have been prepared by melt mixing in an extruder. Consider on impact properties, it is interesting to note that the impact strength of PP is improved as HDPE and LDPE compositions increase and that the impact strength.

Abdel-H (2010) investigated Polyethylene (PE), polypropylene (PP) and their blends. The impact of the thermal aging and blend ratio on the mechanical (tensile and hardness). Samples of PE/PP blends containing 100/0, 75/25, 50/50, 25/75 and 0/100 wt% were prepared via injection molding. The tensile measurements indicated that the yield strength and the modulus decrease with increasing PE content. It was also observed that PE, PP and their blends deform in ductile modes. The strain to break for pure PE is found to be much higher than that for pure PP and for their

blends. The hardness measurements have also revealed that increasing PE content in PE/PP blends reduced the hardness value of PP.

Ultra high molecular weight polyethylene (UHMWPE) has unique properties such as high impact strength, high wear strength, high abrasion resistance, as well as light weight. It has been found that the mechanical properties of the PP/UHMWPE blends were much superior to those of PP/HDPE blends of the same composition. This is most likely attributed to the enhancement of molecular chain entanglement of UHMWPE with PP in the amorphous phase because of the chain flexibility and low crystallinity of UHMWPE. Therefore, low content of UHMWPE might be able to enhance PP properties (Kejian, Chixing, Hongbin, and Delu 2002).

Craig (2010) studied blends of polyethylene (PE) and polypropylene (PP) could potentially be used as matrix for wood-plastic composites (WPCs). Compounding of all blends was performed on twin screw and then injection molded. The tensile modulus and yield properties of the blends were clearly proportional to the relative amounts of HDPE and PP in the blends. However, the nominal strain at break and the notched Izod impact energies of HDPE were greatly reduced by adding as little as 25% of the PP.

2.3.2 Olefin rubber tougheners

In rubber-toughened plastics, the matrix plays an important role in determining the overall toughness. Some matrix tends to craze because of low entanglement density. Massive crazing induced by rubber particles is clearly observed in high impact polystyrene. High molecular weight matrixes are, in general, tougher than their low-molecular counterparts. The effect of rubber concentration on toughness has been studied by a large number of researchers. Mostly semi-crystalline

plastics while others have shown a linear increase in toughness with rubber content (Raymond, Sue, and Yee 2000).

Isotactic polypropylene (iPP), as one of the most important thermoplastics, has been widely used in various industrial fields such as automotive parts, furniture, and packages. However, the application of PP as high-performance engineering plastic is limited by its poor impact toughness, in particular at low temperatures. In the past three decades, the impact strength of PP has been improved by blending it with multiple elastomers such as ethylene-propylene random copolymer (EPR) ethylene-propylene-diene terpolymer (EPDM) styrene-ethylene/ butylenes-styrene triblock copolymer (SEBS) polypropylene-block-poly (ethylene-propylene) copolymer etc (Rongbo et al.2009).

Xiaodong, Hangquan, and Riguang (2006) studied blending systems based on polypropylene (PP) and ultrahigh-molecular-weight polyethylene (UHMWPE). Ethylene-propylene-diene block copolymer (EPDM) use as impact modifier. Binary blends and ternary blends were prepared via a melt extrusion. The notched Izod impact strength, the tensile strength, and the elongation-at break could be improved with increasing UHMWPE content, and achieved optimal values at an 85/15 weight ratio of PP/UHMWPE. EPDM can be used as a compatibilizer to improve the compatibility and the interfacial adhesion between the PP and the UHMWPE, which resulted in more effective toughening and reinforcing effects.

Byung-D, and John. (1997) investigated the mechanical properties of wood-fibre/ toughened PP composite modified by physical blending with an EPDM rubber to improve impact toughness. The concentrations of wood fibres and EPDM were 0-50 wt % and 0-40 wt % respectively. The percent elongation at break

increased with impact modification by EPDM and was reduced by the addition of wood fibres. The flexural modulus and flexural strength followed a similar trend to those of the tensile properties. The strength ratio increased with the addition of EPDM, while it decreased with increasing wood-fibre concentration. The fracture energy dramatically increased with the addition of 10 wt% EPDM. EPDM rubber modification was moderately effective for wood-fibre PP composites.

Dingova, Djiporović, and Miljković (1998) studied improvement the properties of polypropylene/ wood flour (PP/WF_L) composites by using EPDM. The tensile modulus of elasticity and tensile strength values are increased in the cases of PP/ WF_L composites with 10 and 20% of EPDM content, with respect to PP/WF_L control composites. However, in the case of 30% of EPDM content values of these properties decreased. The Izod impact resistance values are increased for all test composites, but most of all in the case of composite with 30% of EPDM.

2.3.3 Filler toughened wood plastic composites

Fillers play important roles in modifying the desirable properties of polymers and reducing the cost of their composites. In conventional polymer composites, many inorganic filers with dimensions in the micrometer range, e.g. calcium carbonate, glass beads and talc have been used extensively to enhance the mechanical properties of polymers. A further improvement of the mechanical properties can be achieved by using filler materials with a larger aspect ratio such as short glass fibres. It is logical to anticipate that the dispersion of fillers with dimensions in the nanometer level having very large aspect ratio and stiffness in a polymer matrix could lead to even higher mechanical performances (Tjong 2006). The addition of filler is known to result in the following, Increase in density and

modulus of elasticity as well as in compressive and flexural strength. Increase the tensile and shear strength as well as the maximum strength at break. Increase of hardness, heat deflection temperature and heat resistance. Improve the impact strength. Increase of hardness, heat deflection temperature and heat resistance (Utracki, and Khanh 1992).

Yong, Qinglin, Craig, Fei, and Yanjun (2007) Studied composites based on high density polyethylene (HDPE), pine flour, and organic clay were made by melt compounding and then injection molding. The dry clay particles are greater than 13 μm in diameter. The flexural and tensile modulus increased slowly with the increase of clay content, but the storage and loss modulus remained at the same level at 1-3% clay loading levels. The impact strength was lowered 7.5% by the addition of 1% clay. However, the clay did not improve the thermal stability of the HDPE/pine composite.

Sanjeev, Amar, and Manju (2010) investigated deals with the development of hybrid composites from wood fibre, talc and a bioplastic. Prepared the composites by extrusion–injection molding. The hybrid green composites showed a pronounced leap of 200% in the Young's and flexural modulus with the dual reinforcement of 20 wt% talc and 20 wt% wood fibre in PHBV matrix. The impact strength of the PHBV does reduce with addition of talc and wood fibre.

Hattotuwa, Premalal, and Baharin (2002) studied polypropylene(PP) with talc and rice husk (RHP) fillers composites. The composite were compounded by internal mixer, which contain 0-60% phr of filler at 15% intervals. Mechanical properties of the composites with reference to filler type and filler loading were investigated. In terms of mechanical properties, Young's modulus and flexural

modulus increased, whereas yield strength and elongation at break decreased with the increase in filler loading for both types of composite. Of these PP composites, the RHP composites exhibited lower yield strength, Young's modulus, flexural modulus, and higher elongation at break than talc composites.

Rai, Kokta, and Daneault (1990) studied linear low density polyethylene (LLDPE) was reinforced with wood fibre, glass fibre, and mica. The effect of aging on mechanical properties of the composites. Samples containing glass fibres showed by far the best results with regard to tensile strength, elongation, and fracture energy. LLDPE filled with mica produced poor results compared to wood fibre composites.

2.3.4 Surface modification

Natural fibres can offer the resulting composites many advantages, the usually polar fibres have inherently low compatibility with non-polar polymer matrix, especially hydrocarbon matrix such as polypropylene (PP) and polyethylene (PE). The incompatibility may cause problems in the composite processing and material properties. Treatment of natural fibres is beneficial to promote interfacial adhesion. Physical treatments (e.g. electronic discharge in the different media such as plasma and corona technologies) may create a hydrophilic or hydrophobic fibre surface by changing the surface energy to consequently increase the compatibility of the treated fibre with the polymer matrix. Chemical modification provides the means of permanently altering the nature of fibre cell walls by grafting polymers onto the fibres crosslinking of the fibre cell walls or by using coupling agents. A coupling agent is a chemical that functions at the interface to create a chemical bridge between the reinforcement and matrix (Yanjun, Callum, Zefan, Holger, and Carsten 2010).

2.3.4.1 Physical modification

Mohamed, David, Stephane, Beatrice, and Andre (2010) investigated the mechanical properties of composites obtained from different combinations of untreated and corona treated fibres and polypropylene. Extrusion-compression molding was used as the method of preparation. Besides, the results show that the treatment of compounds (fibres or matrix) leads to a significant increase in tensile strength. The modification of cellulosic reinforcements rather than polypropylene allows the greater improvement of the composites properties with an enhancement of 30% of Young modulus.

Xiaowen, Krishnan, and Debes (2004) studied argon and air-plasma treatments to modify the surface of wood fibres under suiTable treatment parameters to improve the compatibility between wood fibres and polypropylene. Wood fibres and PP fibres were blended together to form a random mat, which was then vacuum hot-pressed into a composite sheet. The tensile strength and tensile modulus of the composite sheet improved to some extent after the treatment. The storage modulus in the dynamic mechanical properties of wood fibre-PP composites also showed improvement after the treatment.

2.3.4.2 Chemical modification

Beckermann, and Pickering (2008) investigated alkali treated to improve their suitability of Hemp fibres for use as reinforcements in composite materials. Polypropylene copolymer was used as the composite matrix. Hemp fibre reinforced polypropylene composites were produced by extrusion and injection molding. Fibres treated with a solution of 5 wt% NaOH and 2 wt% Na_2SO_3 showed

significant increases in tensile strength and Young's modulus when compared to untreated fibres

Tronc, Hernandez-E, Ibarra-G, Estrada-M, Navarrete-B, and Zaragoza-C (2007) studied blue agave fibre esterification and its use in thermoplastic composite reinforcement. High density polyethylene (HDPE) was used as the composite matrix. Fibre chemical modification the following reagents were used: acetic anhydride, octanoic acid and acetone. Mechanical properties characterization showed that superficial modification was successfully achieved, since a change in the elastic modulus and improved impact resistance were observed when the modified fibre was used.

Rebeca, Maria, Abad-L, and Marcelino (2009) studied the effects of composition and interface modification of wood flour/polypropylene composites. The wood flour was treated with vinyltrimethoxy silane as a coupling agent, and its effect on the WPC properties was examined. The impact strength was maximal for the composites containing 30% of silane-treated wood flour. From studied showed beneficial effects of the coupling agent on the WPC properties were greater in the materials containing a relatively low amount of filler.

Hee-S, Byoung-H, Seung-W, Sumin, and Hyun-J (2007) investigated the effect on the interfacial adhesion of the composites bio-flour-filled, polypropylene composites was examined as a function of five different maleic anhydride-grafted PP (MAPP) types. Result showed enhanced interfacial adhesion, and mechanical and thermal stability of the MAPP-treated composites was strongly dependent on the amount of MA graft (%) and the MAPP molecular weight.

Balasuriya, Ye, Mai, and Wu (2002) studied wood flakes and high density polyethylene (HDPE) and the effects of these modifications on composite properties. An HDPE matrix was modified by a reaction with maleic anhydride (MA) in a twin-screw extruder and then compounded with wood flakes to produce wood–polyethylene composites. Wood flakes were modified by a reaction with a silane coupling agent. The results of MA-modified composites indicate that some maleated HDPE is reacting with wood through a compatibilizer for wood flakes and HDPE. Result coupling agent and maleic anhydride showed significant improvements in tensile strength, ductility, and Izod impact strength were obtained.

2.4 Crosslinked Wood plastic composites

2.4.1 Radiation crosslink

Radiation treatment is a widely accepted technology in polymer processing such as grafting, cross-linking, coating, sterilizing or composite bonding. On exposure to high energy radiation, the polymer becomes electronically excited or ionized after absorption of energy and the excited molecules are able to initiate chemical reactions producing reactive products leading to crosslinking and degradation reactions. In fibre reinforced composites, electron beam treatment of impregnated system can create active centers, with radicals not only in the oligomer matrix but also on the surface of the fibres, which produce the chemical interactions (Chong, Ahmad, Dahlan, and Abdullah 2010). Under UV rays, oxygen reacts with the water to form hydrogen peroxide which causes gradual oxidative breakdown of the polymer which is shown in Figure 2.1 (Quazi, Alam, Mubarak, Saha, and Gafur 2010).

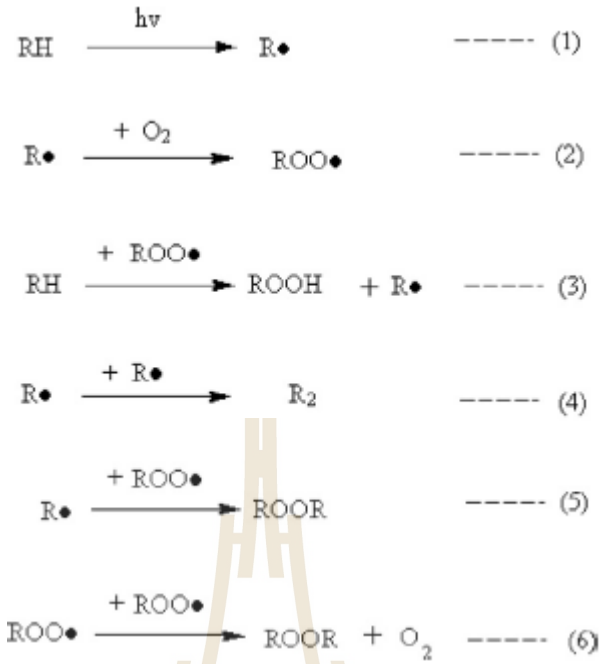

Figure 2.1 Free radical initiation, propagation and termination in polymer by UV (Chong, Ahmad, Dahlan, and Abdullah 2010).

Quazi et al. (2010) studied with Natural silk fibre (20%) reinforced polypropylene (PP) composites were prepared by compression molding. Application of gamma radiation to improve the mechanical properties was successful. Gamma radiation caused increase in both tensile and bending properties up to 250 krad. Maximum increase in tensile and bending strength, tensile and bending modulus by gamma radiation was 16.8%, 28.1%, 64.4% and 51.7%, respectively.

Mubarak, Ali1, Fumio, and Keizo (1999) studied the radiation effect on the physical, thermal, mechanical and degradable properties of biodegradable polymer. Bionolle films prepared by compression molding process and were irradiated with electron beam (EB) radiation of different doses. Tensile strength of Bionolle was enhanced when Bionolle film was exposed under 20 kGy radiations.

Both irradiated and unirradiated films of Bionolle were subjected to different degradation test in outdoor and indoors conditions. Loss of tensile strength of irradiated Bionolle due to storage degradation like in roof, ground and indoors was minimum compared to unirradiated Bionolle.

Sarawut, Sujittra, Sarot, Phiriyatorn, and Sunan (2010) studied polypropylene/wood flour composites at 40 wt% filler content were prepared using a twin-screw extruder and an injection molding machine. The effects of gamma irradiation on the flexural properties, tensile properties, and creep behavior were investigated. The results revealed the improvement of mechanical properties and creep behavior was found in the presence of gamma irradiation at low radiation doses (5 and 10 kGy), while the composites irradiated at radiation doses over 10 kGy rendered the decrease of mechanical properties.

2.4.2 Chemical crosslink

Silane crosslink in WPCs can be present in the polymer matrix but also between the wood flour and the plastic, thereby improving the interfacial adhesion. The silane group is grafted onto the polymer chain by first adding peroxide to create radicals that can induce the grafting of a silane group to the polymer. The resultant silane-grafted polymer matrix is then hydrolyzed and condenses to create –Si–O–Si– bonds between the chains. The bonds between the wood and the plastic have been suggested to comprise a mix of silane-bridges and hydrogen bonds. Silane water crosslinked reaction mechanism was show in Figure 2.8 (Grubbstrom, and Oksman 2009).

Magnus, Nicole, and Kristiina (2007) studied silane cross-linked wood–polyethylene composite profiles were manufactured by reactive extrusion with

addition of only 2% w/w of silane solution during manufacturing. The cross-linked composites showed flexural toughness superior to the non-cross-linked composites. Result showed improved adhesion between the wood fibre and the polyethylene matrix is most likely the reason for the significant improvement in toughness of the cross-linked composites.

Magnus, Paul, and Kristiina (2005) used silane technology in crosslinking composites of wood flour and polyethylene. Composites of vinyltrimethoxy silane grafted high density polyethylene and wood flour were produced by compounding in a twin-screw extruder. The tensile strength for the crosslinked composite with 40% wood flour is much higher than for neat XLPE, while the tensile strength of non-crosslinked composite is lower than for neat HDPE. The elongation at break was also much higher for the crosslinked composite compared to the non-crosslinked. Crosslinking of the composites also reduced the amount of deformation during the creep experiments.

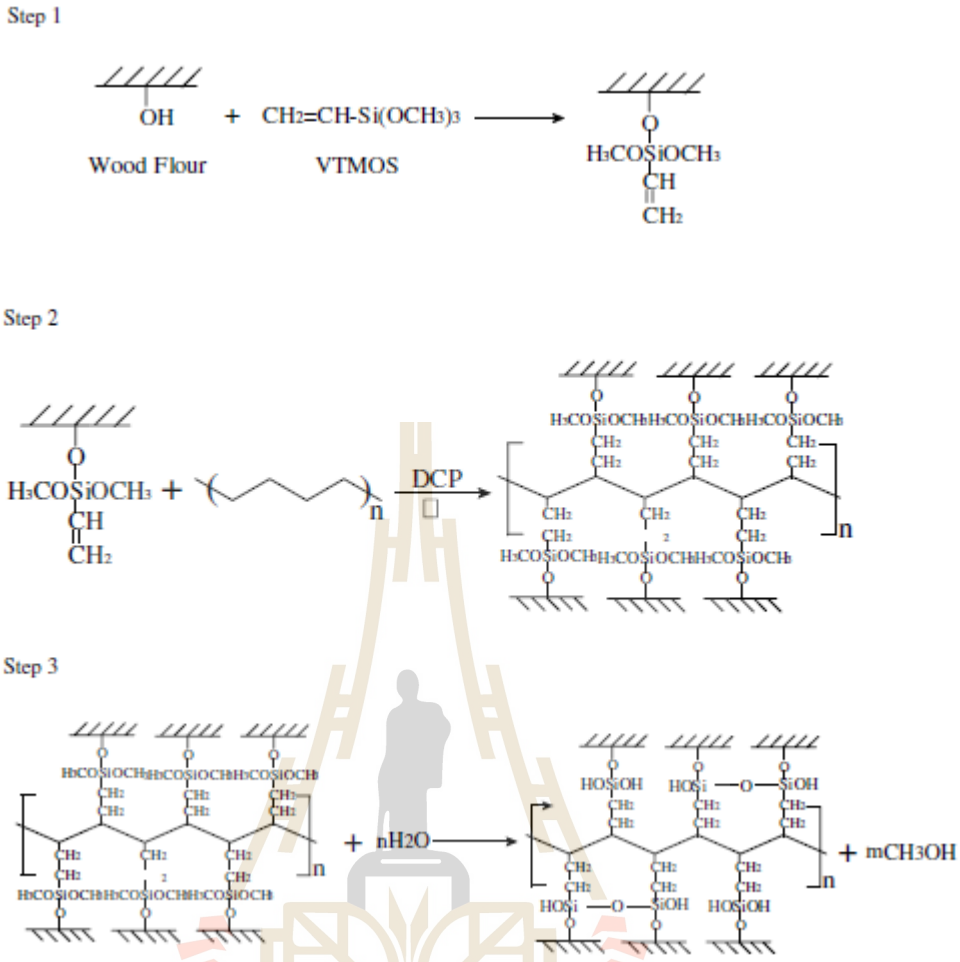

Figure 2.2 The water-crosslinking reaction mechanism of wood fibre/polymer metrics (Chen-Feng, K. et al. 2006).

Chen-Feng, Hsu-Chiang, Chen-Chi, and Chien-Ming (2006) studied Wood flour (WF) reinforced linear low-density polyethylene (LLDPE). Water-crosslinking technique was used to improve the physical properties of wood composite. Composites were compounded in a twin-screw extruder and treated with a coupling agent (vinyltrimethoxysilane, VTMS), and then moisture crosslinked in hot water. Tensile strength, flexural strength and flexural modulus are significantly increased with increasing water crosslinking time. however, tensile elongation and

notched impact strength decreases with the increasing of water crosslinking time. Composite after water crosslinking treatment exhibited better mechanical properties than the non-crosslinked one because of the improved chemical bonding between the wood fibre and the polyolefin matrix. The heat deflection temperature of the composite can be raised.

Goran, Allan, and Kristiina (2010) studied silane-crosslinking of recycled low-density polyethylene wood composites and its effect on composites properties. The composites' compositions were held constant, 50 wt% wood flour, 47 wt% LDPE and 3 wt% of lubricant, and silane-peroxide solution was added to the total material composition as a specific percentage of the total amount. The crosslinked composites were produced using a high and low silane-solution (3 wt% or 1 wt%) content. WPCs were stored in a sauna (SA) at 90°C as well as under room conditions at 21°C (RT). The results showed that crosslinked composite strength, toughness and creep resistance were improved compared to uncrosslinked composites.

Grubbstrom, and Oksman (2009) studied of silane-crosslinking and its relationship to structure–property relations of wood/HDPE composite. WPC were prepared in a compounding extruder. A solution of VTMS and DCP (12:1 w/w) was prepared and added to the composition (4 wt%). The wood-plastic composite was extruded as a profile and immediately pressed in a hot press. The crosslinked composites were stored in either room temperature at 20°C or in a sauna at 90°C. The rest of the crosslinked composites were stored for 3, 6 or 12 hr, 1, 2, 3, 4, 6, 9 or 13 days. The results showed that all crosslinked composites displayed higher strengths and lower creep responses compared with non-crosslinked control samples. Tensile strength and creep resistance improved compared to a non-crosslinked control sample.

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CHAPTER III

DESIGN OF EXPERIMENT: WOOD COMPOSITES BASED ON CROSSLINKED POLYPROPYLENE

3.1 Abstract

Investigation of wood composite based on crosslinked polypropylene was studied. The design of experiment was used to optimize and quantify the amount of the composite constitutes. The 2^k factorial design was conducted to evaluating the statistical effects of material compositions. Three parameters, silane (**A**), wood flour (**B**) and talc (**C**) contents were assigned. Composites were compounded into pellets by co-rotation twin screw extruder at 190°C and test specimens were prepared by injection molding. The measured responds were classified into 2 conditions; original and sauna cured. The original were allowed the samples to anneal at room temperature for approx. a day. The later were achieved by sauna incubation at 105°C for 12 hrs. Impact strength, flexural properties and HDT were tested and obtained as the respond effects. The optimal formulation of WPC was accomplished. Statistical analysis approach using ANOVA testing showed that silane and wood had generally positive effect on the mechanical properties. However talc showed variation effect to properties of WPC. Generally, the mechanical properties were seen to improve after sauna treatment. It evidences that the Crosslink Bridge between polymer matrix and wood flour via silane/water reaction could enhances the interfacial force. SEM was emphasized the crosslink phenomenon and hence the mechanical competency.

3.2 Introduction

Wood Plastic composites (WPCs) are the material manufactured from thermoplastic reinforced with wood fibres. It is used as substitute or alternate for the natural wood which is wildly prohibited or legally controlled by many countries. Most recent applications of WPCs are in the building and decorative industries such as outdoor deck, floors, windows and doors. The most common polymer matirxs are polyolefin types such as PVC, PP and PE. The common reinforcement is wood flour obtained from timber milling. Type of the fibre and its characteristic including the treatment processes can play the important roles of the final properties of WPCs. Nicole, and Robert (2003), Beg, and Pickerin (2008) studied wood flour/polypropylene (PP) composites made from various wood flour particles sizes and found that the mechanical properties of composites depended on the aspect ratio. Zaini, Fuad, Ismail, Mansor, and Mustafah (1996), Febrianto, Setyawati, Karina, Bakar, and Hadi, (2006), Mubarak, Johannes, and Hans-P (2009) also reported that the mechanical properties were affected by the type of the flour added. The commercially available wood composite has some incompetency such as low mechanical strength comparing to those hardwoods. Therefore, the improvements of the long term properties have been interested and explored by many researchers and engineers. The main techniques used for improving the performance of WPCs include grafting, cross linking and blending the matirxs, modification of reinforcement and perhaps adding with other high performance fillers as published by many researchers (Clemons 2010, Magnus, and Kristiina 2006, Yong, Qinglin, Craig, Fei, and Yanjun 2007). Silane grafting followed by water crosslink reaction of polymer matrix especially for PP and PE have received much attention in industrial applications and

fundamental research. Because its provide the obvious advantages, such as easy processing, low capital investment, and favorable properties in the processed materials (Sirisinha, and Kawko 2005). The vinyl type silane was grafted onto the polymer chain by; firstly, adding peroxide to create free radicals that can induce the grafting of the vinyl group of silane into the polymer backbone via addition reaction. The resultant silane grafted polymer matirxs is then hydrolyzed and condensed to create –Si–O–Si– bonds between the chains and/or bonding between wood and polymer. Sirisinha, and Kawko (2005) suggested that the bonding between chains can be either silane bridges or hydrogen interaction. This networking results in the outstanding performance properties. In this studied, WPC based on crosslinked polypropylene and the commercial available wood flour reinforcement was performed. As the crosslink structure of polymer chain enhances the properties of material such as superior in heat and light degradation resistance. Accordingly, it will give rise to outstanding in dimensional stability and durability. As the main ingredients of WPC are PP, wood flour, talc filler and vinyl type silane for the fibre treatment process. These constituent parameters in term of its content used for manufacturing WPC had the significantly effect to the final properties of the wood product. The statistical approach by mean of design of experimental (DOE) on the given parameters, contents, that effect to the properties of WPC will be the prime interests and will be resolved.

3.3 Research methodology

3.3.1 Materials

Commercial grade of isotactic polypropylene homopolymer (PP 700J) typically used for injection molding was employed as a matrix. It is kindly supplied from SCG Chemical Co., Ltd. The property of the PP provided from the manufacturer is summarized in Table 3.1. This PP is designed especially for injection molding applications as it has high melt index, easy to flow. The HDT value is relatively high, 110^{o}C. It is suiTable for heat resistance uses.

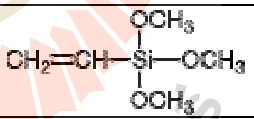
Vinyltrimethoxy silane (VTMS), Silquest® A 171, was used as crosslink agent and purchased from Optimal Tech Co., Ltd. The chemical structure and physical properties of the silane is shown in Table 3.2. It was used as received. It is water clear liquid with very low viscosity. Silane will undergo crosslink reaction via hydroxyl/water condensation.

Dicumyl peroxide (DCP) was employed as free radical initiator. It has chemical formula shown in Figure 3.1. It is commercially grad and available throughout the rubber chemicals suppliers. Again, it was used without further purification. It has low melting point, >50^{o}C. It is normally decomposed and generated quit sTable free radical at the temperature above 120^{o}C. Adding more DCP into PP, especially homopolymer type, is believed to cause the degradation.

Table 3.1 Properties of Polypropylene homopolymer (PP 700J).

Properties	Test Method	Value, Unit
Melting temp	ASTM D2117	160°C
Melt Flow Index	ASTM D1238@230/2.16	12g/10min
Notched Izod impact	ASTM D256@23°C	0.306 J/m
Tensile strength at Yield	ASTM D638 @50 mm/min	32 MPa
Elongation at bleak	ASTM D638 @50 mm/min	650%
Flexural modulus	ASTM D790	1.422 GPa
Heat deflection temperature	ASTM D648 @ 0.455 MPa	110°C

Table 3.2 Properties of VTMS (A171).

Properties	Value, Unit
Chemical formula	CH_2=CHSi(OCH_3)$_3$
Chemical structure	
Boiling point	122°C
Specific gravity, 25°C	0.967

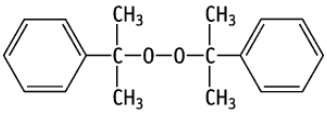


Figure 3.1 Dicumyl peroxide ($C_{18}H_{22}O_2$) (creditchem.chemtt, www, 2010).

Fine white Talc powder, JetFine™ 3CA , with the particle size, given by the manufacturer, at 1.2-1.4 μm was incorporated as filler and is manufactured from Luzenac. It was dried at 105°C in vacuum oven for at least 2 hours priority to use. A property of talc is shown in Table 3.3. This filler not only grant the cost reduction and strength of the WPC product but also provide the atheistic and smoothness of the wood surface.

The mixed free flow powder between Irganox 1076 and Irgafos 168 at the 50:50 by weight ratio was used as thermal/processing stabilizer. The reagents were supplied from Ciba specialty chemicals Co., Ltd. The technical data of these reagents were summarized in Table 3.2 and 3.3. Irganox 1076 is normally used as antioxidant for polymer at high temperature melting point to prevent the color changing. On the other hand, Irgafos 168 is commonly added into polymer to stabilize the polymer chain to undergo chain scission during melt processing by free radical scavenger. It is necessarily to add these chemical into WPC ingredient due to the fact that moisture residue in wood flour would cause the hydrolysis reaction crosslinked by forming Si–O–Si linkages while melt mixing process. This phenomena has the negative significantly effect to both mechanical and physical, appearance, properties of the WPC. The mixed chemical powder was priory and vigorously added into wood flour.

Table 3.3 Properties of Talc, Jetfine 3CA (Luzenac, www, n.d.).

Properties	**Value, Unit**
Particle Size Distribution	Screen Residue >15 µm 0.03% Sedigraph 5100 d50 (1.2 µm) d95 (4.4 µm)
Specific gravity	2.78 g/cm^3
Specific Surface Area	14.5 m^2/g
Hardness	1 (Mohs' scale)
Moisture content (105°C)	≤ 0.3 %
Chemical Composition	SiO_2 (61%), MgO (32%), Al_2O_3 (0.3%), Fe_2O_3 (0.2%) and CaO (0.9%)

Table 3.4 Properties of Irganox 1076 (Ciba Specialty Chemicals Corporation, www, 2000).

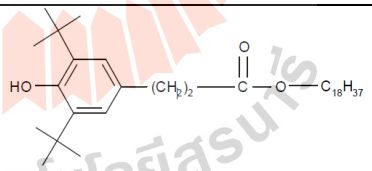
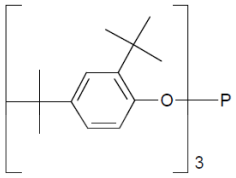
Properties	
Chemical name	Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate
Chemical structure	
Application	IRGANOX 1076, a sterically hindered phenolic antioxidant, is highly efficient, non discoloring stabilizer for organic substrates such as plastics. It protects these substrates against thermo-oxidative degradation.

Table 3.5 Properties of Irgafos 168 (Ciba Specialty Chemicals Corporation, www, 2000).

Properties	
Chemical name	Tris(2,4-ditert-butylphenyl)phosphite
Chemical structure	
Application	IRGAFOS 168 is a hydrolytically sTable phosphite processing stabilizer. It was reacts during processing with hydro peroxides formed by autoxidation of polymers preventing process induced degradation and extending the performance of primary antioxidants.

3.3.2 Design of Experiment

The 2^k factorial design of experiment which *k* equal to 3 was erected to optimizing and quantifying the amount of the wood composite constitutes. Three parameters were silane (**A**), wood flour (**B**) and talc (**C**) contents. Each parameter was divided into two levels; high (+1) and low (-1), respectively. In each level, it was also divided into two sub levels as shown in Table 3.6. For example, silane content at 3 and 5 phr were assigned as low levels, vice versa 8 and 10 phr were assigned as high levels, respectively. According to the rule of design, $2^3 = 8$, eight runs of WPC ingredient was constructed. The design matrix was demonstrated in Table 3.7. The actual mixing batch size was in corresponding to 300 g of PP. The DCP and the stabilizer was constantly added at 0.3 and 2.0 phr into each formulae, respectively

Table 3.6 The parameters and levels of DOE.

Parameters	**High level (+)**		**Low level (-)**	
Silane(phr)	+10	+8	-5	-3
Wood Flour(phr)	+45	+35	-25	-15
Talc(phr)	+40	+30	-20	-10

Table 3.7 Design matrix of both actual and coded factor levels.

Test	**PP (phr)**	**Silane(A) (phr)**	**Wood(B) (phr)**	**Talc(C) (phr)**	DCP (phr)	Stabilizer (phr)
1	100	3(-)	25(-)	20(-)	0.3	2
2	100	5(-)	15(-)	40(+)	0.3	2
3	100	3(-)	45(+)	10(-)	0.3	2
4	100	5(-)	35(+)	30(+)	0.3	2
5	100	8(+)	15(-)	10(-)	0.3	2
6	100	10(+)	25(-)	40(+)	0.3	2
7	100	8(+)	35(+)	20(-)	0.3	2
8	100	10(+)	45(+)	30(+)	0.3	2

3.3.3 Fibre preparation

Wood flour from timber mill was ground into fine powder by hammer mill machine. The size of the fibre was determined by the sieve number or mesh size of the milling. Then it was adequate into integral number. The fibre that passed through the 1 mm sieve, mesh number 18, was verified as fibre having the size less than 1 mm. The bigger fibre was excluded by this method. It was dried in hot oven at

105°C for at least 12 hours to eliminate the trace moisture. Wood flour and VTMS was then mixed by high speed mechanical propeller for 5 minutes. The silane treated wood flour was subsequently stored at room temperature over night, it be able to increasing in grafting between wood and silane before dry blend with the PP and stabilizer before use.

3.3.4 WPC preparation

The mixing scheme of WPC formula conducted in this work is shown in Figure 3.2. Beginning with polypropylene pellets and solid dicumyl peroxide that were pre-mixed and warmed in oven at 60°C for 5 min allowing DCP to melt. The ingredient was then rigorously shaken in plastic bag. By doing so, PP pellet was evenly coated with DCP. The pre dried talc in vacuum oven at 110°C for 1-3 hrs and the silane treated wood flour from 3.3.3 was added into DCP coated PP and utterly pre-blended. Again, it was stored in oven at 80°C before mixing. The ingredient was then constantly controlled and fed into co-rotation twin screw extruder through the single screw feeder for maintaining the fill factor below 1.0 during mixing. The self wiping mixer is consisted of screws with the diameter of 25 mm. and L/D of 20. It is comprised of three triple kneader disks to assist the mixing efficiency. The temperature profiles on the extruder barrel were electrically and constantly controlled at 180, 185, 185, 190 and 190°C from hopper to die zone, respectively. It was observed that mixing at temperature above 190°C would induce the fibre degradation and hence polymer chain scission resulting the darker in color of the WPC stand and also lowers the mechanical properties. The extruded strand was then air cooled and finally granulated in to small pellet using mechanical jaw crusher. The composite pellet was dehumidified at 80°C under vacuum for 2 hr before injection. The test

specimen were prepared by injection molding using Tederic TRX60c injection molding machine at barrel temperature of 170, 170, 175, 190 and 190°C from feed to nozzle tip, graduately. The four cavities rectangular shaped mold with tab gate was employed. The mold temperature was set at 45°C and cooling time of 30 seconds.

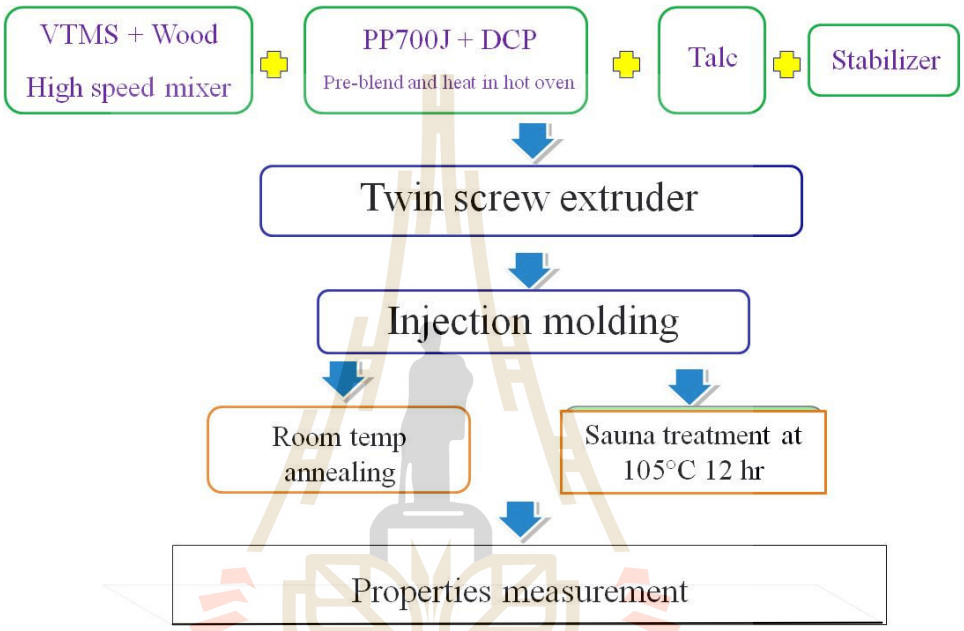


Figure 3.2 Schematic diagram for sample preparation of wood polypropylene composite.

3.3.5 Sauna Treatment of the WPCs

The polypropylene wood composites specimens were divided into 2 sets of samples. One was allowed to anneal at room temperature for at least a day before testing. It was named as original sample. The rest was undergone incubation in the oven that saturated with water vapor at 105°C. They were hatched in the oven for 12 hours and allowed to cool down to room temperature for day prior to test. This process was carried out in order to accelerate the silane/water crosslink reaction. It

would take more than several weeks to complete the crosslink process at the normal atmospheric condition. The sample obtained from this process was called cured or sauna treated WPC.

3.4 Properties measurement and analysis

3.4.1 Rheological testing

The rheological property by mean of melt flow index (MFI) was conducted. The MFI of the wood polypropylene composites pellet was tested in accordance with ASTM D 1238 using the Kayeness melt flow indexer model 4004. The pellet samples obtained was vacuum dried in the oven at 80^{o}C for at least 2 hr to eliminate the residual moisture. Testing samples were melt at 170^{o}C and driven through the capillary die (Ø 1 mm.) using piston load of 2.16 kg. The melting time was set at 240 second. Three cuts were performed and cut times of 15 second The weight of the cut extrudate were calculated into the melt flow index in the standard unit of g/10min.

3.4.2 Impact testing

Impact strength of wood polypropylene composites was tested using ASTM D 256 in Izod mode. The specimen obtained from injection molding with the dimension of 4X13X120 mm was notched using notching machine. The identical injected samples were tested without notching. Notched and Unnotched impact strength was conducted at room temperature using the impact pendulum with impact energy of 2.7 Joule for the notched specimen and 5.4 Joule for the unnotched sample, respectively. The impact values were reported as impact strength (kJ/m^2) that was calculated from lost impact energy divided by the cross section area the fractured

point. Five samples were tested for each composite sample and the average value was obtained and presented.

3.4.3 Flexural testing

Flexural properties by mean of the strength and modulus of the WPC sample were examined in accordance of ASTM D790. Instron universal testing machine (UTM, model 5565) with load cell of 5 kN and three point bending test fixture with span length of 72 mm was employed. The crosshead speed of 10 mm/min was controlled. The test specimen was placed plat-wise to the bending load. The test was conducted at room temperature in normal atmospheric condition. Five samples were tested in each composite sample and the average value was calculated.

3.4.4 Heat deflection temperature testing

Heat deflection temperature (HDT) of the wood composites was obtained in accordance with ASTM D 648. A samples tested in the edgewise position, with the support span length of 100 mm, as a simple beam with the load applied at its center to give maximum stress of 0.455 MPa (66 psi). The standard testing machine from Atlas ,model HDV 1, was employed. The raising temperature at a uniform rate of 2±0.2^{o}C/min was assigned. Liquid silicone oil was used as heating transfer media. The HDT value was reported in degree Celsius (^{o}C) as soon as the specimen had been deflected to 0.25 mm or 0.01 inch that monitored by dial gauge. This temperature was recorded as the deflection temperature under flexural load of the test specimen. Three samples were examined.

3.4.5 Morphological investigation

Morphology of the fractured surface of wood polypropylene composites was examined using scanning electron microscope (SEM). The broken

piece of notched specimen from impact test was cut in to small piece of sample. It was then attached onto the sample holder. The samples were coated with layers of gold for 5 min by ionization before analysis. SEM photograph was taken using JOEL machine model JSM6400 at the accelerating voltage of 20 keV.

3.4.6 Interpretation of DOE

According to the 2^k factorial approach with k = 3, eight run were designed to evaluating the statistical effects of the recipe composition factor on the given responds. The effect of the factor is define as the change in response produce (Y) by a change in the level of the factor such high (+) and low (-) level. It is called main effect (E_f) and calculated as follow:

$$E_f = \frac{\Sigma Y_{E+}}{n/2} - \frac{\Sigma Y_{E-}}{n/2} \quad (3.1)$$

where E_f = main effect of factor

y_{E+} = the responses of high level factor

y_{E-} = the responses of low level factor

Analysis of variance (ANOVA) and regression techniques are useful to determine if there is a statistically significant difference between treatments and levels of variables. After calculating the main effect and interaction effect of factors then graph plotting between normal probability and effect of factor into normal probability plot. The significant effect from the normal plot is again evaluation by ANOVA by statistical mean. In this work the commercial computer software, Design Expert™ version 7, was using to assist the statistical calculation. The level of significant (α) was assigned at 0.05 or 95% confidential. Base on *P*-value from statistical calculation

if the calculated *P*-value is less than 0.05, it is implied that statistical model and also the given factor were significant. Finally, the accepted factor derived from ANOVA was used to calculate the predicted regression model for properties of WPCs.

3.5 Results and discussions

3.5.1 Analysis of MFI

Table 3.8 MFI of wood polypropylene composite.

Test	PP (phr)	**Silane(A) (phr)**	**Wood(B) (phr)**	**Talc(C) (phr)**	DCP (phr)	Stabilizer (phr)	MFI@170/2.16 (g/10 min)
1	100	3(-)	25(-)	20(-)	0.3	2	12.73
2	100	5(-)	15(-)	40(+)	0.3	2	11.63
3	100	3(-)	45(+)	10(-)	0.3	2	8.61
4	100	5(-)	35(+)	30(+)	0.3	2	9.02
5	100	8(+)	15(-)	10(-)	0.3	2	20.41
6	100	10(+)	25(-)	40(+)	0.3	2	12.54
7	100	8(+)	35(+)	20(-)	0.3	2	9.95
8	100	10(+)	45(+)	30(+)	0.3	2	7.24

Rheological properties by mean of melt flow index, obtained at 170/2.16, of wood polypropylene composite are summarized in Table 3.8. They were taken into the calculation of the standard effects of the individual parameter and also the interacted parameters by assisting of Design Expert™. Consequently, the plot of the normal % probability and pareto chart are constructed as illustrated in Figure 3.3

and 3.4 respectively. Based on the analyzed result, it is seen that only amount of wood (**-B**) has the tendency to be negatively and significantly affected to the melt index of WPC as it is located outside the regressed linear trend line.

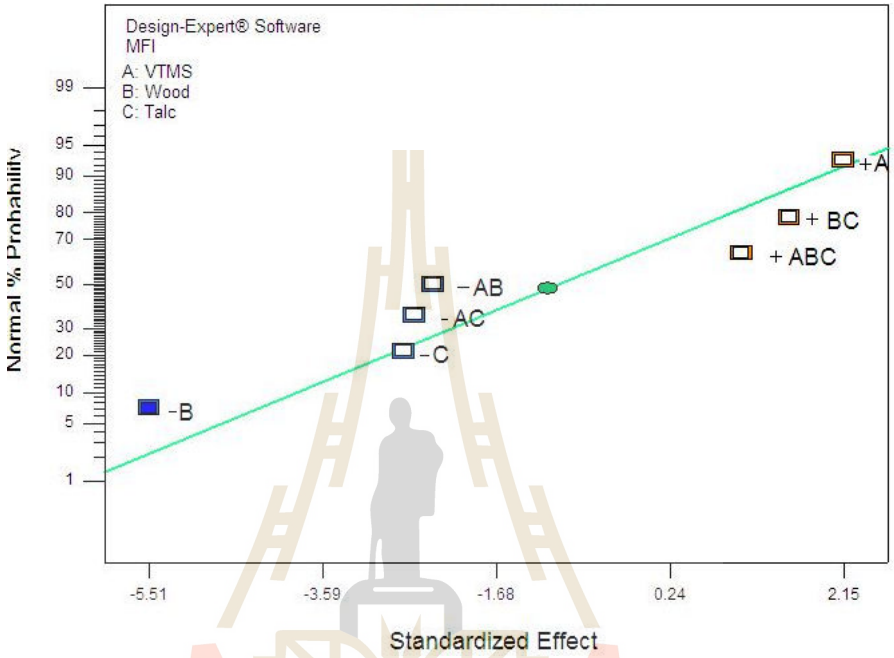


Figure 3.3 Normal probability plot of MFI.

To confirm this proposition, the ANOVA testing was analyzed and the test result is given in Table 3.9. According to the statistical conclusion, the levels of designed parameters to manufacture the WPC is significantly affected to MFI of the wood composite as it is indicated by the calculated *P*-value, 0.0472, of the model less than the critical value, 0.05. The pareto chart in Figure 3.4 is reinforced that wood flour content (**-B**) had negatively and significantly affected to the flow ability of the composite. It is meant that increasing the wood content will decrease the MFI, higher viscosity process but benefit for the manufacturing by extrusion in melt.

Table 3.9 ANOVA test for MFI.

Analysis of variance Table for MFI					
Source	Sum of Squares	df	Mean Square	F-value	*P*-value
Model	60.71	1	60.71	6.58	0.0427
B-Wood	60.71	1	60.71	6.58	0.0427
Residual	55.4	6	9.23		
Cor Total	116.11	7			

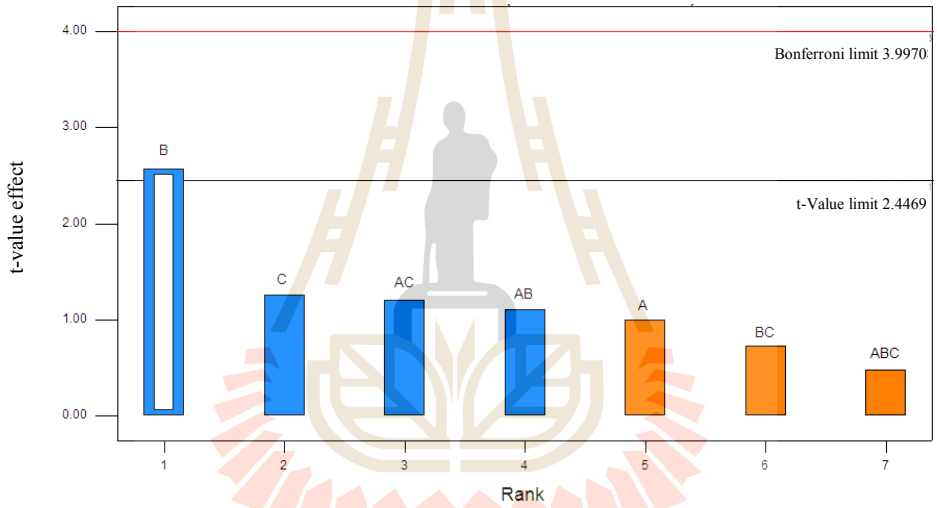


Figure 3.4 Pareto chart analysis of MFI.

3.5.2 Analysis of flexural properties

Flexural strength and its modulus of are summarized in Table 3.10 for the original and sauna cured samples, respectively. General observation, it is seen that the test values obtained from sauna cured sample are slightly higher that the sample without curing. It is might be due to the increasing the crosslink network though the silane/water condensation reaction. The parameter

effects of flexural strength of original samples were calculated and plotted with the normal % probability and pareto chart are given in Figure 3.5 and 3.6 respectively. From the standard effects plot shows that silane (+**A**) and the interaction effect between silane and talc (-A**C**) are and the greatest effect on the flexural strength of WPC without sauna treatment. They are positive (+) and negative (-) effects on the strength, respectively. With the assistance of ANOVA testing at 95% of confidential, the conclusion confirms that these two parameters are significantly effect on the flexural strength as the calculated *P*-values of the model and also the parameters are less than 0.05 as shown in Table 3.11.

Table. 3.10 Flexural properties of wood polypropylene composite.

Test run	Flexural Strength(MPa)		Flexural Modulus(GPa)	
	Original	Cured	Original	Cured
1 (-,-,-)	53.57 ± 0.71	53.57 ± 0.73	1.84 ± 0.16	1.96 ± 0.74
2 (-,-,+)	55.57 ± 0.63	54.17 ± 0.79	2.34 ± 0.07	2.41 ± 0.92
3 (-,+,-)	53.81 ± 0.83	53.75 ± 2.03	2.16 ± 0.06	2.18 ± 0.36
4 (-,+,+)	54.66 ± 1.19	55.69 ± 1.52	2.34 ± 0.05	2.35 ± 0.14
5 (+,-,-)	55.87 ± 0.72	57.67 ± 0.96	1.84 ± 0.02	1.88 ± 010
6 (+,-,+)	54.69 ± 1.91	54.12 ± 0.98	2.43 ± 0.10	2.58 ± 0.08
7 (+,+,-)	56.12 ± 1.21	57.44 ± 0.98	2.29 ± 0.10	2.23 ± 0.05
8 (+,+,+)	55.79 ± 1.33	56.04 ± 1.17	2.47 ± 0.13	2.57 ± 0.10

For the cured sample by sauna incubation, the normal plot is illustrated in Figure 3.7. The similar consequences are observed. Talc (-**C**) content also indicates the significantly and negatively effect on the flexural strength of WPC after sauna curing. However, the ANOVA testing and pareto chart as shown in Table 3.12 and Figure 3.8. concludes that only silane (+**A**) and interaction between silane and talc (-**AC**) are significantly effect on the flexural strength of the composite but not talc. Taking only the statistical results into consideration, it suggests that adding only silane(**A**) at high level content (+), the flexural strength of WPC both without and with moisture incubation would be elevated. Similarly, high silane content with low level of talc would also superior the flexural strength of the composite.

The normal plot the standard effect of the parameters on the flexural modulus the WPC sample without and with sauna cured are given in Figure 3.9 and 3.11, respectively. Pareto chart analysis of original and sauna cured samples are show in Figure 3.10 and 3.12 respectively. The flexural modulus of both sample conditions is seemingly and greatly influenced by only the talc content (**C**+). The *p*-values obtained from ANOVA testing, in Table 3.13 and 3.14, for the design models of original and cured samples are 0.0244 and 0.0071, respectively. They are confirmed that the factor **C**, talc content, is significant effect on flexural modulus of WPC. It is meant that mixing the talc into the WPC at high level of content, it will give rise to the wood with higher stiffness but also brittle.

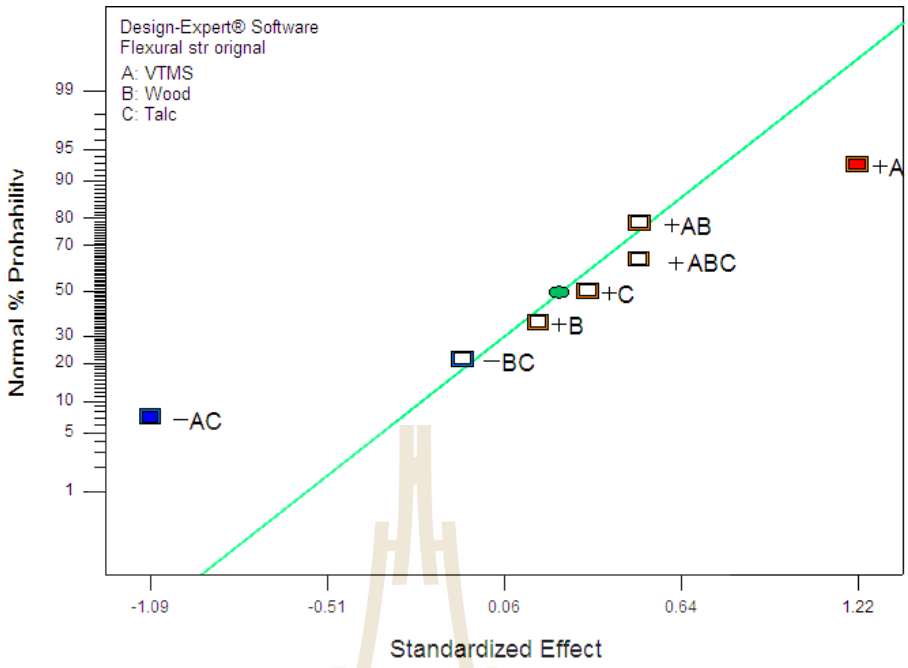


Figure 3.5 Normal probability plot of flexural strength (original).

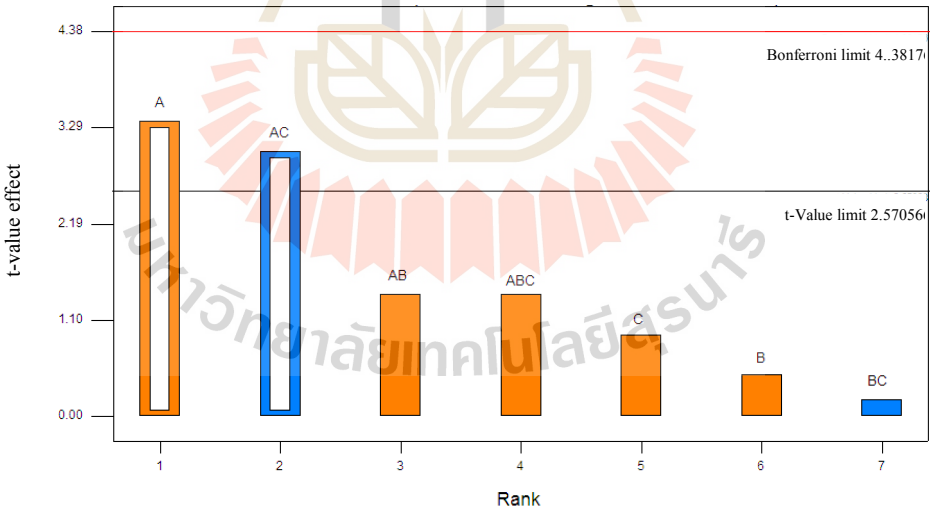


Figure 3.6 Pareto chart analysis of flexural strength (original).

Table 3.11 ANOVA test for flexural strength (original).

Analysis of variance Table for flexural strength (original)					
Source	Sum of Squares	df	Mean Square	F Value	*P*-value
Model	5.34	2	2.67	10.16	0.0173
A-VTMS	2.95	1	2.95	11.25	0.0202
AC	2.38	1	2.38	9.07	0.0297
Residual	1.31	5	0.26		
Cor Total	6.65	7			

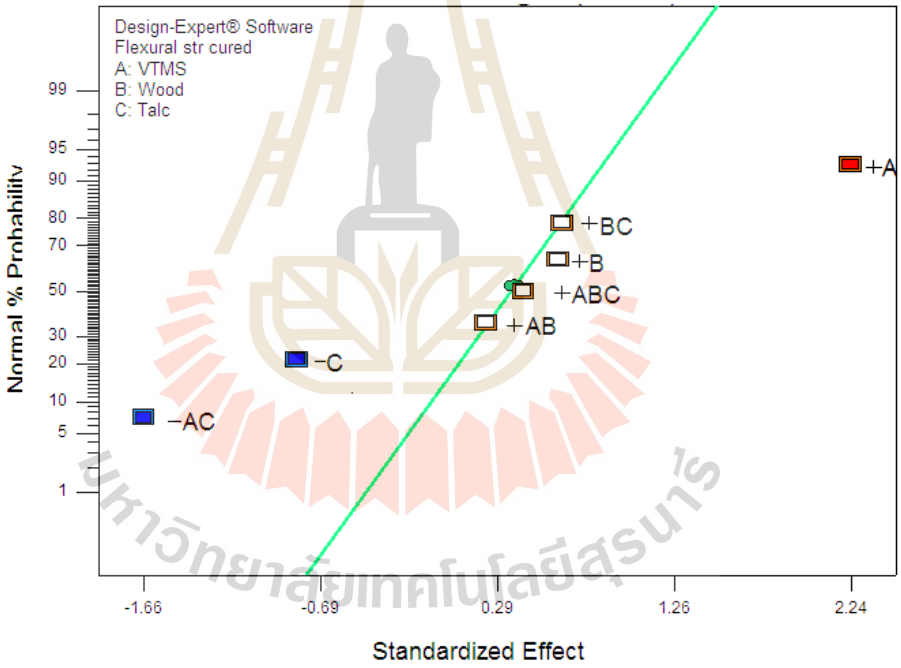


Figure 3.7 Normal probability plot of flexural strength (cured).

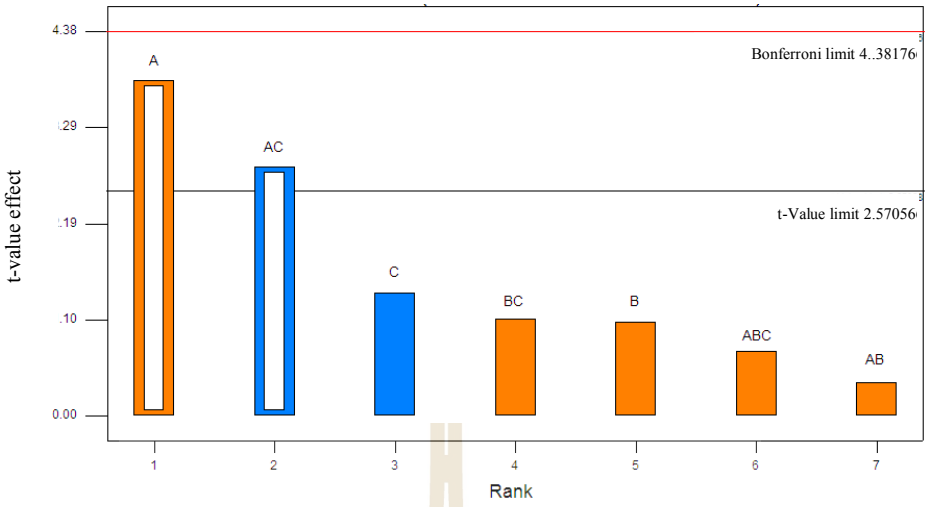


Figure 3.8 Pareto chart analysis of flexural strength (cured).

Figure 3.12 ANOVA test for flexural strength (cured).

Analysis of variance Table for flexural strength (cured)					
Source	Sum of Squares	df	Mean Square	F Value	*P*-value
Model	16.84	3	5.61	10.81	0.0218
A-VTMS	9.99	1	9.99	19.25	0.0118
C-Talc	1.33	1	1.33	2.57	0.1841
AC	5.51	1	5.51	10.62	0.0311
Residual	2.08	4	0.52		
Cor Total	18.92	7			

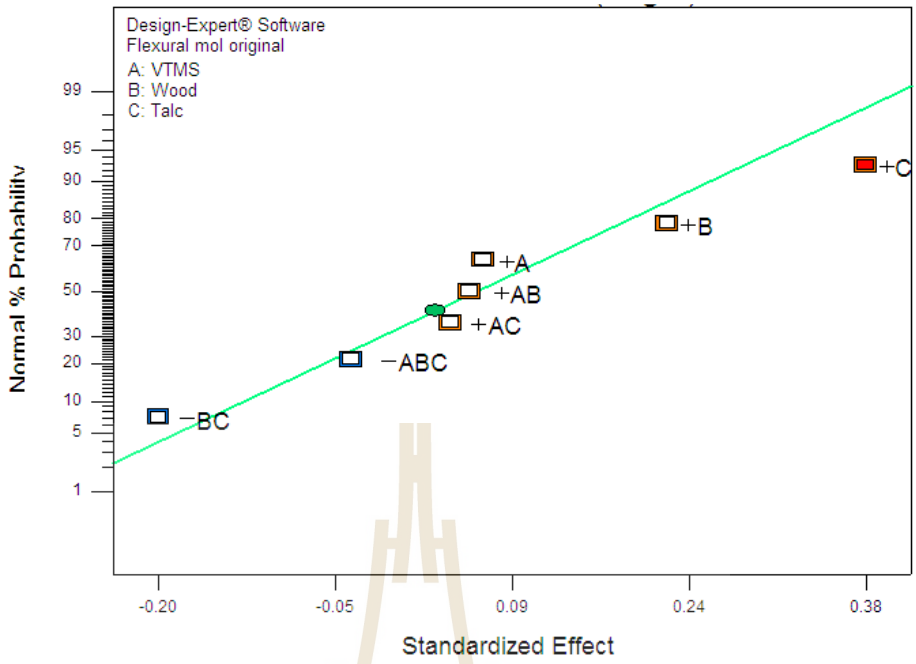


Figure 3.9 Normal probability plot of flexural modulus (original).

Table 3.13 ANOVA test for flexural modulus (original).

Analysis of variance Table for flexural modulus (original)					
Source	Sum of Squares	df	Mean Square	F Value	*P*-value
Model	0.2911	1	0.291	8.92	0.0244
C-Talc	0.2911	1	0.291	8.92	0.0244
Residual	0.1959	6	0.033		
Cor Total	0.4870	7			

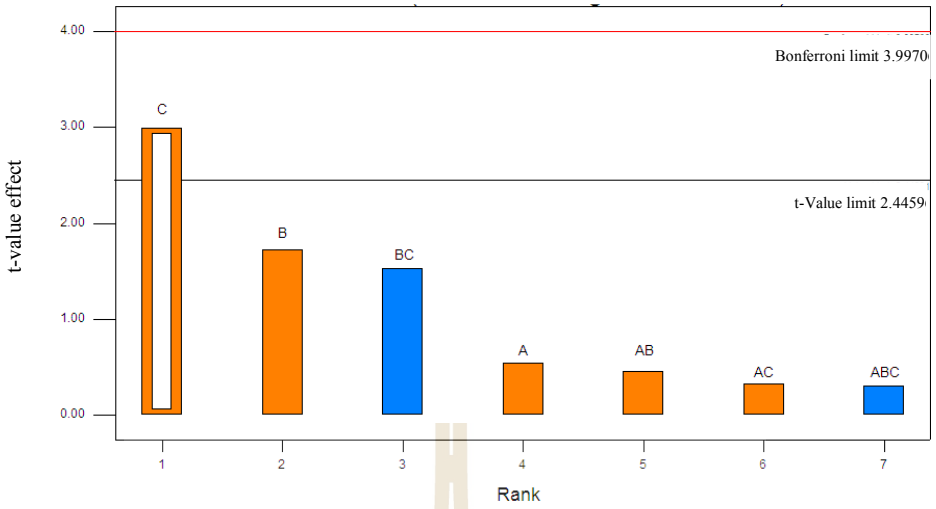


Figure 3.10 Pareto chart analysis of flexural modulus (original).

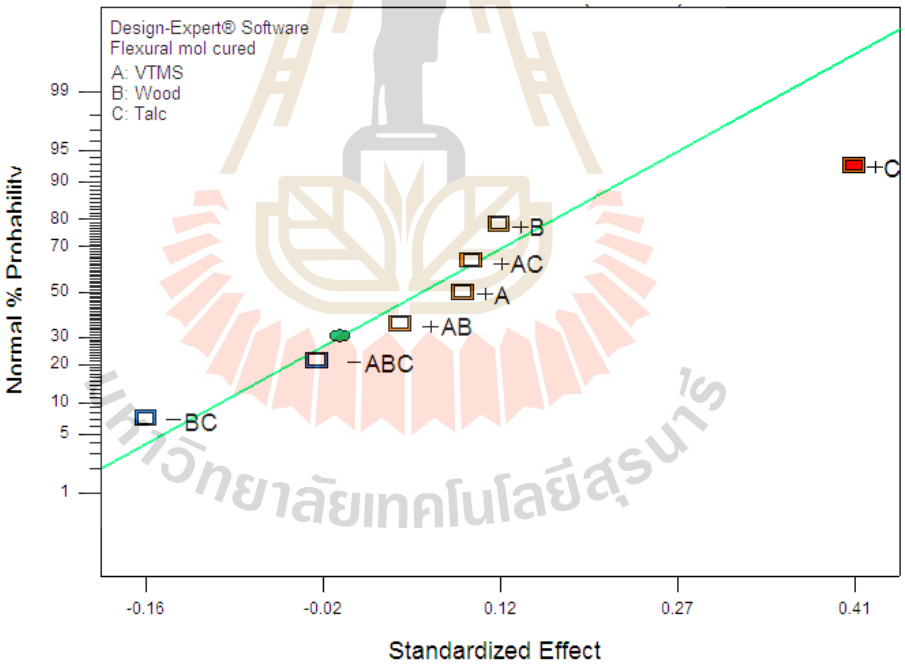


Figure 3.11 Normal probability plot of flexural modulus (cured).

Table 3.14 ANOVA test for flexural modulus (cured).

Analysis of variance Table for flexural modulus (cured)					
Source	Sum of Squares	df	Mean Square	F Value	*P*-value
Model	0.3321	1	0.3321	16.06	0.0071
C-Talc	0.3321	1	0.3321	16.06	0.0071
Residual	0.1241	6	0.0207		
Cor Total	0.4562	7			

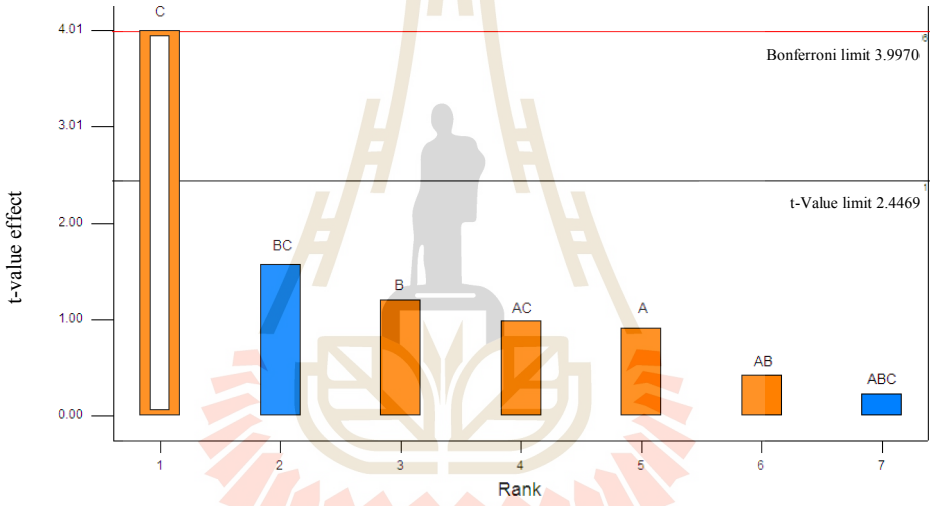


Figure 3.12 Pareto chart analysis of flexural modulus (cured).

3.5.3 Analysis of impact strength

Test values of the notched and unnotched impact strength of WPCs for both original and cured samples are summarized in Table 3.13. Evidently, results show that notched impact strength of cured samples was higher than the original ones. It is confident to postulate that silane water crosslink via sauna treatment can enhance the toughness of WPCs. The statistical analysis using normal plot and pareto chart as

seen in Figure 3.13 and 3.14, respectively illustrate that the notched impact strength for the uncured WPCs is affected from the talc content **(C**) and interacted parameters between silane and talc (A**C**) which are negative (-) and positive (+) effects, respectively. In contradictory, the ANOVA result shown in Table 3.14 indicates that *P*-value of model is 0.2430 which higher than the critical value, 0.05. It is implied that talc (-**C**) and interacted between silane and talc (+**AC**) are not significant effect to the notched impact strength of the virgin WPCs.

Table. 3.15 Impact strengths of wood polypropylene composite.

Test run	Notched Impact Strength (kJ/m^2)		Unnotched Impact Strength (kJ/m^2)	
	Original	Cured	Original	Cured
1 (-,-,-)	0.973 ± 0.14	1.428 ± 0.18	9.177 ± 0.25	8.940 ± 1.58
2 (-,-,+)	0.910 ± 0.10	1.352 ± 0.27	7.563 ± 1.39	7.703 ± 1.32
3 (-,+,-)	1.210 ± 0.26	1.320 ± 0.20	7.329 ± 1.27	8.685 ± 1.81
4 (-,+,+)	0.989 ± 0.19	1.478 ± 0.34	8.924 ± 1.16	6.279 ± 1.06
5 (+,-,-)	0.958 ± 0.11	1.351 ± 0.26	8.022 ± 2.33	11.48 ± 2.06
6 (+,-,+)	1.056 ± 0.11	1.411 ± 0.25	8.022 ± 0.92	8.541 ± 0.94
7 (+,+,-)	1.107 ± 0.35	1.337 ± 0.24	9.495 ± 1.08	8.962 ± 0.58
8 (+,+,+)	1.305 ± 0.16	1.101 ± 0.14	9.114 ± 0.30	8.497 ± 0.79

For the analysis of cured sample as shown in Figure 3.15, the silane (+**A**) and the interaction of all parameters (-**ABC**) shows positive and negative effect,

respectively. But these parameters are not significant effect to the impact of cured sample as it is confirmed by the ANOVA and pareto plot as presented in Table 3.15 and Figure 3.16, respectively. However, the results indicate that adding high amount of silane it would increase the notched impact strength of the sample after sauna curing process.

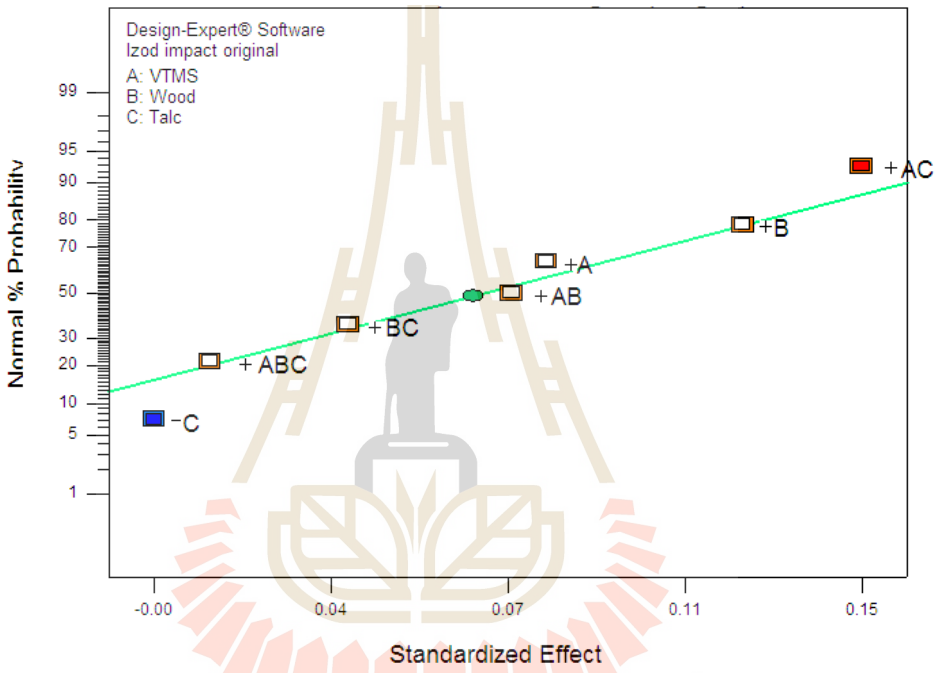


Figure 3.13 Normal probability plot of notched impact strength (original).

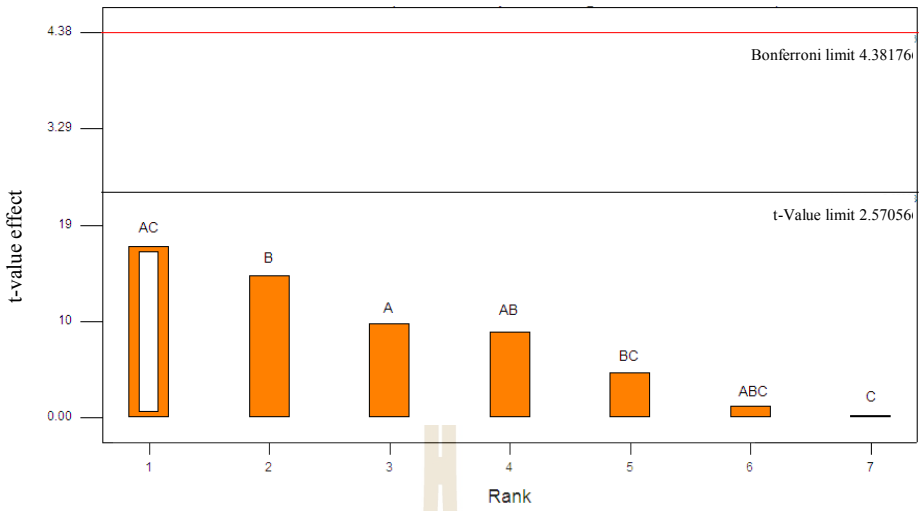


Figure 3.14 Pareto chart of notch impact strength (original).

Table 3.16 ANOVA test for notched impact strength (original).

Analysis of variance Table for notch impact (original)					
Source	Sum of Squares	df	Mean Square	F Value	*P*-value
Model	0.0449	2	0.0224	1.90225	0.2430
C-Talc	0.0000	1	0.0000	0.00052	0.9827
AC	0.0449	1	0.0449	3.80398	0.1086
Residual	0.0590	5	0.0118		
Cor Total	0.1038	7			

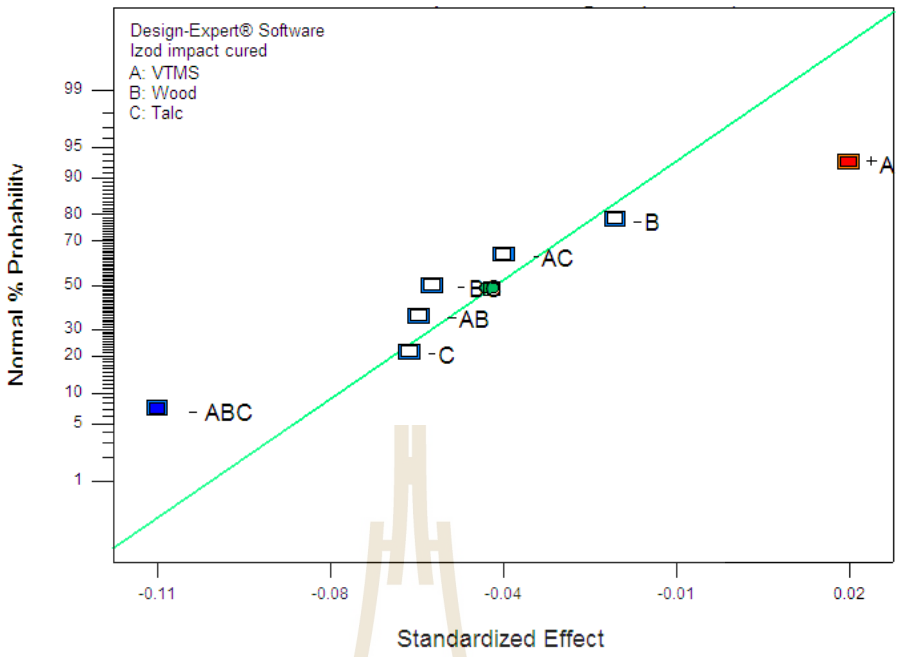


Figure 3.15 Normal probability plot of notched impact strength (cured).

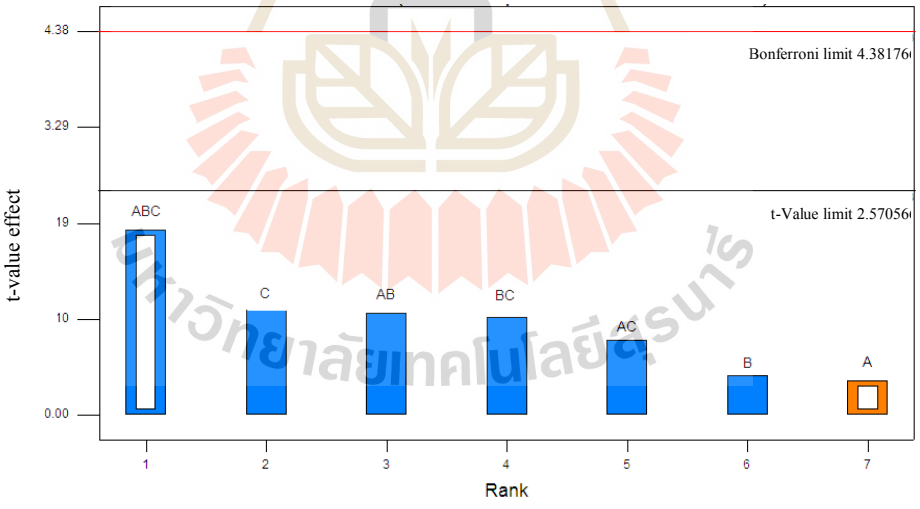


Figure 3.16 Pareto chart of notched impact strength (cured).

Table 3.17 ANOVA test for notched impact strength (cured).

Analysis of variance Table for notch impact (cured)					
Source	Sum of Squares	df	Mean Square	F Value	*P*-value
Model	0.0248	2	0.0124	2.3118	0.1946
A-VTMS	0.0008	1	0.0008	0.1538	0.7111
ABC	0.0240	1	0.0240	4.4697	0.0882
Residual	0.0268	5	0.0054		
Cor Total	0.0516	7			

Figure 3.17 show the normal plot of unnotched impact of WPCs before the sauna cured. The plot reveal that all single and interacted parameters are well fitted with the linear trend except the interaction between silane and talc (-**AC**) had negative effect. It indicate that this interacted parameters is probably had the significant effect to the unnotched impact of the uncured WPC. Taking the ANOVA result into account as summarized in Table 3.18, it is uncovered that the experimental model conducted for the test and also the -**AC** are not significant effect to the unnotched WPC without sauna treatment. The pareto chart provided in Figure 3.18 emphasis that unnotched impact of the WPC is not significantly affected by the designed model and parameters.

Vice versa, the normal plot of the strength of cured WPCs given in Figure 3.19 manifested that silane (+**A**), Wood content (-**B**) and talc (-**C**) have the tendency to be the pronounce effect to the unnotched impact strength as there are excluded from the linear regression line. The ANOVA conclusion as given in Table 3.19 supports that the designed model and both silane (+**A**) and talc (-**C**) are significantly effects on the impact respond. due to unnotched impact strength of sauna treatment WPCs. The

result from the pareto plot is also strengthened the conclusion of the design. Superior unnotched impact property of the WPC after moisture incubation can be achieved by incorporating high level of silane but low level of talc contents.

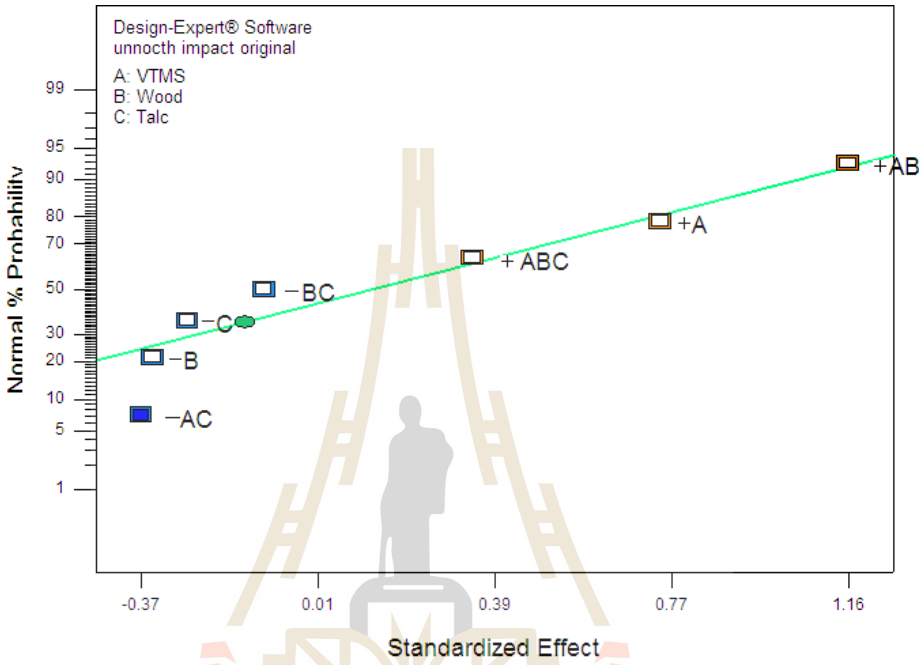


Figure 3.17 Normal probability plot of unnotched impact strength (original).

Table 3.18 ANOVA test for unnotched impact strength (original).

Analysis of variance Table for unnotch impact (original)					
Source	Sum of Squares	df	Mean Square	F Value	*P*-value
Model	0.2738	1	0.2738	0.37025	0.5652
AC	0.2738	1	0.2738	0.37025	0.5652
Residual	4.4370	6	0.7395		
Cor Total	4.7108	7			

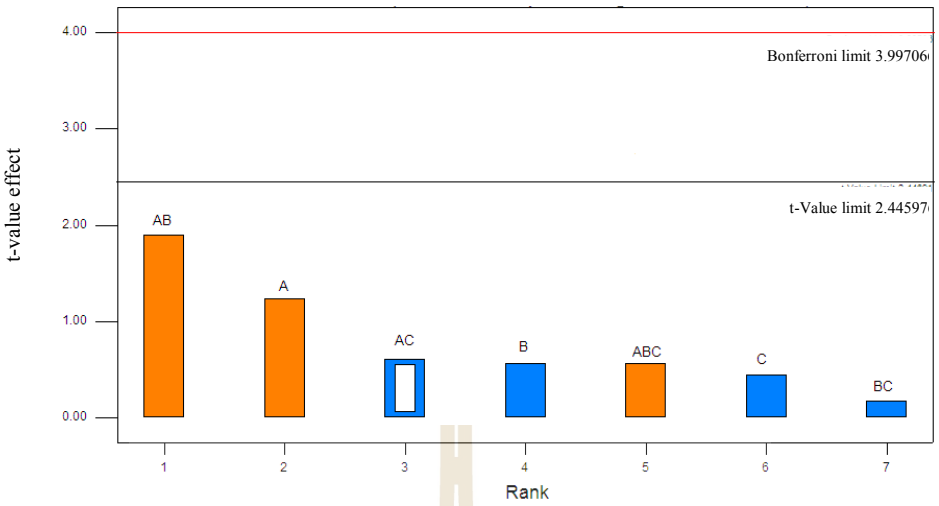


Figure 3.18 Pareto chart of unnotched impact strength (original).

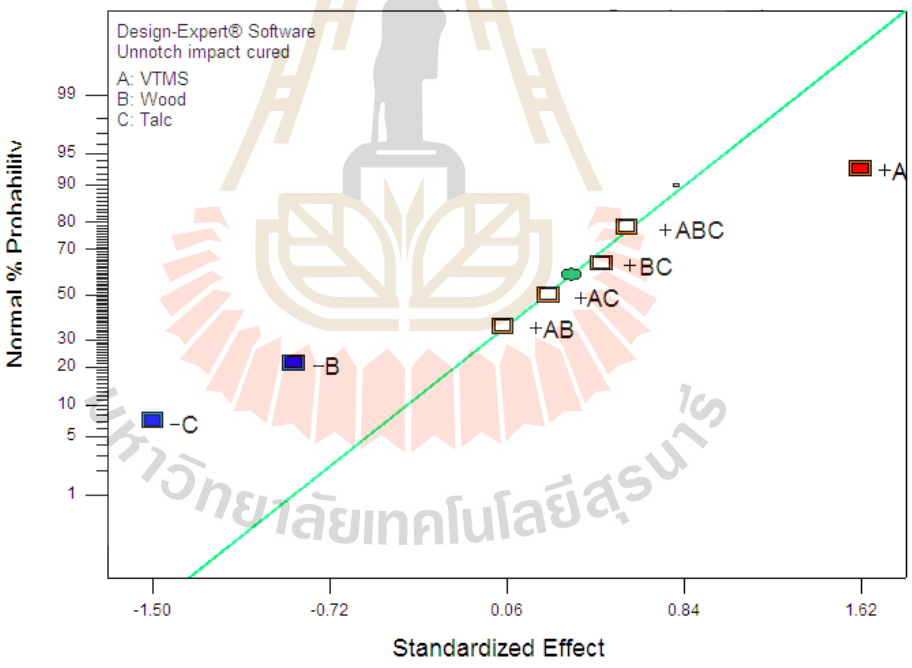


Figure 3.19 Normal probability plot of unnotched impact strength (cured).

Table 3.19 ANOVA test for unnotched impact strength (cured).

Analysis of variance Table for unnotch impact (cured)					
Source	Sum of Squares	df	Mean Square	F Value	*P*-value
Model	11.2884	3	3.7628	11.9841	0.0182
A-VTMS	5.2225	1	5.2225	16.6332	0.0151
B-Wood	1.5501	1	1.5501	4.93704	0.0904
C-Talc	4.5157	1	4.5157	14.3821	0.0192
Residual	1.2559	4	0.3140		
Cor Total	12.5443	7			

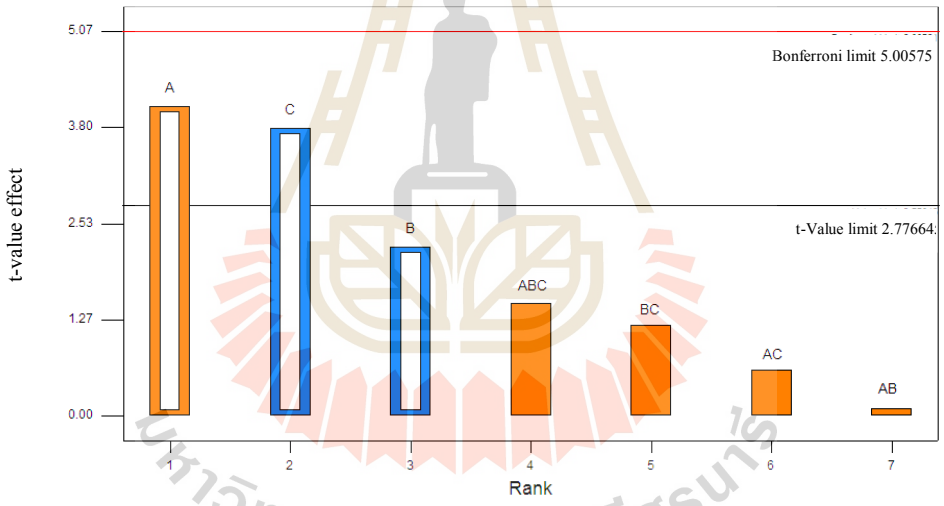


Figure 3.20 Pareto chart of unnotched impact strength (cured).

3.5.4 Analysis of HDT

Thermal properties by mean of heat deflection temperature (HDT) of wood polypropylene composite, derived from the DOE testing, for the original and after sauna cure are summarized in Table 3.20. It is observed that HDT of WPC sample are the range of 130 - 142°C. Generally, the values obtained from cured

sample are noticeably higher than the original ones. The change in thermal property of WPC sample from the sauna treatment might be influenced either from the silane/water reaction or the increase in the crystallinity of the PP matrix during incubation period. Both phenomena had the positive effect to the HDT of the WPC.

The statistic result of the original samples by using the normal plots as presented in Figure 3.21 obviously indicates that the wood flour (+**B**) and talc (+**C**) at high level of contents have positive effect to HDT. It is commonly known that filler and/or fibre addition normally enhance the thermal property of the composite material. Table 3.19 shows the *P*-values of the ANOVA testing. The analysis conclusion confirms that the HDT of WPCs is significantly and positively affected by wood and talc contents. Not only the ANOVA but also the pareto plot as given in Figure 3.22 verifies that those two parameters had great effect to the HDT.

On the other hand, the HDT analysis of cured WPCs by the normal plot is presented in Figure 3.23. It is seen that the interaction between silane and wood (AB-), which is negative effect, was largely deviated from the line trend. It shows the tendency to be significant effect on HDT of crosslinked WPC after sauna incubation. The pareto chart which is plotted between the calculated t-value and the rank of the effects on HDT shown in Figure 3.24 review that the interacted parameters, -AB, is below the critical t-value. It manifest that the effect is not significantly effect to the HDT of cured WPC. The conclusion is confirmed by the ANOVA result that summarized in Table 3.20. The statistical conclusion reviews that the model, the designed parameters, is not significantly effect to the HDT of WPC after sauna curing. Because the calculated *P*-value is 0.2497 which are higher than the assigned

critical *P*-value at 0.05. Hence, the interaction parameter between silane (A) and wood (B) contents is not significantly effect to the HDT as well.

Table. 3.20 Heat deflection temperature of wood polypropylene composite.

Test run	Heat deflection temperature (^{o}C)	
	original	cured
1 (-,-,-)	130.0 ± 2.0	136.7 ± 2.1
2 (-,-,+)	138.0 ± 0.0	138.7 ± 2.5
3 (-,+,-)	141.0 ± 1.7	141.0 ± 3.0
4 (-,+,+)	141.3 ± 1.2	143.3 ± 0.6
5 (+,-,-)	134.5 ± 2.7	140.3 ± 0.6
6 (+,-,+)	139.3 ± 1.5	142.3 ± 1.2
7 (+,+,-)	140.3 ± 2.5	139.0 ± 1.0
8 (+,+,+)	142.3 ± 1.5	142.3 ± 1.5

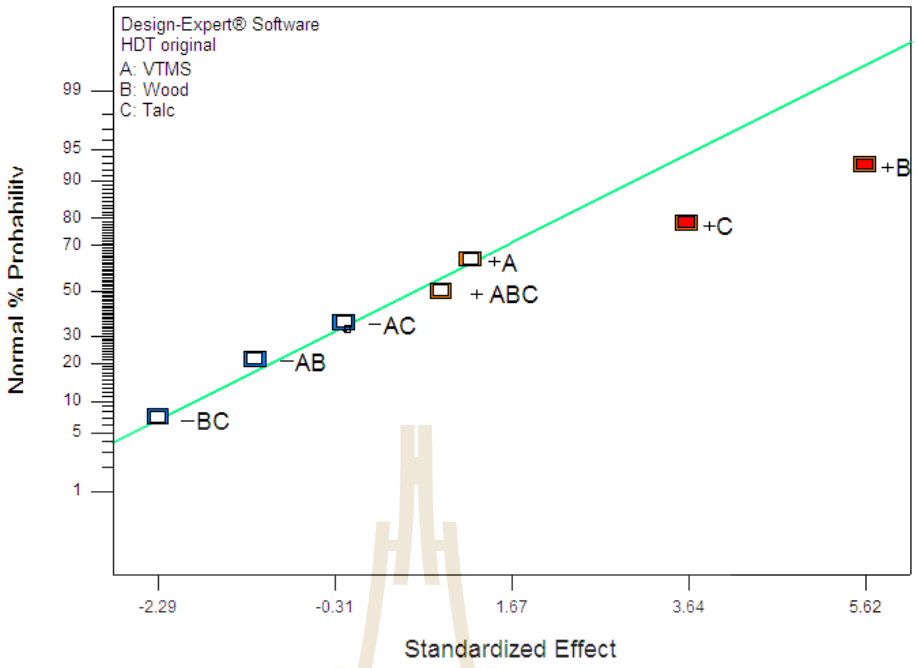


Figure 3.21 Normal probability plot of HDT (original).

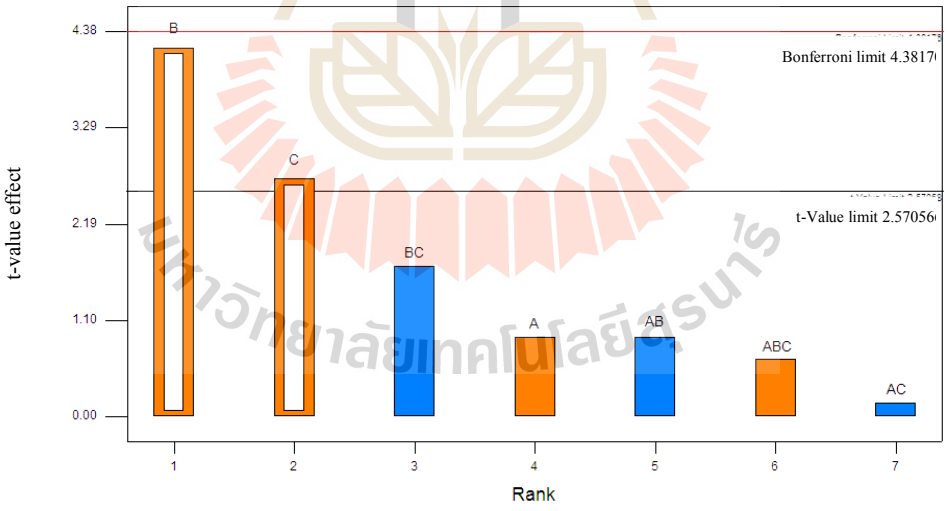


Figure 3.22 Pareto chart of HDT (original).

Table 3.21 ANOVA test for HDT (original).

Analysis of variance Table for HDT (original)					
Source	Sum of Squares	df	Mean Square	*F* Value	*P*-value
Model	89.4700	2	44.73501	12.4475	0.0114
B-Wood	63.2250	1	63.22501	17.5923	0.0085
C-Talc	26.2450	1	26.24501	7.30267	0.0427
Residual	17.9695	5	3.593892		
Cor Total	107.4395	7			

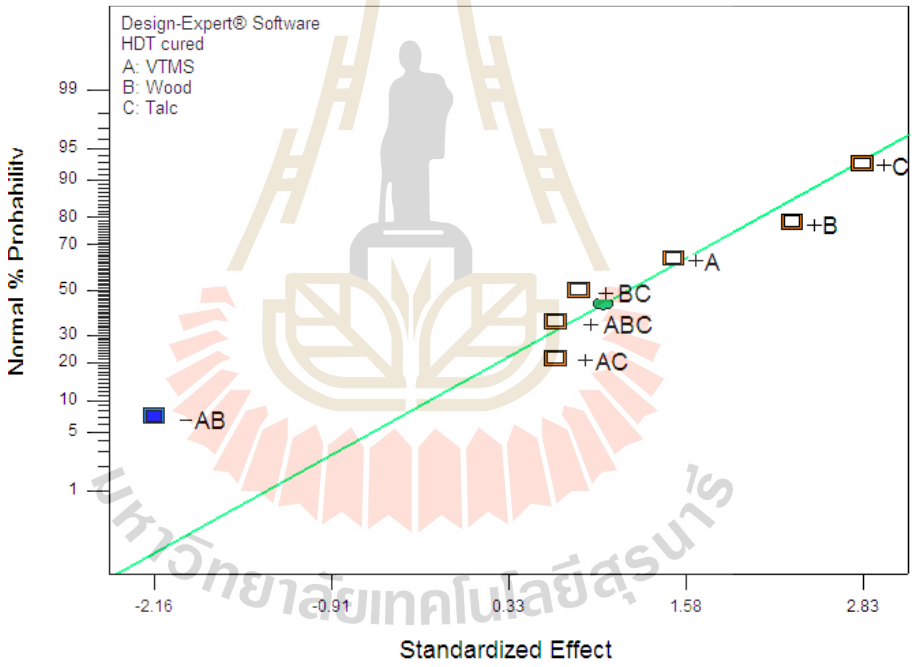


Figure 3.23 Normal probability plot of HDT (cured).

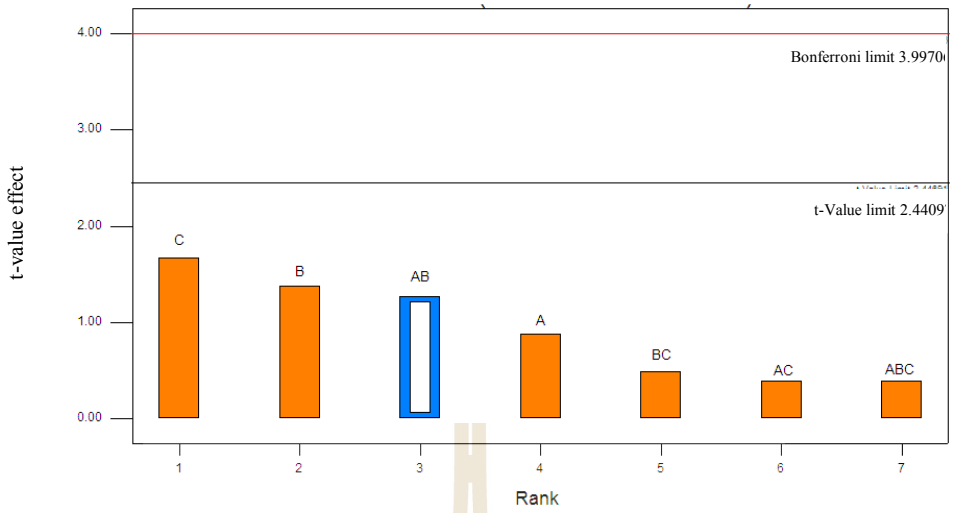


Figure 3.24 Pareto chart of HDT (cured).

Table 3.22 ANOVA test for HDT (cured).

Analysis of variance Table for HDT (cured)					
Source	Sum of Squares	df	Mean Square	*F* Value	*P*-value
Model	9.3658	1	9.3658	1.62396	0.2497
AB	9.3658	1	9.3658	1.62396	0.2497
Residual	34.6036	6	5.7673		
Cor Total	43.9694	7			

Within the statistical approach in this section, the primary conclusion can be drawn that the flow ability by mean of MFI of the crosslinked PP wood composite depends largely on the wood content. Higher in wood loading will inhibit the flow ability, lower in MFI, of the sample. General speaking, the wood content is significantly and negatively effect to the MFI. The flexural strength of WPC which refer to the bending toughness of the material has significantly controlled by silane

(+**A**) and combination between silane and talc (-**AC**) contents, respectively. It suggests that adding only silane (**A**) at high level content(+), the flexural strength of WPC both without and with moisture incubation would be elevated. Similarly, high silane content (+**A**) with low level of talc (-**C**) would also superior the flexural strength of the composite. The bending elasticity measured as flexural modulus of the sauna cured WPC is high when using high level of talc content (+**C**). The similar toughness properties of WPC were found for impact strengths especially in the unnotched mode. Finally, the service temperature by mean of HDT of WPC before sauna cured will be elevated if it is compounded at high level of wood flour. However, after the complete silane/moisture condensation the HDT does not affect by the given parameters.

3.5.5 Morphology investigation

Morphological observation by SEM of the fractured surface of the crosslinked polypropylene wood composites analyzed from Run#1. 7 and 8 are shown in Figure 3.25 (***a***) to 3.25 (***f***). Run# 1 and Run#8 samples are represent the formula which are derived from inclusively low level and high level parameters, respectively. They are shown quite interesting impact properties. WPC obtained from all low level of contents result in lowest strength for the original specimen but become highest in test value after sauna cured process. In contradictly, for Run#8, at all high loading parameters, the strength reviews the highest Figure before sauna cured but become the lowest after the process. Similarly, Run#7 indicates the highest toughness by mean of flexural strength for both before and after moisture incubation. Figure 3.25 (***a***) and 3.25 (***b***) illustrates the surface of WPC before and after sauna cured for Run#1's samples. The picture shows poor adhesion between wood and matrix that indicated by

the space between matrix and fibre for the original one. The surface delamination is diminished after the moisture treatment. Picture from Run#7, Figure 3.25 (***c***) and (***d***), at high silane and wood content but low level of talc, it is seen that the adhesion between those two phases is slightly improved by moisture incubation. The toughness strengths, both flexural and impact, are considerably increased through the treatment. Figure 3.25 (***e***) and 3.25 (***f***) are the original and sauna cured WPC sample of Run#8 with all high levels. It is shown the relative superior in all properties. However, the test values are slightly declined after silane/water crosslinked. This can be explained that as increasing the fibre/filler loading, they tendency to be agglomerated and absorbed excess moisture during the incubation. Hence, the material becomes weaker. From the SEM photographs, they suggest that sauna treatment on WPC compounded using high silane is achieved through silane/water macro crosslink reaction. Hence, the crosslink bridge between polymer matrix and wood flour could play the important role for enhance the surface interaction/adhesion and bonding strength between matrix and reinforcement, accordingly. Increasing in silane content would increase the mechanical properties, especially toughness, of WPC. Also as adhesion between the fibre/filler cluster particle increased through the silane/water reaction, the particle become too dense. Therefore, stress transfer from matrix to filler and flexibility of chain is inferior. As the result, the impact toughness is decreased as explained elsewhere (Hattotuwa, Premalal, Ismail, and Baharin. 2002).

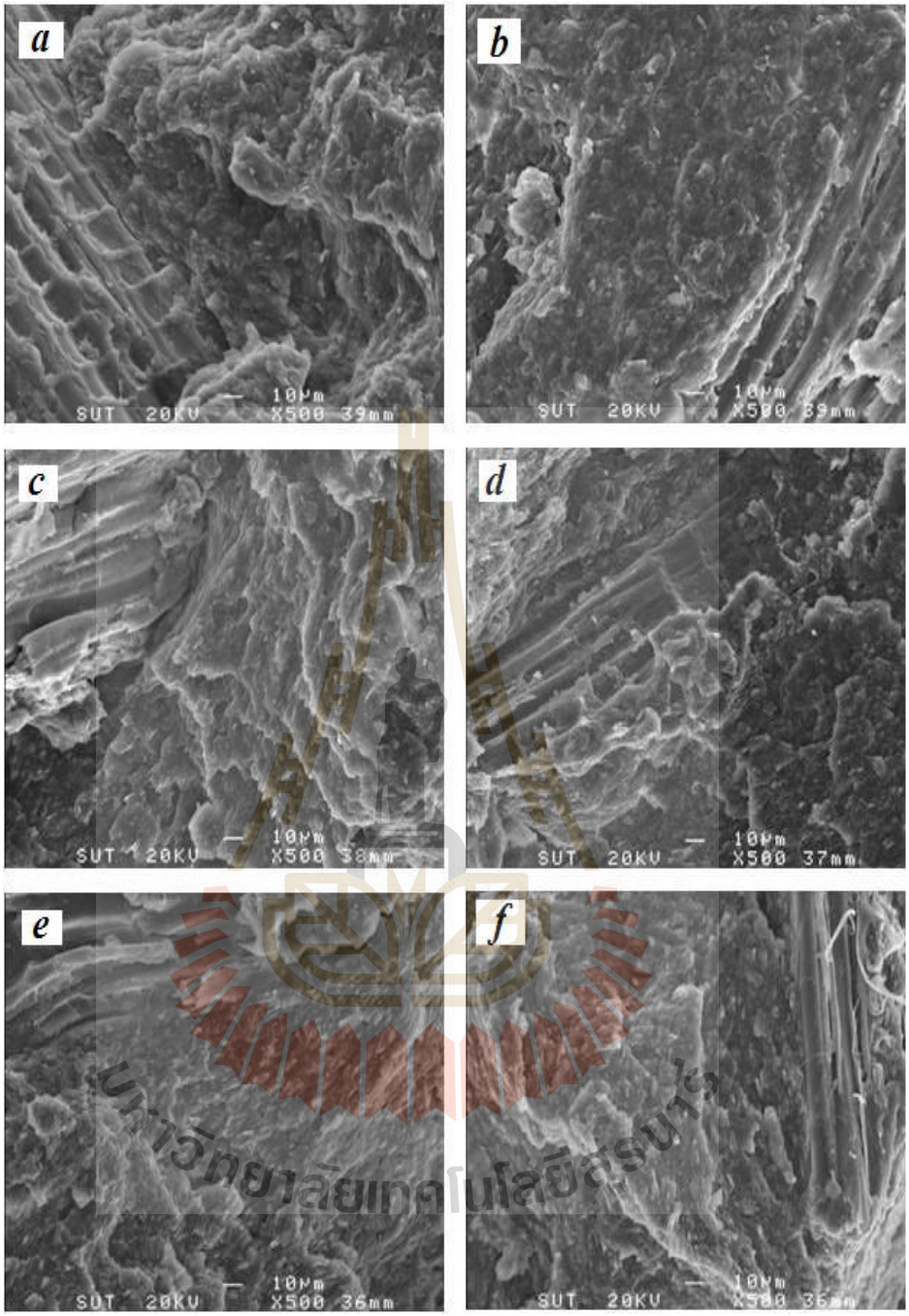


Figure 3.25 SEM micrograph of; (***a***) Run.1 original, (***b***) Run.1 cured, (***c***) Run.7 original, (***d***) Run.7 cured (***e***) Run.8 original and (***f***) Run.8 cured (X500).

3.5.6 Optimization

Taking the ANOVA conclusion presented above, the regression model obtained from the statistical calculation is also constructed and summarized in Table 3.23. The parameters seen in the equations are the significant parameters by mean of ANOVA analysis. The equation can be used to predict the properties Figure of the WPC to the required value. For example, the equation for HDT of the original is 138.52+2.81 (**B**)+1.81 (**C**). It is implied that maximized HDT of WPC can be achieved if it is compounded in twin screw mixing and injected at 190^{o}C by using high level of wood flour (**B** = +1) and high level of talc (**C** = +1), accordingly. The rest can be estimated as the identical manner. By using the DOE approach, the optimal formulation of WPC from crosslinked PP can be accomplished. The optimum response level of factor(s) from the Design Expert® given by plotting the desirability depended on silane and wood level of contents shown in Figure 3.26. It means that the maximum attraction, *e.g.* equal to 0.700 or 70% confident of WPC formula is suggested at high level (+1) of silane and wood but low level (-1) of talc contents. It recommended for better in properties of composite for both original and cured WPC. Therefore, test run no.7 (Run#7) compounded at 8 phr (+1) of silane, 35 phr (+1) of wood flour and 20 phr (-1) of talc are selected for optimal crosslinked PP wood composite constituent.

Table 3.23 The predicted regression models for the properties of WPCs derived from ANOVA testing.

Test	Regressed models
Original :	
MFI	11.46-2.75(B)
Flexural strength	55.01+0.61(A)-0.55(AC)
Flexural modulus	2.21 +0.19(C)
Notch impact	No significant
Unnotch impact	No significant
HDT	138.52+2.81(B)+1.81(C)
Sauna cured :	
Flexural strength	55.20+1.12(A)-0.41(C)-0.83 (AC)
Flexural modulus	2.27+0.20(C)
Notch impact	No significant
Unnotch impact	8.64+0.73(A)-0.53(B)-0.88(C)
HDT	No significant

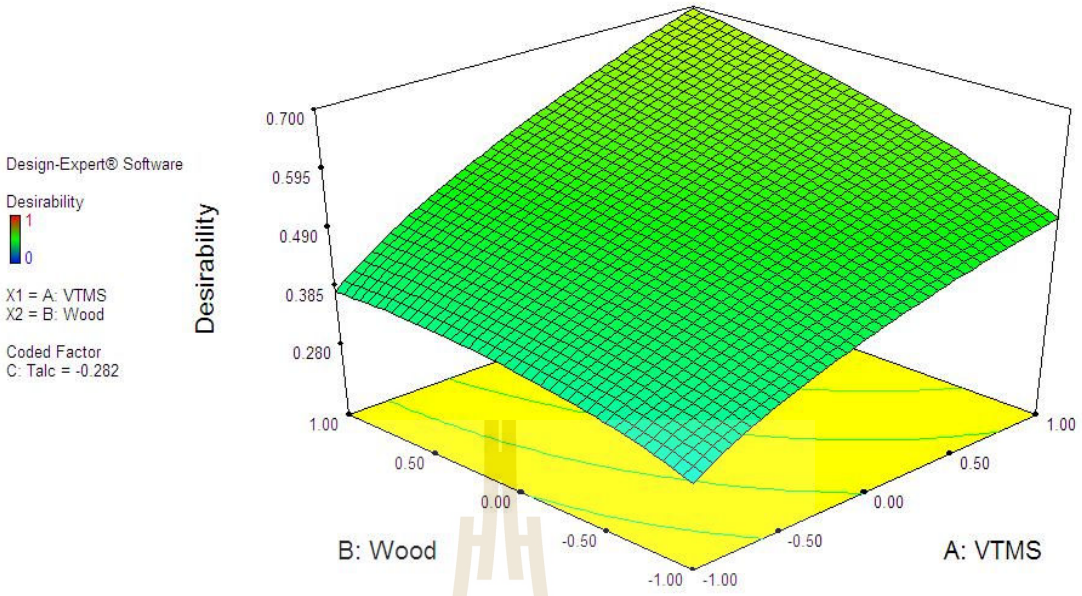


Figure 3.26 3D surface graph of desirability from Design-Expert®

3.6 Conclusions

The optimal formula of the composite material based on crosslinked PP matrix consisting of silane (**A**), wood flour (**B**) and talc (**C**) was concluded. By the DOE, statistical analysis approach, was shown that the flow ability of WPC was significantly and negatively controlled by the addition of wood flour (**-B**). There had no significant parameter the effect on notched and unnotched impact strength for both original and sauna cured WPC. Flexural strength of original WPCs had been strongly affected by silane (+**A**) and interaction between silane with talc (-**AC**). The similar effects were also detected for moisture cured sample. The flexural modulus of samples before sauna treatment were also influenced by wood (+**B**), talc (+**C**), and interaction of wood and talc (-**BC**), but talc (+**C**) was a positive effect on sauna cured specimen. The wood flour (+B) and talc (+C) at high level of contents obviously increased the heat deflection temperature (HDT) for original wood composite. For

cured samples, the ANOVA conclusion was shown no significant parameters on HDT. Scanning electron microscopy (SEM) evidenced the improvement of matrix/fibre adhesion of the WPC and hence the measured mechanical properties, accordingly. So, the optimal contents of WPC based on crosslinked PP should at high level (+) of silane, wood flour and lower (-) talc contents. This formula would produce the composite with generally good mechanical and thermal properties. Sauna cured via silane/water macro crosslinked reaction facilitated the interfacial adhesion between fibre and matrix and hence enhanced the mechanical properties.

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CHAPTER IV

TOUGHENING OF WOOD COMPOSITE

4.1 Abstract

Investigation of wood composite based on crosslinked polypropylene was studied. In this studied aim to improve toughness of composite. Ultra-high molecular weight polyethylene (UHMWPE) and Ethylene propylene diene terpolymer (EPDM) were employ to improve impact strength via blend matrix. Composites were compounded into pellets by co-rotation twin screw extruder and test specimens were prepared by injection molding. Sauna incubation at 105^{o}C for 12 hr in oven chamber was performed to accelerate the final silane condensation crosslink reaction. Impact strength, flexural properties and heat deflection temperature testing were conducted. Impact strength, HDT and flexural modulus can be improve with increasing UHMWPE content, and achieved optimal values at 5-10 phr of UHMWPE. Adding an EPDM elastomer to the matrix blends, reduced flexural strength and modulus but increased impact strength. When incorporation of EPDM into the PP/UHMWPE blends was exhibited much higher impact strength than that of the PP/UHMWPE binary blends. Silane crosslinked by sauna treatment can improve the impact strength, HDT were also much higher for the crosslinked composite compared to the non-crosslinked.

4.2 Introduction

From previous discussion, the toughness by mean of the notched impact strength of crosslinked PP wood composite was relatively low especially when compare with the virgin PP. Commonly, fracture toughness and impact resistance of WPC are among the most important properties as the material is normally subjected to the bending load. To achieve the highest load bearing of the composite, various modifying means have been used such as blending with other thermoplastics, rubbers, fibre reinforcement or through the filling with inorganic particles (Hristov, Lach, and Grellmann 2004). Polymer blends were extensively studied with a view improving the properties. The benefits claimed include, for example, improvement in impact strength, tensile strength, environmental stress cracking, low temperature impact properties and so on. A study on blends of polypropylene with conventional polyolefins is of continued interest, and much of the research paid attention to the PP/PE blend (Xiaodong, Riguang, and Hangquan 1995).

On the other hand, rubber toughened plastics are also had great attentions. The polymer matrix plays an important role in determining the overall toughness. Some matrix tend to craze because of low entanglement density. Massive crazing induced by rubber particles is clearly observed in high impact polystyrene. High molecular weight matrix are, in general, tougher than their low molecular counterparts (Raymond, Sue, and Yee 2000).

In this study aim to improve the toughness of wood polypropylene composite by both blending matrix with ultra high molecular weight polyethylene (UHMWPE) and also rubber toughening by ethylene propylene diene terpolymer (EPDM) addition.

4.3 Research methodology

4.3.1 Materials

In this studied, composite constitutes based on isotactic polypropylene homopolymer (PP700J) supplied from SCG Chemical Co., Ltd. Vinyltrimethoxy silane (VTMS), Silquest A 171, purchased from Optimal Tech Co., Ltd. Dicumyl peroxide (DCP) was employed as free radical initiator. It is commercial grad. Talc, JetFine 3CA, particle size of 1.2-1.4 μm was employed as filler. Blending of Irganox 1076 and Irgafos 168 at 50:50 (w/w) were used as thermal/processing stabilizer.

Table 4.1 Properties of UHMWPE (UH900) (Asahi Chemical Industry. Co., Ltd, www, n.d.).

Properties	Test Method	Value, Unit
Average molecular weight	Viscosity method	33×10^4
Melting temp	DSC	136 ^oC
Charpy impact (15J)	JIS K7111	Non folding
Tensile strength at Yield	JIS K7161	24 MPa
Elongation at bleak	JIS K7161	330%
Flexural modulus	JIS K7171	0.11 GPa
Heat deflection temperature	JIS K7191	85^oC

In addition, ultra high molecular weight polyethylene (UHMWPE), UH900, was available from Asahi Chemical Industry. Co., Ltd. Properties of UHMWPE is summarized in Table 4.1. Ethylene propylene diene terpolymer (EPDM)

was also used as rubber toughener. Properties of EPDM as given by the manufacturer are shown in Table 4.2. All the ingredients employed to prepare the WPC sample were used as received.

Table 4.2 Properties of EPDM (Lioncopolymer, www, n.d.).

Properties	Test Method	Value, Unit
Mooney Viscosity	ZS 1223B @ 125ºC	52/67
E/P Weight Ratio	ZS 1231	68/32
Specific Gravity	ASTM D792	0.87 g/cc
Tensile Strength,	ASTM D412	1350 MPa
% Elongation	ASTM D412	260 %

4.3.2 Experimental formula

In order to study the effectiveness of the both toughness, UHMWPE and EPDM, the composites formula were comprised of PP matrix, 35 phr of wood flour, 20 phr of talc, 8 phr of VTMS and 0.3 phr of DCP. In the investigation of UHMWPE as toughener, the UHMWPE contents of 0, 5, 10, 15, 20, 25 phr was designed. Then, optimal content of UHMWPE was resolved. Further improvement by addition of EPDM rubber was investigated. The rubber content of 0, 2, 4, 6, 8 and 10 phr was incorporated into the PP/UHMWPE system. Finally, PP/UHMWPE/EPDM tertiary matrix were studied.

4.3.3 Fibre preparation

Wood flour from timber mill was ground by hammer mill machine into fine particle. The size of the powder was determined by the sieve size. The fibre passed through the 1.0 mm sieve size was collected and verified as fibre with the average size of 1.0 mm. It was dried in hot air oven at 105^{o}C for at least 12 hr to eliminate the moisture residue. The wood flour and desired amount of VTMS were then mixed by high speed mechanical mixer for 5 minutes. The silane treated wood flour was subsequently stored in air tight container at room temperature over night priory undergo dry mix with other ingredients.

4.3.4 WPC preparation

4.3.4.1 UHMWPE toughening

Polypropylene pellets and Dicumyl peroxide were pre mixed and warmed in oven at 60°C for 5 min to allow the DCP to melt. The ingredient was then rigorously shaken in plastic bag. By doing so, PP pellet is evenly coated with DCP. The pre died talc in vacuum oven at 110°C for 1 - 3 hrs was added. All the dried ingredients, silane treated wood flour, DCP coated PP, thermal/processing stabilizer and talc were then brought together into plastic bag and utterly physically blended. Again, it was stored in oven at 80°C before melt mixing. The ingredient was then constantly controlled and stave fed into co-rotation twin screw extruder through the single screw feeder. The twin screws diameter of 25 mm. with L/D of 20 was employed. The segmented screws configurations are comprised of three triple kneader disk sections. The temperature profiles for mixing were 180, 185, 185, 190 and 190^{o}C from hopper to die zone, respectively. Mixing at temperature above 190^{o}C would induce the fibre degradation and hence polymer chain scission and lower in both

physical and mechanical properties. The extruded strand was air cooled and granulated in to small pellet using the crusher. The composite pellet was dried at 80°C in vacuum oven for 2 hours before injection. Injection molding process was performed on Tederic TRX60c injection molding machine at barrel temperature of not over than 190°C.

4.3.4.2 UHMWPE/EPDM toughening

For PP/UHMWPE/EPDM system, EPDM and DCP were well mix on the two roll mill. Then, UHMWPE powder, talc and solid thermal/process stabilizer were added onto the mixed rubber. All ingredients were further mixed. Thoroughly dispersion was achieved by folding the rubber bale before it re-entry to the mixing gap. The process was repeatedly 50 rounds of mixing. The rubber mixture was frozen in the freezer overnight. Then, the frozen rubber was immediately crushed into small pieces using the crushing machine. Finally, The rubber flaks were rigorously blended with PP pellet in plastic bag. The rest of the melt mixing with the wood flour in the twin screw extruder was same manner as described in the PP/UHMWPE preparation system. The test samples were also prepared by injection molding.

4.3.5 Sauna Treatment of the WPCs

The polypropylene wood composites specimens were divided into 2 sets of samples. One was allowed to anneal at room temperature for at least a day. It was named as original sample. The other was undergone incubation in the moisture saturated oven at 105°C for approximately 12 hours. This process was employed to accelerate the silane/water condensation reaction. The reaction might be lead to the polymer chain crosslink or the interfacial bonding between wood flour and the

polymer matrix. The sample obtained from this process was classified as sauna cured WPC or shortly as cured sample.

4.4 Properties measurement and analysis

4.4.1 Rheological testing

The rheological property by mean of melt flow index (MFI) was conducted. The MFI of the wood polypropylene composites pellet was tested in accordance with ASTM D 1238 using the Kayeness melt flow indexer model 4004. The pellet samples obtained was vacuum dried in the oven at 80^{o}C for at least 2 hours to eliminate the residual moisture. Test pellet was molten at 170^{o}C and the static force driven through the capillary die (Ø 1 mm.) using piston loaded at 2.16 kg. The melting time was chosen at 240 seconds. Three extrudate cuts were performed with the cut time of 15 seconds. The weight of the extrudate was used to compute the melt flow index in the standard unit of g/10min.

4.4.2 Impact testing

Impact strength of wood polypropylene composite was tested using ASTM D 256 in Izod mode. The specimen obtained from injection molding with the dimension of 4X13X120 mm. was v-notched by the notching machine. For the sample without the designed stress intensity crake tip, or unnotched, the identical injected samples were tested. Notched and unnotched impact strengths were conducted at room temperature using the impact pendulum with impact energy of 2.7 Joule for the notched specimen and 5.4 Joule for the unnotched sample, respectively. The impact values were reported as impact strength (kJ/m^2) that was calculated from lost impact

energy divided by the cross section area the fractured point. Five samples were tested for each of composite sample and the average value was obtained and recorded.

4.4.3 Flexural testing

Flexural properties both the strength at maximum load and modulus of the WPC sample were examined in accordance of ASTM D790. Instron universal testing machine model 5565 with the load cell of 5 kN and three point bending test fixture with span length of 62 mm was employed. The crosshead speed of 10 mm/min was electronically controlled. The flexural test specimen obtained by injection molding had the dimension of 4X13X120 mm.WPC sample was placed plat wise under the bending load. The test was conducted at room temperature in normal atmospheric condition. Five samples were tested in each composite sample and the average values were calculated.

4.4.4 Heat deflection temperature testing

The WPC specimen with exactly the same dimension to those flexural testing was used to measure the Heat deflection temperature (HDT). The standard ASTM D 648 was followed. A samples was tested in the edgewise position with the support span length of 100 mm. Add on weight with equivalent to the standard load applied at its center to give maximum stress of 0.455 MPa (66 psi) was appointed. The standard testing machine from Atlas Electric Device Co. Ltd., model HDV 1, was employed. The constantly elevating temperature at a uniform control rate of 2 ± 0.2^{o}C/min was assigned. Liquid silicone oil was used as heating transfer media. The HDT value was recorded in degree celsius (^{o}C) as soon as the specimen had been deflected to 0.25 mm or 0.01 inch that monitored by dial gauge. This temperature was

defined as the deflection temperature under flexural load of the test specimen or HDT. Three samples were examined and each individual result was averaged and reported.

4.4.5 Morphological investigation

Morphology of the fractured surface of the wood sample was examined using scanning electron microscope (SEM). The broken piece of notched specimen from the impact test was prepared in to small piece of sample. It was then attached onto the SEM sample holder. The samples were coated with layers of gold for 5 mins by ionization before analysis. SEM photograph was taken using JOEL machine model JSM 6400 at the accelerating voltage of 20 keV.

4.5 Results and discussions

4.5.1 UHMWPE toughening

Table 4.3 WPCs formula for UHMWPE toughening.

Test	PP (phr)	**Silane (phr)**	**Wood (phr)**	**Talc (phr)**	DCP (phr)	Stabilizer (phr)	UHMWPE (phr)
1	100	8	35	20	0.3	2	0
2	100	8	35	20	0.3	2	5
3	100	8	35	20	0.3	2	10
4	100	8	35	20	0.3	2	15
5	100	8	35	20	0.3	2	20
6	100	8	35	20	0.3	2	25

4.5.1.1 Melt flow index

Rheological properties by mean of melt flow index (MFI) of the UHMWPE toughened WPC formula, as summarized in Table 4.3, is summarized in Table 4.4 and plotted against the UHMWPE contents in Figure 4.1. As expected that the melt index was exponentially decreased with increasing the UHMWPE content from 0 to 25 phr. It is known that the high molecular weight or long chain branching polymer has strongly effect to rheological. The viscosity of the polymer is typically increased, lower the melt index, with increasing the molar mass or chain entanglement. So, adding the ultra high molar mass of PE into the composite would increase the flow ability of the material.

Table 4.4 Effect of UHMWPE on melt flow index.

UHMWPE (phr)	Melt flow index (g/10min)
0	4.961± 0.115
5	3.959 ± 0.039
10	3.601 ± 0.185
15	2.519 ± 0.059
20	2.391 ± 0.142
25	2.163 ± 0.067

4.5.1.2 Heat deflection temperature

Heat deflection temperature of wood composites based on PP/UHMWPE matrix is illustrated in Table 4.5 and plotted in Figure 4.1. Within the

standard deviation, the result shows that the HDT of both original and cured composite are decreased with increasing the UHMWPE addition. The obvious lower in the HDT is found when more than 5 phr of UHMWPE is added. As the UHMWPE content exceed 5 phr the deflection temperatures of composites reduce with increase UHMWPE. For the sauna cured composites the reduction in the deflection is found when adding more than 10 phr of UHMWPE.

Table. 4.5 Heat deflection temperature of PP/UHMWPE matrix wood composite.

UHMWPE (phr)	Heat deflection temperature (°C)	
	Original	Cured
0	135.0 ± 1.4	140.0 ± 1.0
5	138.3 ± 0.6	140.5 ± 2.1
10	134.7 ± 2.9	140.7 ± 2.1
15	130.3 ± 1.5	133.3 ± 0.6
20	128.0 ± 1.4	132.3 ± 1.2
25	128.5 ± 2.1	131.0 ± 1.0

According to the Fox's equation, for the miscible system, increasing in weight fraction of low HDT polymer would decrease the service temperature of the mixed polymers. HDT of UHMWPE is normally 70-75^{o}C. However, with the assisting of peroxide/silane crosslink system, the small amount of UHMWPE added into the matrix system would introduce the macro crosslink structure in the matrix phase. Consequently, the deflection temperature would be

either retained or sometimes slightly increased as observed in this research result. Limit amount of the crosslink gents would be completely consumed when excess of UHMWPE is found. Hence, the rule of mixture will dominate the thermal property of the composite.

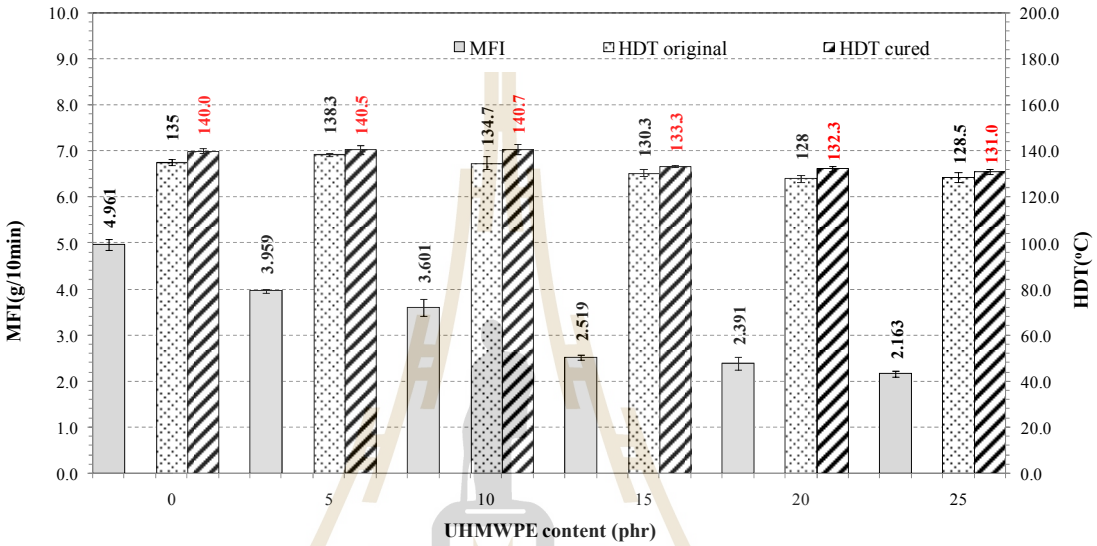

Figure 4.1 Effect of UHMWPE on MFI and HDT.

4.5.1.3 Flexural properties

Table 4.6 summarized the flexural properties of the WPC composites. Figure 4.2 is the plot between the strength and modulus against the UHMWPE contained in WPC matrix. It is seen that both flexural strength and modulus are slowly decreased with increasing the ultra high polymer. Within the standard deviation and comparing between the original and cured samples, it is evidenced that the test values of the sauna cured are marginally higher than the sample without curing. The maximum flexural strength and modulus of composites is found in the non toughened specimen. The decreasing in the flexural properties with

addition of UHMWPE is might be due to the fact that there is no fusion of the high molecular weight polymer during melt mixing.

Table. 4.6 Flexural properties of PP/UHMWPE wood composite.

UHMWPE (phr)	Flexural strength (MPa)		Flexural modulus (GPa)	
	Original	Cured	Original	Cured
0	57.10 ± 0.19	57.28 ± 1.12	2.35 ± 0.08	2.29 ± 0.13
5	53.99 ± 2.09	54.65 ± 0.56	2.09 ± 0.16	2.34 ± 0.07
10	51.95 ± 1.93	52.18 ± 0.91	2.07 ± 0.09	2.21 ± 0.11
15	50.62 ± 0.51	51.77 ± 0.86	1.88 ± 0.16	2.16 ± 0.11
20	49.14 ± 0.37	49.88 ± 1.57	1.93 ± 0.15	1.92 ± 019
25	48.48 ± 0.98	49.28 ± 0.80	1.84 ± 0.98	1.89 ± 0.15

Recalling from the experimental section, the melt temperature was controlled at 190^{o}C. The increasing the temperature above this level would cause the wood flour degradation. However, as the processing temperature of UHMWPE normally above 300^{o}C, the polymer fusion of this polymer cannot be achieved at the given mixing temperature. As the result, the high molecular weight polymer would only act as the foreign particle in the composite matrix, not the matrix toughener. Consequently, the flexural properties would be decreased as increasing the UHMWPE loading. The more increasing the solid ultra high molar mass powder into the material, the higher in solid agglomeration onto the matrix phase is found. The

evidence for this explanation will be discussed by the morphological investigation later on.

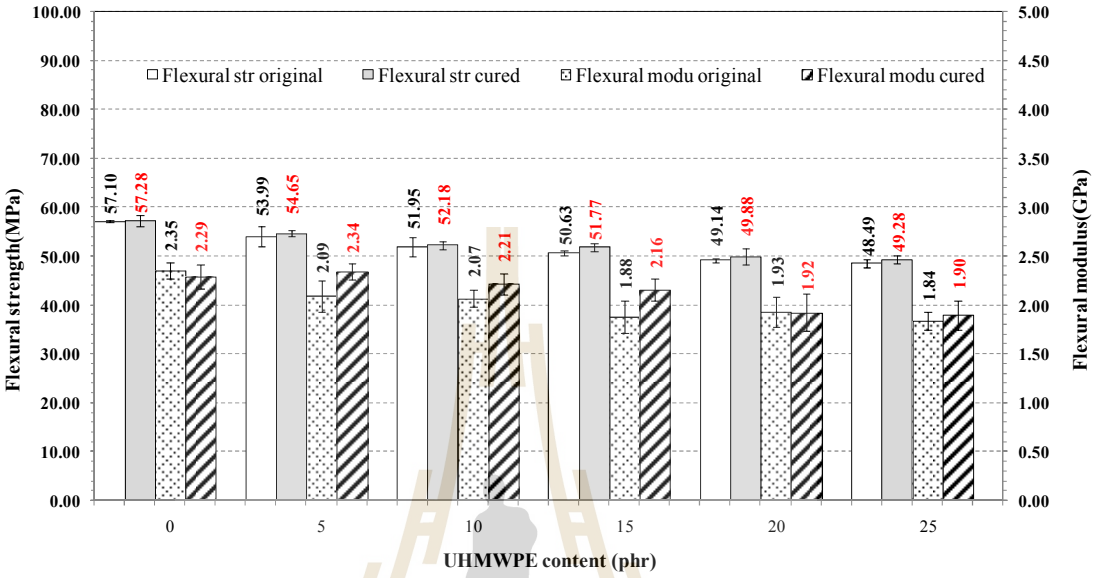

Figure 4.2 Effect of UHMWPE on flexural properties of original and sauna cure WPC.

4.5.1.4 Impact strength

The Izod notched and unnotched impact strengths of wood composites with PP/UHWMPE binary matrix blends was reported in Table 4.7 and they are plotted in corresponding with the amount of UHMWPE content as shown in Figure 4.3. As expected for both impact tests, the strength of cured sample is higher than the original one. The condensation reaction of silane/moisture is majorly responsibility for this increasing. It is also observed that the notched impact strength is increased with increase in the UHMWPE content with the optimal loading at 10-15 phr. Further increase the high molecular weight the strength is depleted. The

maximum strength is 2.19 kJ/m^2 and 2.24 kJ/m^2 at 10 phr of UHMWPE for original and cured sample, respectively. However, for the unnotched mode, the strengths are relatively constant. They seem not to be any relationship with the UHMWPE contents. The decreasing of the strength at high content of UHMWPE will be explained by the particles agglomeration of the solid powder of the added UHMWPE. As purpose in previous section that compounding the WPC at low processing temperature of UHMWPE, there is not enough heat to fuse this polymer but it is only soften and agglomerated into large particle. The more large foreign particle generated the more interfacial void would be created. As the result, the impact toughness of the material would become weak, especially when the stress intensity crake tip is formed.

Table 4.7 Impact strengths of PP/UHMWPE matrix wood composite.

UHMWPE (phr)	Notched impact (kJ/m^2)		Unnotched impact (kJ/m^2)	
	Original	Cured	Original	Cured
0	1.40 ± 0.60	1.49 ± 0.18	11.48 ± 1.28	12.77 ± 0.50
5	1.88 ± 0.14	2.21 ± 0.33	12.55 ± 0.68	13.78 ± 0.86
10	2.19 ± 0.11	2.24 ± 0.11	10.66 ± 1.10	11.10 ± 1.65
15	2.03 ± 0.22	2.14 ± 0.14	11.13 ± 0.40	12.44 ± 0.81
20	1.49 ± 0.01	2.01 ± 0.25	11.77 ± 0.82	12.07 ± 0.94
25	1.31 ± 0.19	1.85 ± 0.14	11.82 ± 0.98	11.52 ± 1.25

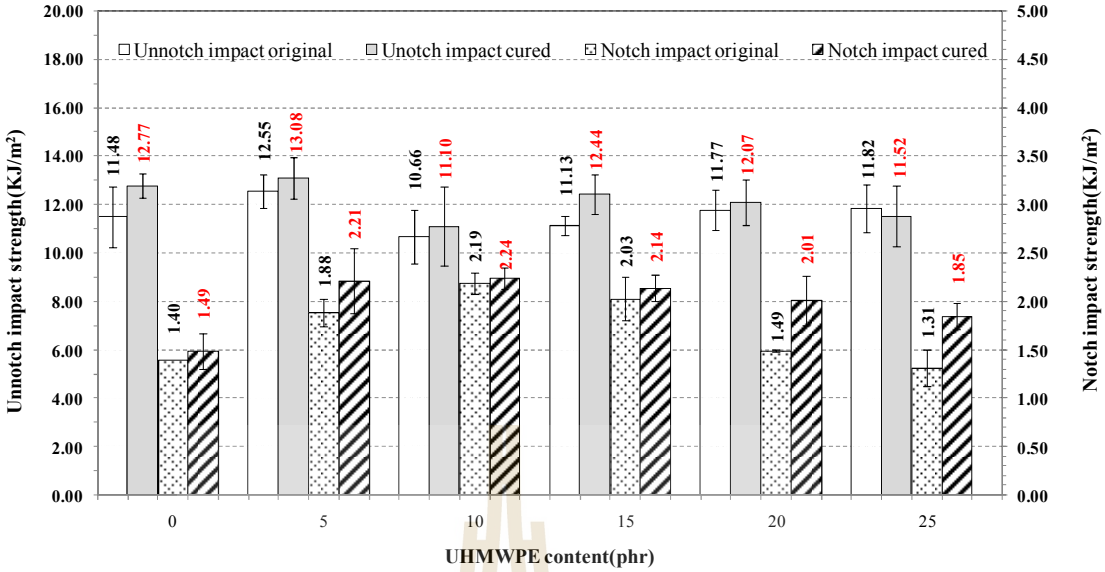

Figure 4.3 Effect of UHMWPE on notched and unnotched impact strengths of original and sauna cured WPC.

4.5.1.5 Morphology investigation

Scanning electron microscopy (SEM) was employed to investigate the morphology of the composites to resolve the surface adhesion between fibre and matrix and also the dispersion of UHMWPE toughener in the matrix phase. The SEM photographs of the fractured surface obtained from notched impact specimen are summarized in Figure 4.4 (***a***) to 4.4 (***d***), respectively. It is obviously seen that there is relatively poor dispersity of UHMWPE in matrix phase. The sizes of UHMWPE agglomeration is increased with increased the polymer content, from 0 – 25 phr. It is in agreement with the notched impact strength which is generally decreased with increasing the size of agglomeration.

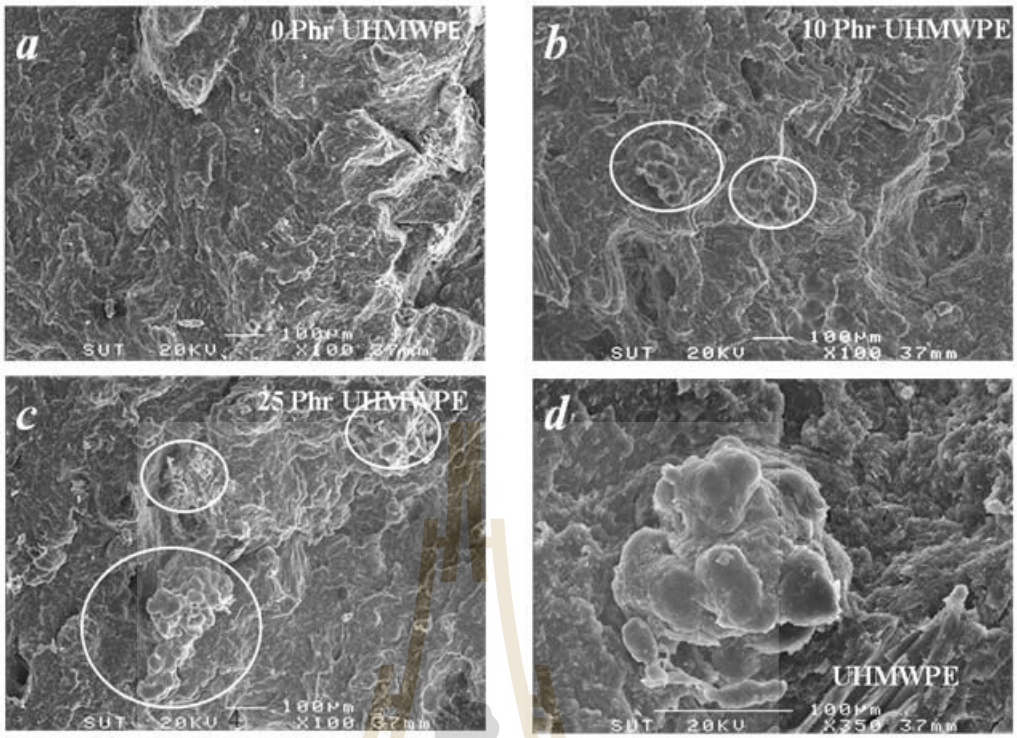

Figure 4.4 SEM of fractured surface of the original wood polypropylene composite with various UHMWPE contents: (***a***) 0 phr, (***b***) 10 phr, (***c***) 25 phr of UHMWPE at X100, and (***d***) 10 phr of UHMWPE at X350 magnification, respectively.

However, good adhesion between the agglomerated particle and PP matrix phase is observed as shown in Figure 4.4.(***d***). It is meant that at low content of UHMWPE the high toughness characteristic of this polymer is overcome the incompetency of dispersion therefore the ability of being the toughener is met as evidence at 10-15 phr of addition. Not only UHMWPE was added in the composite but also the wood flour was incorporated as reinforcement. The interfacial adhesion between the fibre and matrix is also important. Figure 4.5 (***a***) and 4,5 (***b***) are the higher magnification SEM photographs of fibre/matrix bonding of the composite with

adding 10 phr of UHMWPE before and after sauna curing, respectively. Better interfacial bonding due to the silane/moisture incubation is observed from the electron scanning analysis. Again, this result strengthen that sauna treatment via silane/moisture condensation reaction can improve the surface adhesion between fibre and matrix and perhaps between the UHMWPE dispersed particle and PP phase, as well. As the result, the fracture toughness is increased.

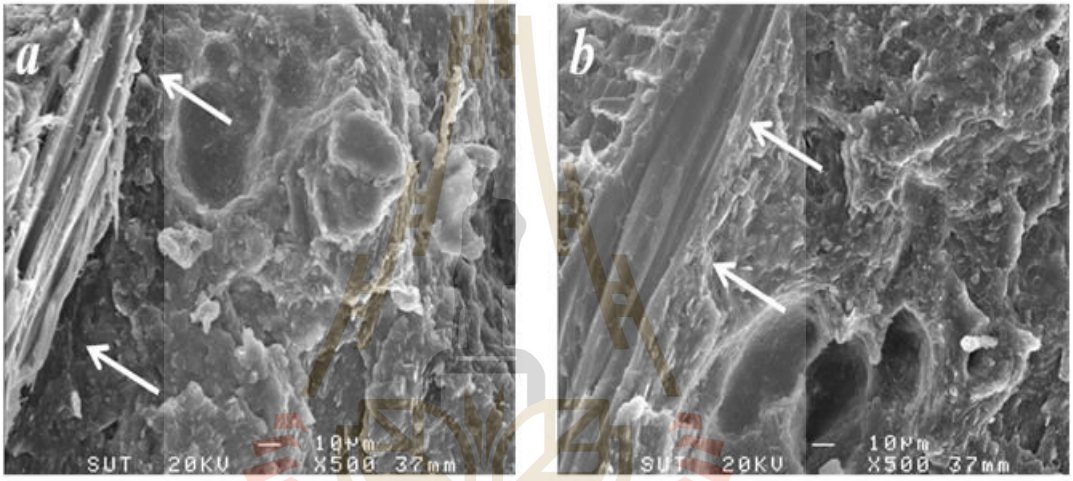

Figure 4.5 SEM photographs of; (***a***) 10 phr UHMWPE and (***b***) crosslinked samples with sauna treated (X500).

The result from the present experiment shows that small amount of UHMWPE, 5-10 phr, can be used to improve fracture toughness of the composite material. However, the flexural properties and also the service temperature by indicating of HDT are slightly decreased with increasing the amount of UHMWPE content. The agglomeration of UHMWPE particle as the result of high melting temperature and also the lower service temperature of the polymer are responsible for

the explanation. The sauna cured is still the better choice for interfacial improvement between fibre and the matrix phase and hence the superior in the mechanical properties. Based on the results of this experiment, the optimal amount of UHMWPE that can be added into the composite constituent and shown the obvious improvement of the mechanical properties are 10-15 phr. However, further improvement in the fracture toughness of the composite is required. The next discussion will be focused on the addition of synthetic rubber in conjunction with UHMWPE as complementary toughener.

4.5.2 UHMWPE/EPDM binary toughens

Table 4.8 WPCs formula for EPDM toughening.

Test	PP (phr)	Silane (phr)	Wood (phr)	Talc (phr)	DCP (phr)	Stabilizer (phr)	UHMWPE (phr)	EPDM (phr)
1	100	8	35	20	0.3	2	10	0
2	100	8	35	20	0.3	2	10	2
3	100	8	35	20	0.3	2	10	4
4	100	8	35	20	0.3	2	10	6
5	100	8	35	20	0.3	2	10	8
6	100	8	35	20	0.3	2	10	10

From the previous outcome found that only UHMWPE only was not fully effective in term of the ability to enhance the fracture toughness of the WPC. Only fraction of impact strength was increased at tiny amount of UHMWPE powder added. That is because the high molecular weight polymer could not be fused at the

low processing temperature. In this section additional toughener by mean of elastomer addition in conjunction with the toughener UHMWPE are discussed. EPDM and UHMWPE were used in the form of rubber flake prepared by two roll mill mixing as described in the experimental section. The properties of WPC ingredient shown in Table 4.8 and compounded be the twin screw mixer are being presented.

4.5.2.1 Melt flow index

Table 4.9 and the plot in Figure 4.9 shows the relationship between rheological properties by mean of melt flow index (MFI) and the EPDM contents of the WPC compound. It is found that MFI is gradually decreased with increasing the EPDM content. On the other words, EPDM has the positive effect on the viscosity the wood composite. It is known that the adding rubber would undergo crosslink in the presence of free radical initiator, DCP. Therefore, the viscosity of the compound would be increased with increasing the rubber content.

Table 4.9 Effect of EPDM on melt flow index.

EPDM (phr)	Melt flow index (g/10min)
0	3.303 ± 0.123
2	2.905 ± 0.036
4	2.633 ± 0.041
6	2.698 ± 0.034
8	2.433 ± 0.133
10	2.429 ± 0.091

4.5.2.2 Heat deflection temperature

The relation between heat deflection temperature (HDT) of composites and the amount of EPDM are summarized in Table 4.10 and also plotted in Figure 4.6. It is observed that the heat deflection temperature of the sauna cured sample is higher than the original sample regardless to the addition EPDM. However, the service temperature is obviously decreases with increasing the EPDM content, especially for the sample before sauna curing. It is hardly seen the huge difference in the HDT with the rubber content. The HDT is approximately 133°C for the WPC sample that was sauna cured. The lowering of HDT with increasing amount of EPDM is might the fact from the rule of mixture that EPDM has much lower in HDT than PP or PP/UHMWPE blends. Therefore, incorporate more EPDM would lower the HDT of the compound. However, free radical cured EPDM might has the better thermal resistivity and then the obvious lowering in the service temperature is diminished.

Table. 4.10 HDT of PP/UHMWPE/EPDM matrix wood composite.

EPDM (phr)	Heat deflection temperature (°C)	
	Original	Cured
0	133.7 ± 0.6	135.3 ± 1.2
2	123.0 ± 0.0	133.7 ± 1.5
4	123.3 ± 2.0	132.7 ± 0.6
6	121.3 ± 0.6	132.0 ± 1.0
8	119.3 ± 0.6	132.3 ± 0.6
10	119.0 ± 0.0	132.7 ± 0.6

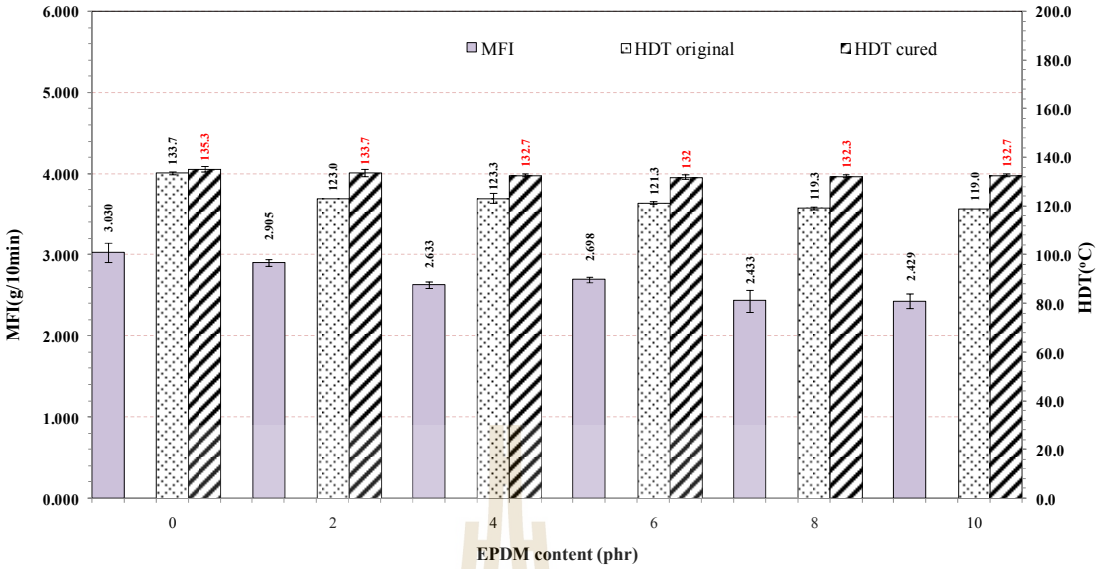

Figure 4.6 Effect of EPDM on MFI and HDT of the WPC.

4.5.2.3 Flexural properties

Bending toughness of the rubber toughened WPC samples measured by flexural strength and modulus are illustrated in Table 4.11 and their plots with respect to the rubber contents is demonstrated in Figure 4.7, respectively. It is seen that the flexural strength is slowly decreased with increasing the EPDM addition for both original and cured conditions. At the given amount of rubber addition, the silane/moisture condensation reaction through the sauna incubation at 105°C has marginally increased the strength. through all fraction of EPDM. The identical trend is also observed for the modulus property. Decreasing both flexural strength and modulus of the WPC with increasing the amount of the EPDM rubber addition mean that the flexural strength, ductility, of the sample is inferior. Further increase in the modulus but not significant improve in the strength of the sauna cured WPC emphasis that the flexural properties of the samples are ruined. It is meant that further adding

the EPDM rubber in conjunction with the UHMWPE is not effective in term of toughening phenomena of the WPC. This could be due to the explanation that the added rubber could not be well dispersed into the PP matrix phase or adhere with the wood fibre but it is penetrated within the interface of UHMWPE and the matrix. Consequently, the toughness of the main phase cannot be enhanced by the rubber. Therefore, the flexural properties are incompetency. This piece of evidence will be presented later on the SEM investigation.

Table 4.11 Flexural properties of PP/UHMWPE/EPDM wood composite.

EPDM (phr)	Flexural strength (MPa)		Flexural modulus (GPa)	
	Original	Cured	Original	Cured
0	48.50 ± 0.82	49.19 ± 1.55	1.81 ± 0.17	2.00 ± 0.08
2	44.01 ± 0.56	46.32 ± 0.35	1.81 ± 1.16	1.85 ± 0.15
4	42.41 ± 0.92	42.67 ± 0.92	1.70 ± 0.77	1.74 ± 1.04
6	40.19 ± 0.55	39.87 ± 0.69	1.57 ± 0.99	1.62 ± 0.01
8	37.63 ± 0.68	38.83 ± 0.71	1.54 ± 1.15	1.52 ± 0.65
10	37.96 ± 0.50	38.19 ± 0.90	1.51 ± 0.03	1.51 ± 0.01

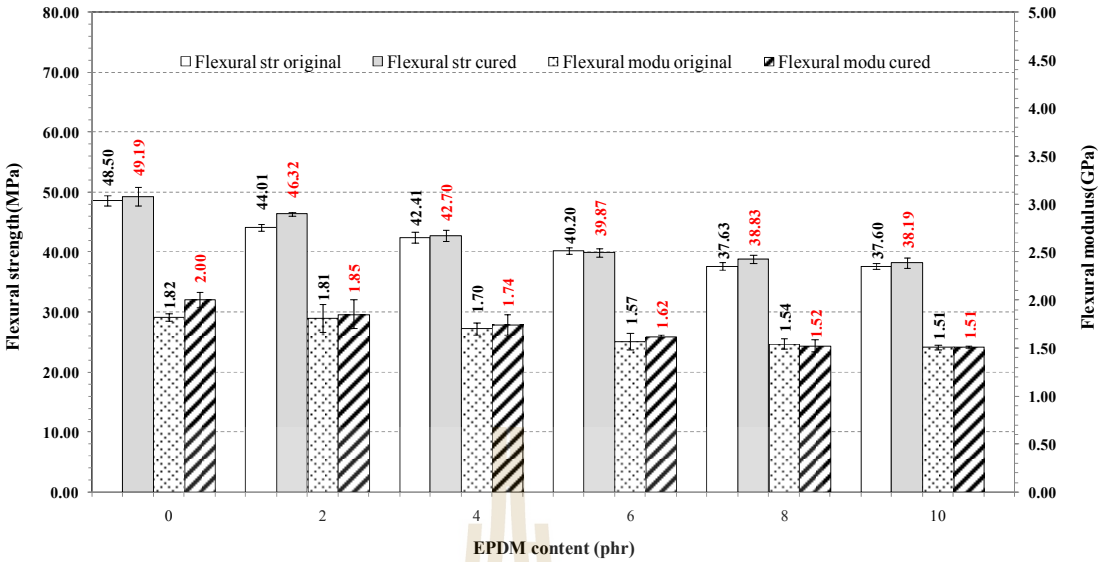

Figure 4.7 Effect of EPDM on flexural properties of original and sauna cured WPC.

4.5.2.4 Impact strength

Impact strengths, notched and unnotched, test results of both original and cured WPCs are illustrated in Table 4.12. They are also plotted with the respect of the EPDM contents as given in Figure 4.12. Within this experiment boundary, the results indicate that notched impact strength of wood composites obtained from PP/UHWMPE/EPDM ternary matrix is obviously elevated with raising the EPDM concentration for both with and without sauna treatment. As expected, the strength of the sauna cured is superior than the sample without moisture treatment. The similar trend is also found for the unnotched testing mode. But the elevation of the strength is less obvious than the v-notched specimen. According this study, the maximum strengths are found at 10 phr of EPDM addition. Further increasing in the EPDM content is believed to be better in the fracture toughness. But, as previously discussed, the thermal property of the WPC would be lower. Balancing between the

high toughness but low service temperature would be considered. The high energy absorption and the stress distribution ability of the rubber are highly possibility to be taken into explanation of the better impact strengths with correspondence the EPDM addition. The improve in the toughness of the polymer matrix phase by the rubber toughener rather than in the surface adhesion between reinforcement and continuous phase is evidenced as provided in the later discussion.

Table 4.12 Impact strength of PP/UHMWPE/EPDM matrix wood composite.

EPDM (phr)	Notched impact (kJ/m^2)		Unnotched impact (kJ/m^2)	
	Original	Cured	Original	Cured
0	1.80 ± 0.27	2.41 ± 0.15	11.62 ± 0.17	11.82 ± 1.37
2	2.20 ± 0.11	2.62 ± 0.14	11.83 ± 1.16	11.92 ± 0.61
4	2.82 ± 0.11	3.23 ± 0.22	12.05 ± 0.77	12.57 ± 1.06
6	2.97 ± 0.21	3.60 ± 0.14	12.58 ± 0.99	12.74 ± 0.56
8	3.22 ± 0.21	3.87 ± 0.29	12.44 ± 1.15	12.45 ± 0.92
10	3.68 ± 0.15	4.23 ± 0.19	12.72 ± 1.67	12.66 ± 1.13

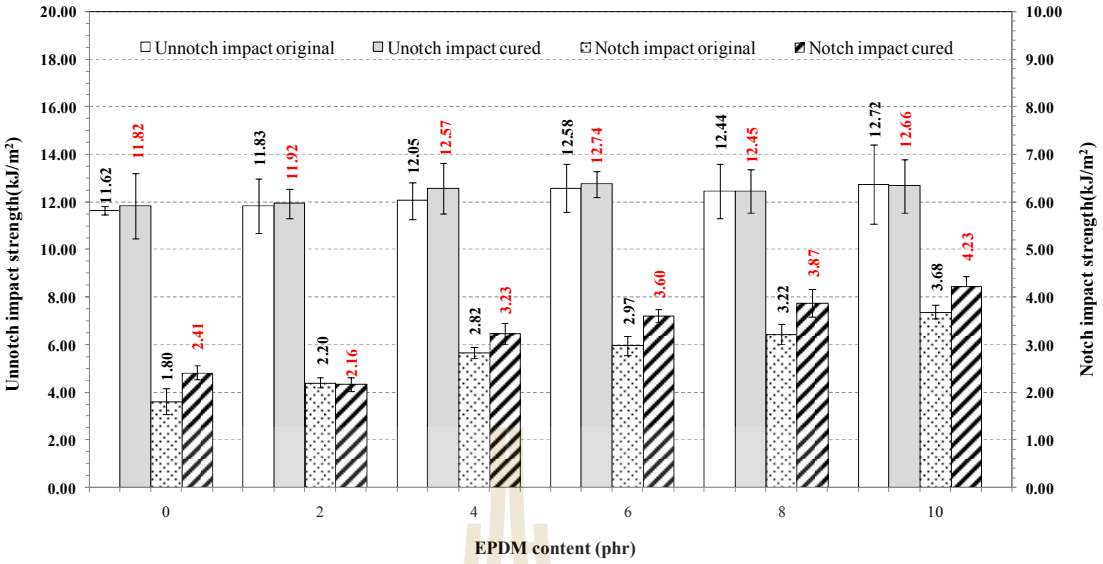

Figure 4.8 Effect of EPDM on notched and unnotched impact strength of original and sauna cured WPC.

4.5.2.5 Morphology investigation

Decreasing in the flexural strength but increasing in the impact strengths as presented needed to be explained in term of fracture behavior. Scanning electron microscopy (SEM) of notched fractured surface of the WPC samples without and with 10 phr of EPDM addition are shown in Figure 4.9. Figure 4.9 (***a***) and (***b***) are the composite without EPDM before and after sauna incubation, respectively. It is observed that the fracture surfaces of the matrix phase are brittle like material in nature. When comparing with the SEM photographs of the WPCs with 10 phr of EPDM content, Figure 4.9 (***c***) and (***d***), the fractured traces are tougher in nature. The rubber toughener fibril is distinguished on the fractured surface. Moreover closer look at the surface adhesion between PP/UHMWPE as shown in Figure 4.10 (***a***) and 4.10 (***b***). It is obviously evidenced that adding EPDM into the PP phase assists the

adhesion between PP and UHMWPE unmelted particle. Hence, the toughness strength of the matrix would be improved. With the combination of better matrix toughness and good interfacial adhesion between fibre and polymer phase arising from the silane/moisture reaction, the fractured strength of the WPC with addition of EPDM rubber is increased with increasing the rubber content as established.

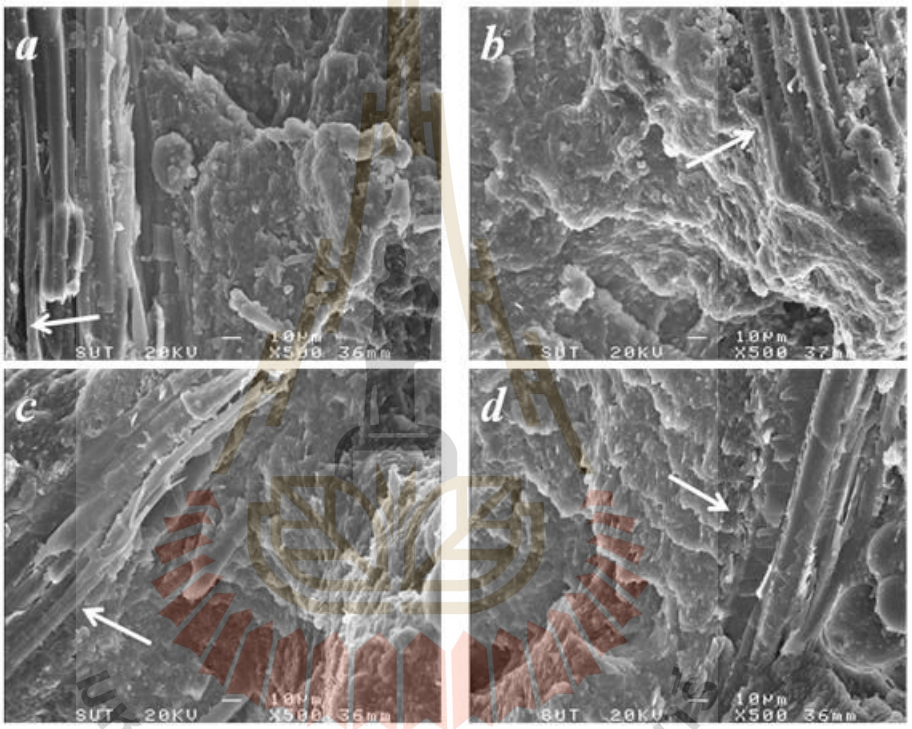

Figure 4.9 SEM of fracture surface of wood PP/UHMWPE/EPDM composite: (***a***) original sample without EPDM (***b***) cured sample without EPDM (***c***) original sample with 10 phr of EPDM (***d***) cured sample with 10 phr of EPDM. at magnification X500.

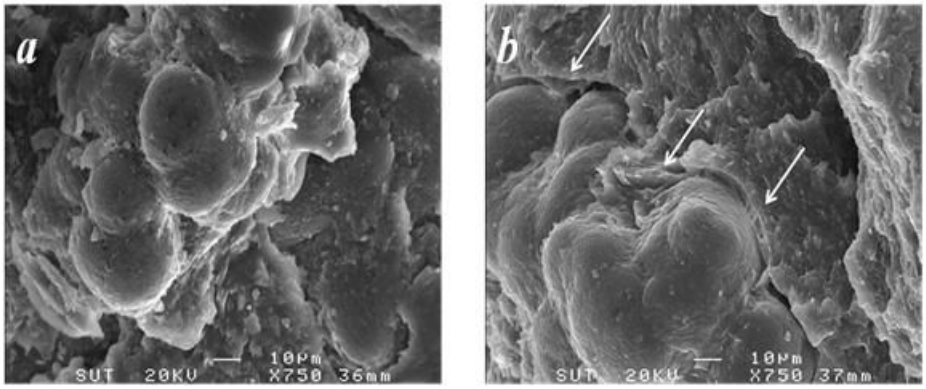

Figure 4.10 SEM images of wood composites; (***a***) 0 phr of EPDM and (***b***) 10 phr of EPDM.

4.6 Conclusions

WPC prepared from the polymers matrix systems, PP/UHMWPE and PP/UHMWPE/EPDM, in the present of peroxide/silane crosslinked system was achieved in the twin screw mixer. Sauna curing by incubation the sample in the oven saturated with moisture vapor at 105^{o}C for 12 hours was conducted. It was found that agglomeration of UHMWPE unmelted particle at high contents were responsible for the lower in the toughness of the sample. The optimal usage of UHMWPE derived from this study was at 10 phr. Further addition of EPDM rubber as fracture toughener into the PP/UHMWPE was found that the more EPDM concentration the more in impact strengths but vastly lower in the HDT. The added EPDM rubber was responsible for improvement of the toughness of the PP/UHMWPE/EPDM tertiary phase.

4.7 References

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CHAPTER V

EFFECT OF PEROXIDE, SILANE AND PP COPOLYMER IN CROSSLINKED PP WOOD COMPOSITE

5.1 Abstract

Investigation of wood composite based on crosslinked polypropylene was studied. Addition of DCP as free radical initiator and Vinyltrimethoxy silane as crosslink agent were employ to improve properties of composite. Composites were compounded by co-rotation twin screw extruder and test specimens were prepared by injection molding. Crosslink process by sauna incubation at 105^{o}C for 12 hr. Degree of crosslinking, mechanical properties, HDT and morphology of composite was performed. The result shows that mechanical properties and HDT of both original and cured composite were diminish with increase in DCP concentration. Result from MFI and gel content exhibit that free radical induced chain degradation via free radical back biting reaction is repeated mentions. Accordingly, properties of composite were reduced. Subsequently, effect of VTMS addition was studied. It observed that, addition of VTMS can improve mechanical strength and HDT of composite. Degree of crosslink was rising with increase silane crosslink agent. Cured sample via sauna incubation process still the better choice to improve properties of composite.

PP copolymer was used as impact modifier. Propylene-ethylene copolymer has efficient to improve impact strength but not for flexural properties and HDT. Durability by mean of anti termite testing shows that PP wood composite has ability to termite resistant as hard wood. General observation, when compare between original and sauna cured samples, it is noticed that the interfacial adhesion between fibre and PP based matrix is improved via the sauna curing process.

5.2 Introduction

Crosslinking is one of the important methods to improve the thermal and chemical resistance of polymers. In general, there are three crosslinking methods, i.e. radiation crosslinking, peroxide crosslinking and silane crosslinking. The vinyl based silane crosslinking technique is cost-effective, easily operated and improvements in many useful properties of polyolefins. In producing of the silane crosslink able polyolefins, peroxide, silane and polyolefins are mixed by a melt process. During the process, the silane is grafted onto the backbones of polyolefins via free radical initiation of vinyl silane. The silane grafted polymer chains are then hydrolyzed and crosslinked by forming Si–O–Si linkages. Silane grafting reactions and the properties of crosslinked polyolefins dependence on reaction parameters such as content of free radical initiator and silane curing agent. This process of polyolefin crosslinked is efficiently worked with the polyethylene chains. The crosslink density is directly proportion to the peroxide and silane content at given mixing conditions (Kalyanee 2005, Miao, Zhengzhou, Baojun, and Keliang 2006, Zhengzhou, Xiusheng, Zhou, Yuan, and Weicheng 2005). It is, however, difficult to have the effective amount of crosslink in the PP system. At the certain mixing condition the polymer can either go

crosslink or degradation (Kalyanee 2005 and Kalyanee, and Keskanok 2005). Precise amount of crosslink agents; both vinyl silane an peroxide, and also the mixing condition such as temperature profile have to be established. Degradation of PP would lead to the brittle material and incompetency in mechanical characteristics.

Polypropylene has advantages of high rigidity, light weight, and high recyclability. In view of these advantages, it is the most popularly used plastic in the world. Polypropylene can be classified into three types: homo-polypropylene, random polypropylene, and high-impact polypropylene (hiPP). Isotactic polypropylene (iPP), with its high crystallinity and excellent rigidity, is mainly used as homo polypropylene. It is used in injection-molding products and high-heat-resistant sheets (Kiyokazu, Shojiro, and Nobuhide 2011). Impact copolymer polypropylene (ICPP) is a complicated copolymer and is widely used. In general, impact polypropylene copolymer is a copolymer consisting of propylene and a small amount of ethylene. It is a material combining appropriate strength and impact strength and is used in high-performance (Chunhui, Yonggang, Ruifen, and Qiang 2011).

Biodegradation of wood by termites is recognized as one of the most serious problems for wood. Termites live in the soil and travel to the wood to feed. Therefore, wood that is in close contact with the soil (or with a cracked slab that is over soil) is most at risk to termite attack. One goal of the wood product protection should be to exploit the natural defences mechanisms of durable wood species or simply use the naturally resistant wood itself. Some methods, including chemical modification and the use of arsenic/chromium-free preservatives, have been developed to enhance the durability of wood. Chemical modification is accomplished by treating the wood with selected chemicals that modify the cell wall wood polymers without leaving toxic

residues within the wood. Wood composite with polymer or with plastic has been proposed to extend their service life because the resulting product is more resistant to biodegradation and safe to living organisms (Hadi, Hadjib, and Jasni 2002, Lang-D, Yi, and Ming 2009).

From previous chapters, only statistical analysis by mean of DOE was used to conclude the effect of the composite constituent on the properties of WPC obtained. There was no hard evidence on the crosslink process of the PP matrix. Only macro responds that were used to hypothesis the crosslink ability of the polymer. In this chapter, more detail of crosslink ability of the matrix using the gel content determination will be emphasis on the existing of the crosslinked polymer chains. Moreover, UHMWPE and EPDM were also used to investigate as fracture toughened of WPCs. It was found that only impact strengths were improved but not for flexural and HDT properties. In the present study, further fine tune on the amount of DCP and vinyl silane on the crosslinking process of PP will be reported. In hope, proper amount of DCP and silane used that gives rise to the actual crosslink of PP would improve the properties of the toughened wood PP composite. In addition PP copolymer (PP740J) will be blend in composite matrix to improve impact strength of composite.

5.3 Research methodology

5.3.1 Materials

In this studied, composite constitutes based on isotactic polypropylene homopolymer (PP700J) supplied from SCG Chemical Co., Ltd. Vinyltrimethoxy silane (VTMS), Silquest A 171, purchased from Optimal Tech Co., Ltd. Dicumyl

peroxide (DCP) was employed as free radical initiator. It is commercial grad. Talc, JetFine 3CA, particle size of 1.2-1.4 μm was employed as filler. Blending of Irganox 1076 and Irgafos 168 at 50:50 (w/w) were used as thermal/processing stabilizer. Ultra high molecular weight polyethylene (UHMWPE), UH900, was available from Asahi Chemical Industry. Co., Ltd. Ethylene propylene diene terpolymer (EPDM) was also used as rubber toughener. In addition, PP copolymer with 1% ethylene content (PP740J) was used to impact modifier. It supplied from SCG Chemical Co., Ltd. The property of the PP copolymer provided from the manufacturer is summarized in Table 5.1. All the ingredients employed to prepare the WPC sample were used as received.

Table 5.1 Properties of homo (PP 700J) and copolymer (PP 740J) polypropylenes (SCG Chemical Co., Ltd, www, n.d.).

Properties	**Test Method**	**PP700J**	**PP740J**
Melting temp	ASTM D2117	160°C	160°C
Melt Flow Index	ASTM D1238@230/2.16	12g/10min	27g/10min
Notched Izod impact	ASTM D256@23°C	0.306 J/m	0.816 J/m
Tensile strength at Yield	ASTM D638 @50 mm/min	32 MPa	32 MPa
Elongation at bleak	ASTMD638@50 mm/min	650%	150%
Flexural modulus	ASTM D790	1.422 GPa	1.225 GPa
HDT	ASTM D648@0.455 MPa	110°C	110°C

5.3.2 Experimental formula

In order to study the effectiveness of DCP, free radical initiator and VTMS, crosslink agent, the composites formula were comprised of PP matrix, 35 phr of wood flour, 20 phr of talc, 10 phr of UHMWPE, 10 phr of EPDM. In the investigation of DCP, the DCP contents of 0, 0.05, 0.1, 0.15, 0.2, 0.3 phr was designed. The designed formula is summarized in Table 5.2. Then, optimal content of DCP was resolved. Further improvement by addition of VTMS content was investigated. The vinyl silane content at 8, 10, 15 and 20 phr was added into the wood composites. The WPC formula with varying of vinyl silane contents is given in Table 5.8. Finally, binary PPs matrix ratio of homopolymer and block copolymer of 100/0, 80/20, 50/50, 20/80 and 0/100 %weight was blended. The propose formula of PPs matrix is summarized in Table 5.13. Effect of DCP, VTMS and PP740J content on properties of WPC were evaluated.

5.3.3 Fibre preparation

Wood flour from timber mill was ground by hammer mill machine into fine powder. The size of the powder is determined by the sieve grid. The fibre powder that passed through the 1 mm sieve grid will be verified as fibre having the average size of less than 1 mm. It was dried in hot oven at 105^{o}C for at least 12 hr to eliminate the excess moisture. Dried wood flour and VTMS were then mixed by high-speed mechanical mixer for 5 minutes at room temperature. The silane treated flour was subsequently stored at room temperature over night before dry blend with other ingredient.

5.3.4 WPC preparation

EPDM and solid DCP were well mixed on the two roll mill. The DCP/EPDM was repeatedly kneaded with the rubber mixing action for several minutes. Then, UHMWPE powder, talc and solid thermal/process stabilizer were consequently and graduately added onto the mixed rubber. All ingredients were further kneaded in normal mill mixing actions for more than 5 mins. Thoroughly dispersion was achieved by repeatedly folding the rubber bale before its re-entry to the mixing gap. The process was repeatedly at least 50 rounds of mixing. The rubber mixture was frozen in the freezer overnight. Then, the solid hard frozen rubber was immediately crushed into small pieces using the jaw crushing machine. Finally, the rubber flaks were rigorously blended with PP pellet in plastic bag. The rest of the melt mixing with the wood flour in the twin screw extruder was achieved in the identical manner as described previous chapter. The test samples were also prepared by injection molding.

5.3.5 Sauna Treatment of the WPCs

The injected toughened polypropylene wood composites specimens were divided into 2 sets of samples. One was allowed to anneal at room temperature for at least a day. It was, again, named as original sample. The other set was undergone incubation in the moisture saturated oven at 105^{o}C for approximately 12 hours. This process was employed to accelerate the silane/water condensation reaction. Normally, the polymer chain crosslink reaction or the interfacial bonding between wood flour and the polymer matrix would be occurred during the incubation process. The sample obtained from this process was classified as sauna cured WPC or shortly as cured sample.

5.4 Properties measurement and analysis

5.4.1 Rheological testing

The rheological property by mean of melt flow index (MFI) was conducted. The MFI of the wood polypropylene composites pellet was tested in accordance with ASTM D 1238 using the Kayeness melt flow indexer model 4004. The pellet samples obtained was vacuum dried in the oven at 80^{o}C for at least 2 hours to eliminate the residual moisture. Test pellet was molten at 170^{o}C and the static force driven through the capillary die (Ø 1 mm.) using piston loaded at 2.16 kg. The melting time was chosen at 240 seconds. Three extrudate cuts were performed with the cut time of 15 seconds. The weight of the extrudate was used to compute the melt flow index in the standard unit of g/10min.

5.4.2 Impact testing

Impact strength of wood polypropylene composite was tested using ASTM D 256 in Izod mode. The specimen obtained from injection molding with the dimension of 4X13X120 mm. was v-notched by the notching machine. For the sample without the designed stress intensity crake tip, or unnotched, the identical injected samples were tested. Notched and unnotched impact strengths were conducted at room temperature using the impact pendulum with impact energy of 2.7 Joule for the notched specimen and 5.4 Joule for the unnotched sample, respectively. The impact values were reported as impact strength (kJ/m^2) that was calculated from lost impact energy divided by the cross section area the fractured point. Five samples were tested for each of composite sample and the average value was obtained and recorded.

5.4.3 Flexural testing

Flexural properties both the strength at maximum load and modulus of the WPC sample were examined in accordance of ASTM D790. Instron universal testing machine model 5565 with the load cell of 5 kN and three point bending test fixture with span length of 62 mm was employed. The crosshead speed of 10 mm/min was electronically controlled. The flexural test specimen obtained by injection molding had the dimension of 4X13X120 mm. WPC sample was placed plat wise under the bending load. The test was conducted at room temperature in normal atmospheric condition. Five samples were tested in each composite sample and the average values were calculated.

5.4.4 Heat deflection temperature testing

The WPC specimen with exactly the same dimension to those flexural testing was used to measure the Heat deflection temperature (HDT). The standard ASTM D 648 was followed. A samples was tested in the edgewise position with the support span length of 100 mm. Add on weight with equivalent to the standard load applied at its centre to give maximum stress of 0.455 MPa (66 psi) was appointed. The standard testing machine from Atlas Electric Device Co. Ltd., model HDV 1, was employed. The constantly elevating temperature at a uniform control rate of 2±0.2^{o}C/min was assigned. Liquid silicone oil was used as heating transfer media. The HDT value was recorded in degree Celsius (^{o}C) as soon as the specimen had been deflected to 0.25 mm or 0.01 inch that monitored by dial gauge. This temperature was defined as the deflection temperature under flexural load of the test specimen or HDT. Three samples were examined and each individual result was averaged and reported.

5.4.5 Morphological investigation

Morphology of the fractured surface of the wood sample was examined using scanning electron microscope (SEM). The broken piece of notched specimen from the impact test was prepared in to small piece of sample. It was then attached onto the SEM sample holder. The samples were coated with layers of gold for 5 mins by ionization before analysis. SEM photograph was taken using JOEL machine model JSM 6400 at the accelerating voltage of 20 keV.

5.4.6 Gel content determination

The gel content of the composites was determined using *p*-xylene extraction according to ASTM D 2765. The specimens to be analyzed were ground and the precise amount of the solid WPC was placed in filter paper, Whatman No. 42 with particle retention of 2.5 μm and tightly wrap and secured with cotton wire. The package was placed in round bottom flask filled with *p*-xylene. It was brought to boil and refluxed for at least 6 hours. The extracted package was then dried at 130^{o}C in vacuum oven until a constant weight was attained and the package paper was subsequently re-weighed. Four digit of weigh was recorded. The gel content was determined as the average of three separate replicates sample. The gel-content was calculated according to the following equations;

$$\%\text{Gel content} = \frac{\text{weight loss during extraction}}{\text{(weight of original specimen) - (weight of filler)}} \times 100 \qquad (5.1)$$

5.4.7 Termite resistant test

In this studied, termite resistant of 4 type of sample such: Eucalyptus, Teak, wood composite (original and cured sample) was performed. Teak and Eucalyptus obtain from natural. All of sample weight and record before immerge in water for one night. The test specimen was placed depth of 5 centimetre underground near the mounds. The termite activity in each sample was observed and monitored every 2 week for 5 times. Three replicate samples were examined and each individual result by weight averaged and reported by weight remains (%).

$$\%\text{Weight of sample} = \frac{\text{weight of sample after termite attack}}{\text{weight of original sample}} \times 100 \qquad (5.2)$$

5.5 Result and discussion

5.5.1 Effect of DCP concentration

Table 5.2 summarizes the WPC compound formula with increasing the amount of DCP. The rest of the ingredients, polymer matrix, talc filler, wood flour, silane, UHMWPE, EDPM and processing stabilizer, which are the optimal ratio for producing WPC and presented in the previous chapter. Only DCP content is varied from 0.0 to 0.30 phr in order to find out its effect on the properties of the WPC. The test results of the specimen in corresponding with the DCP used are being discussed.

Table 5.2 WPCs formula for DCP experiment.

Test	PP (phr)	Silane (phr)	Wood (phr)	Talc (phr)	Stabilizer (phr)	UHMWPE (phr)	EPDM (phr)	DCP (phr)
1	100	8	35	20	2	10	10	0.00
2	100	8	35	20	2	10	10	0.05
3	100	8	35	20	2	10	10	0.10
4	100	8	35	20	2	10	10	0.15
5	100	8	35	20	2	10	10	0.20
6	100	8	35	20	2	10	10	0.30

5.5.1.1 Melt flow index

The effects of the DCP content on the melt flow index (MFI) of WPC is shown in Table 5.3 and plotted against the amount of the peroxide in Figure 5.1. It is seen that the melt flow ability of WPCs is graduately decreased with increasing use of DCP. This indicates that the polymer matrix would be undergone chain scission through the free radical chain degradation reaction. It is quite common that PP chain is easily broken down the presence of free radical (Miao Hu et al. 2006). In this case, vast probability of chain reduction via increasing the free radical concentration would be responsible for the decreasing in melt viscosity of the compound, higher in melt flow index.

Table 5.3 Effect of DCP on melt flow index.

DCP (phr)	Melt flow index (g/10min)
0.00	1.413 ± 0.076
0.05	2.409 ± 0.135
0.10	3.015 ± 0.114
0.15	4.111 ± 0.148
0.20	4.463 ± 0.110
0.30	5.816 ± 0.096

5.5.1.2 Heat deflection temperature

Figure 5.1 and Table 5.4 show the HDT of wood composites with the higher in DCP content. The result shows that the HDT of the composite before sauna treatment is more or less constant with the amount of DCP. Except that at 0.05 phr, the test value is the highest. However, when compare with the sample without DCP addition, the test results are superior. After the sauna curing process, it observes that the HDT of DCP initiated WPC constant at around 138^{o}C with no effect of the peroxide used. The numbers are again noticeable higher than the system with no DCP addition. The outcome may explain that the chain scission via the radical induced degradation has no effect on the thermal property of the WPC. Not only the fibre and matrix adhesion improve via the silane/moisture reaction but it also elevate the service temperature of the composite.

Table 5.4 Effect of DCP on Heat deflection temperature of wood composites.

DCP (phr)	Heat deflection temperature (°C)	
	Original	**Cured**
0.00	130.7 ± 3.96	133.7 ± 3.06
0.05	138.3 ± 2.31	138.5 ± 2.21
0.10	135.0 ± 1.73	138.0 ± 1.73
0.15	134.3 ± 1.53	137.0 ± 2.83
0.20	134.7 ± 0.58	137.0 ± 1.73
0.30	135.0 ± 0.00	137.0 ± 1.73

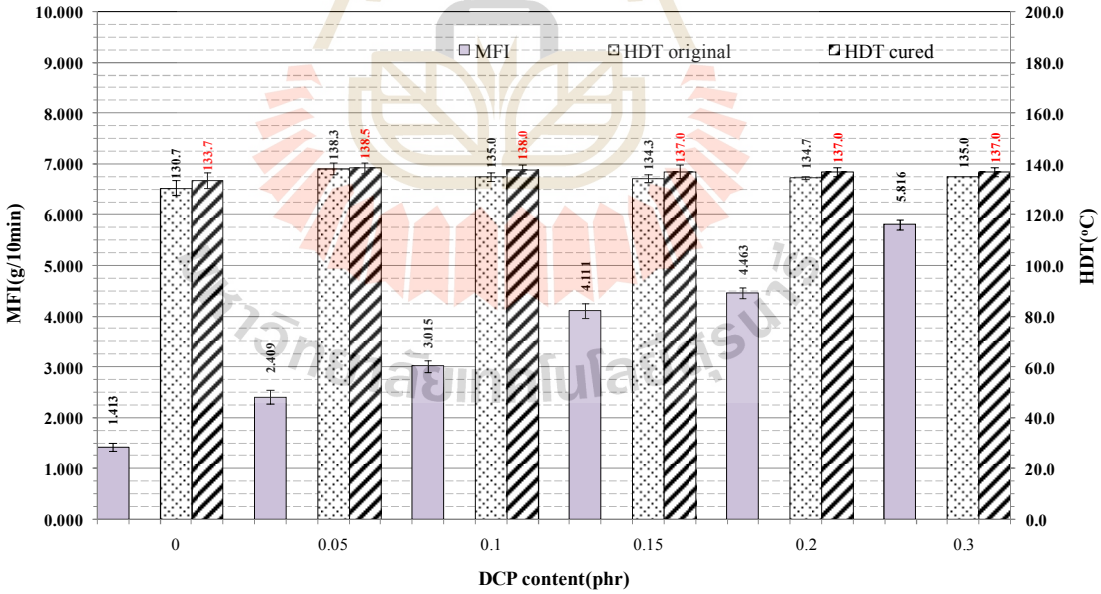

Figure 5.1 Effect of DCP on MFI and HDT.

5.5.1.3 Flexural properties

The effect of DCP on the flexural strength and modulus of PP wood composite are given in Table 5.5 and they are plotted in Figure 5.2, respectively. It is seen that flexural strength of WPC using DCP is higher in bending strength than composites without DCP for both original and cured samples. As typically found for this system, sauna curing can tiny improve the strength. From the test result is also noticed that increasing in DCP addition is generally and marginally decreased the strength. Within this experiment, DCP at 0.05 phr shows the highest value in flexural strength for both sample conditionings. The possible chain degradation through the free radical chain scission phenomenon would be respond for the decreasing of the strength with increasing the peroxide usage.

The similar trend between amount of DCP and the flexural modulus is detected. Except that, the modulus of the WPC sample without DCP shows the fractionally higher in test value than the sample with peroxide addition. Adding 0.05 phr of free radical initiator again is the optimal amount used in this experiment. The decreasing in both strength and modulus means that the material is less in toughness strength. From the results, it can roughly say that adding the peroxide initiator into the WPC ingredient would inferior the bending toughness of the material due to the chain degradation via the free radical chain scission process.

Table 5.5 Effect of DCP on flexural properties of wood composites.

DCP (phr)	Flexural strength (MPa)		Flexural modulus (GPa)	
	Original	Cured	Original	Cured
0.00	44.49 ± 0.84	47.20 ± 2.14	2.53 ± 0.06	2.61 ± 0.05
0.05	54.55 ± 1.03	54.84 ± 1.98	2.59 ± 0.08	2.62 ± 0.07
0.10	52.75 ± 0.74	52.90 ± 2.27	2.43 ± 0.04	2.47 ± 0.04
0.15	52.33 ± 1.01	52.46 ± 0.63	2.38 ± 0.06	2.36 ± 0.04
0.20	51.61 ± 1.72	52.68 ± 0.36	2.43± 0.06	2.48 ± 0.01
0.30	51.12 ± 0.30	52.09 ± 1.87	2.45 ± 0.05	2.43 ± 0.06

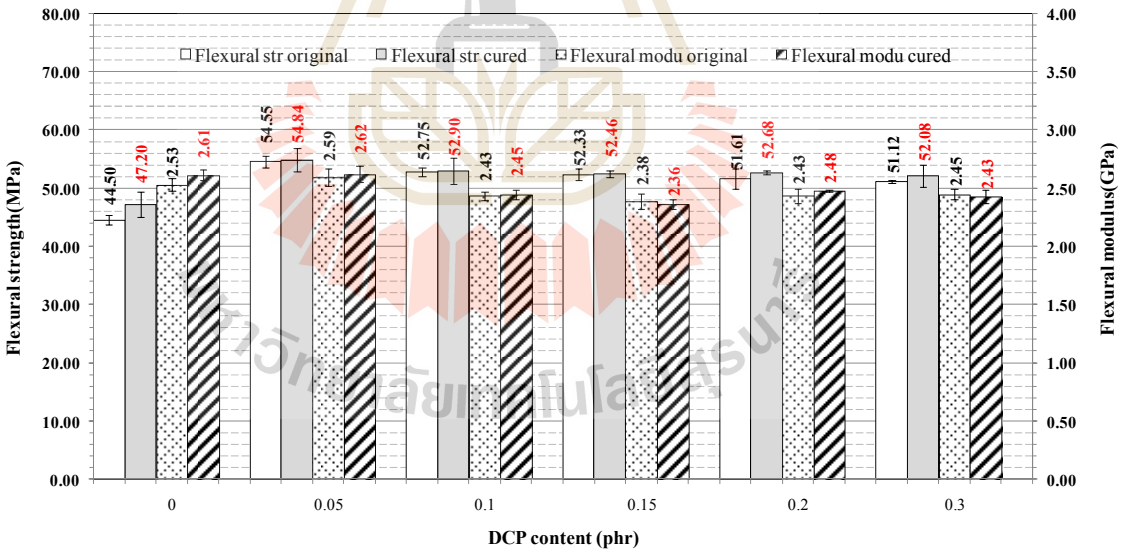

Figure 5.2 Effect of DCP on flexural properties.

5.5.1.4 Impact strengths

Similar trend in the impact to those flexural properties would be expected for the WPC with DCP adding. Because both properties reflect the toughness characteristic of the WPC. Table 5.6 and Figure 5.3 demonstrate the notched and unnotched impact strengths of the WPC obtained with the amount of DCP, respectively. Notched impact of the WPC with 0.05 DCP shows better test value than the sample without DCP for both conditioned samples. However, further increased the amount of peroxide the impact toughness is noticeably decreased, especially in the original sample. When comparing between original and cured samples, it is found that sauna treatment can obviously improve the notched impact strength of the WPC.

Table 5.6 Effect of DCP on impact strengths of wood composites.

DCP (phr)	Notched impact (kJ/m^2)		Unnotched impact (kJ/m^2)	
	Original	Cured	Original	Cured
0.00	1.87 ± 0.13	2.44 ± 0.15	8.62 ± 0.46	9.38 ± 1.33
0.05	2.15 ± 0.13	2.50 ± 0.12	12.34 ± 0.81	11.98 ± 0.57
0.10	2.10 ± 0.15	2.56 ± 0.24	11.95 ± 0.92	12.06 ± 0.93
0.15	1.82 ± 0.10	2.38 ± 0.15	12.00 ± 0.99	11.37 ± 0.69
0.20	1.61 ± 0.14	2.26 ± 0.25	11.79 ± 0.77	10.50 ± 1.99
0.30	1.46 ± 0.11	2.05 ± 0.12	10.06 ± 0.57	11.22 ± 0.80

The similar trend is found for the unnotched mode of testing. But the magnitude of decreasing with increasing the peroxide content is less than the notched test mode. At 0.1 phr of DCP is still the best concentration in term of the impact strengths. The more DCP usage and the chain shortening would be the best explanation for the impact strengths incompetency of the WPC manufactured in this research study.

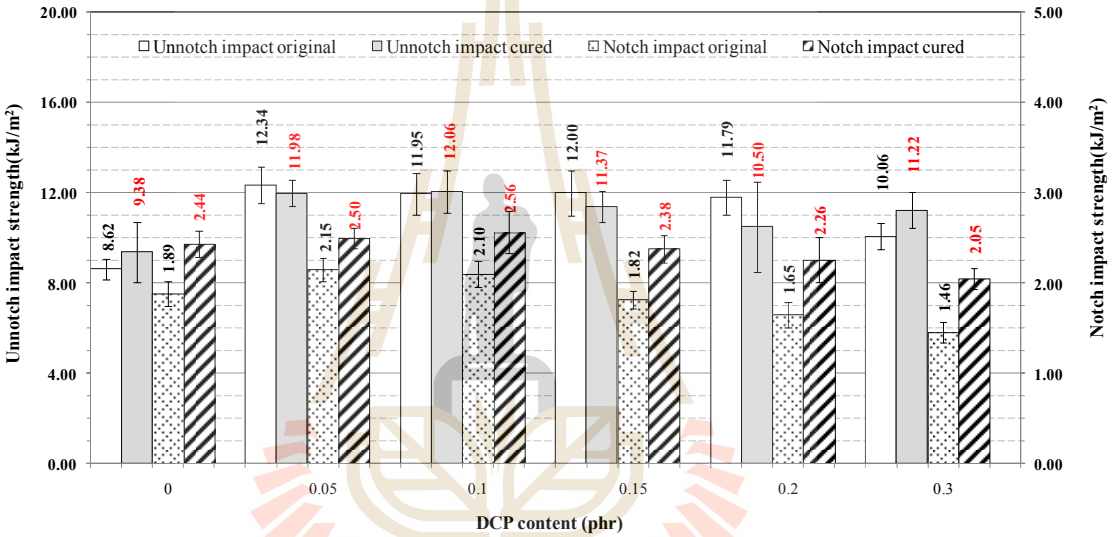

Figure 5.3 Effect of DCP on impact properties.

5.5.1.5 Gel content

According to the mechanical and thermal testing results found from the above discussion, the chain degradation via free radical back biting reaction is repeated mentions. It is worth to verify the existing and decreasing of the crosslinked fraction the matrix phase of the WPC sample. Therefore, the degree of crosslinking, non xylene dissolvable fraction, in the composites was determined and reported as gel content. According standard tested performed, the gel content obtained

from the WPC sample with and without DCP addition before and after sauna curing is summarized in Table 5.7 and Figure 5.4, respectively. As expected, the gel content is almost linearly decreased with increased the use of DCP from 0.05 to 0.3 phr for both original and cured WPC. However, from the test Figures, sauna curing increases the non dissolve fraction. Interestingly to found that the gel fraction of the matrix without DCP addition is higher than the system with DCP. This might be because of that insufficient efficiency of xylene to dissolve long chain PP in this experiment.

Table 5.7 Effect of DCP on gel content of wood composites.

DCP (phr)	Gel content (%)	
	Original	**Cured**
0.00	40.6 ± 4.5	54.6 ± 2.0
0.05	28.1 ± 4.7	39.5 ± 9.9
0.10	25.0 ± 12.0	36.5 ± 25.4
0.15	12.7 ± 8.3	33.5 ± 2.8
0.20	9.7 ± 8.4	32.0 ± 4.3
0.30	13.9 ± 10.8	24.7 ± 7.5

When the chain is shortened by the peroxide degradation, it can be easily dissolved by the solvent. Shorter of polymer chain lesser in non dissolved solid fraction. This % gel fraction experiment found is important evidence to make the solid conclusion that the decreasing the properties, especially toughness, are related to the change of the polymer chain length. DCP undergone free radical initiation and

consequently chain scission resulted in the chain shortening of the matrix has the negative effect to the mechanical properties of the WPC.

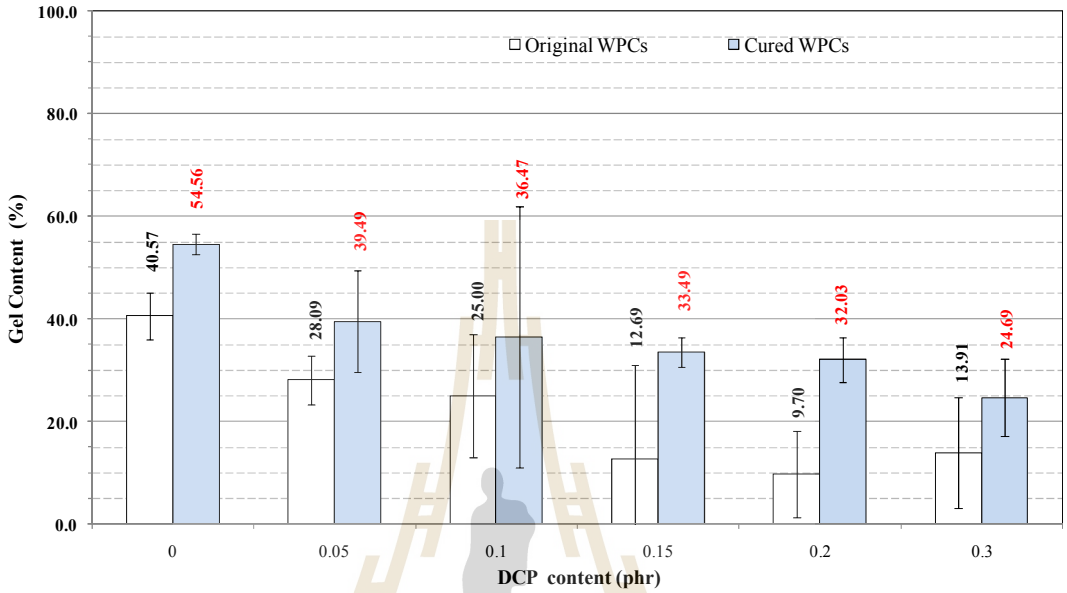

Figure 5.4 Effect of DCP on gel content of te crosslinked wood composites.

5.5.1.6 Morphological investigation

Figure 5.5 (***a***) to 5.5 (***f***) present the SEM photographs at X500 of the composite fractured surface before and after sauna incubation, respectively. The images will review the difference at the wood flour/matrix interfacial adhesion before and after sauna treatment. Figure 5.5 (***a***) and (***b***) are the composite without DCP before and after the treatment, respectively. WPCs with 0.1 phr and 0.3 phr of DCP are show in Figure 5.5 (***c***) to 5.5 (***e***), respectively. General observation, when compare between original and sauna cured samples, it is noticed that the interfacial adhesion between fibre and PP based matrix is improved via the sauna curing process regardless to the presence of DCP.

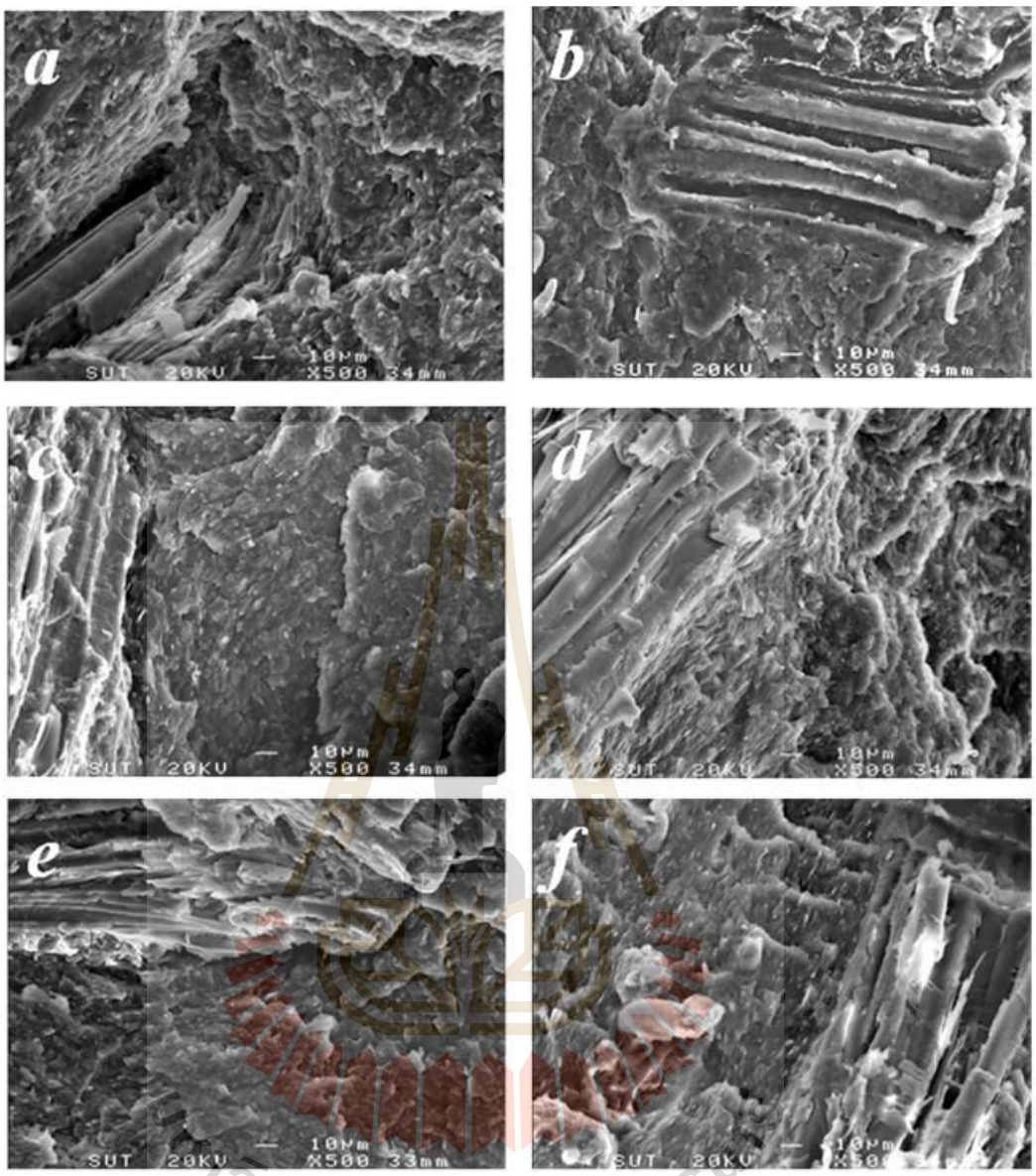

Figure 5.5 SEM of fractured surface of PP wood composite: (***a***) sample without DCP (original), (***b***) sample without DCP (cured), (***c***) original sample with 0.1 phr of DCP, (***d***) cured sample with 0.1 phr of DCP, (***e***) original sample with 0.3 phr of DCP, (***f***) cured sample with 0.3 phr of DCP at magnification X500.

It is seen that the gap between the two phases is diminished or disappeared after the incubation process. This observation is in agreement with the notched impact test result where the impact was superior after the treatment. From SEM evidence only, it is hardly to see the effect of DCP addition on the crosslinking/degradation phenomenon either at matrix or interfacial phases of the sample.

According to the summarized data derived from MFI and gel content show that increase DCP content will increase the melt flow of the molten composite and reduce the degree of crosslink, respectively. It probably means that free radical induced chain degradation of PP is the main reason those changes. At this present experiment, addition of DCP does not improve neither mechanical properties nor HDT of wood composite. Especially, it was found that the impact strength of the sample was dramatically decreased. The chain scission via the free radical depolymerisation would be the main hypothesis for the properties inferior.

5.5.2 Effect of VTMS concentration

From the previous outcome found that adding DCP into the matrix system of WPC did not improve the mechanical and thermal properties of the material. In contradictedly, the polymer chain degradation while increasing the DCP free radical initiator was found and hypothesised explanation. As the preliminary called crosslink system, the vinyl silane/peroxide induced condensation reaction was adopted in this research work. In theoretical point of view, increasing peroxide concentration with limited amount of vinyl silane, or vice versa, the amount of crosslink density would not linearly increase with increasing peroxide. Because the vinyl group presented on silane molecule, which act as the crosslink points, is the

limiting agent. Therefore, the excess free radical generated will likely to react with the polymer chain and hence free radical chain degradation would be occurred. According to the results found, at the given amount of excess DCP at 0.10 phr but further increase the amount of VTMS from 8 to 20 phr to investigate the optimal usage of this peroxide/vinyl silane system on the WPC formula were investigated. The designed formula for manufacturing the WPC test samples are shown in Table 5.8.

Table 5.8 WPCs formula and the amount of VTMS.

Test	PP (phr)	Wood (phr)	Talc (phr)	Stabilizer (phr)	UHMWPE (phr)	EPDM (phr)	DCP (phr)	VTMS (phr)
1	100	35	20	2	10	10	0.10	8
2	100	35	20	2	10	10	0.10	10
3	100	35	20	2	10	10	0.10	15
4	100	35	20	2	10	10	0.10	20

5.5.2.1 Melt flow index

Table 5.9 and Figure 5.6 show the effect of VTMS on the melt flow index (MFI) of the WPC compound. It is observed that MFI is slowly decreased with increasing the VTMS content. It is reversed trend with the previous found on the DCP where the MFI was increased with increasing the peroxide content. Normally, the decreasing in MFI values is directly functioned with the increasing in the polymer chain length. From the result obtained, it is suspected that the molecular chains of polymer matrix could be increased via either branching or macro crosslink reaction.

The enlarging of the chain would inhibit the mobility of the PP chains and hence decrease in the MFI. Further evidences are needed to strongly enforce this hypothesis.

Table 5.9 Effect of VTMS on melt flow index.

VTMS (phr)	Melt flow index (g/10min)
8	2.749±0.156
10	2.737±0.076
15	2.590±0.075
20	1.999±0.039

5.5.2.2 Heat deflection temperature

The results of HDT with respect to the amount of vinyl silane addition crosslink are summarized in Table 5.10 and also Figure 5.6. It is seen that the HDT of both original and sauna cured WPCs are risen against the VTMS addition. There is two folds explanation for the changes. Not only the increasing in the molar mass of the polymer matrix through the peroxide initiated silane chain extension but also the enhancement of the interfacial adhesion between matrix and reinforcement due to the silane addition. Both phenomenons have the positive effect on the service temperature of WPC sample especially for the sauna cured samples.

Table 5.10 Effect of VTMS on HDT.

VTMS (phr)	Heat deflection temperature(°C)	
	Original	Cured
8	120.7 ± 1.2	128.0 ± 1.0
10	123.0 ± 1.0	129.0 ± 1.0
15	126.0 ± 0.0	131.0 ± 1.0
20	125.7 ± 0.6	133.3 ± 1.0

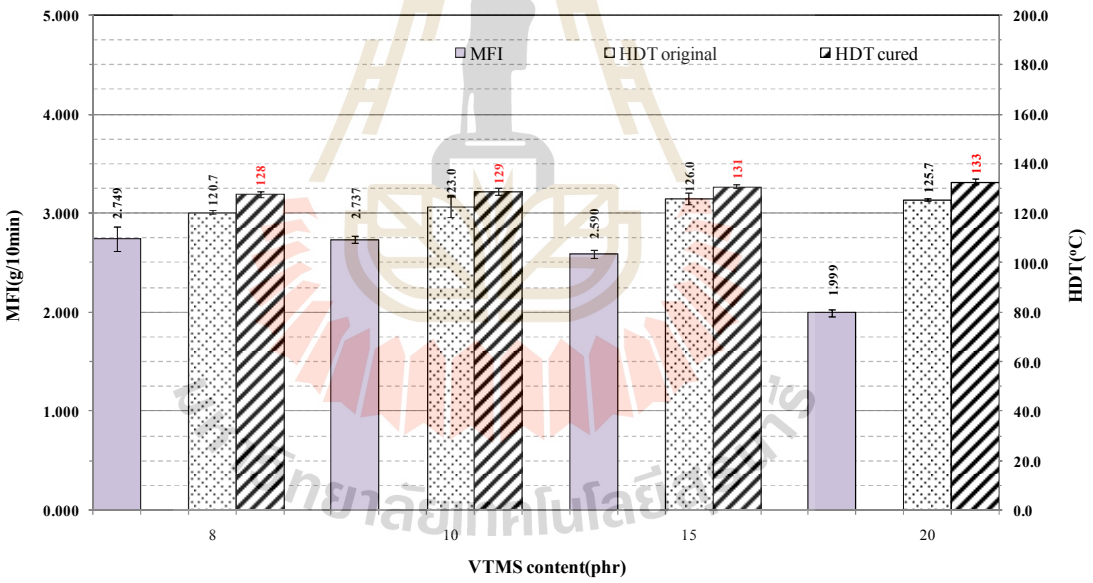

Figure 5.6 Effects of VTMS on MFI and HDT of the WPC.

5.5.2.3 Flexural properties

Table 5.11 shows the result of the flexural properties of wood composite with various VTMS addition. The plot of test values and the vinyl silane concentration is given in Figure 5.7. Within the standard deviation, it is found that the strengths of both original and cured WPC are increased with increasing the amount of the silane used. When compare between original and cured, it is seen that the bending strength of cured sample is insignificant higher than the original ones. Similar to those flexural strengths, the modulus of WPC composites are again insignificantly increased with increasing the VTMS content for both original and cured. The increasing in the flexural properties with increasing amount of VTMS added is might be due to the effect of the molar mass raised and enhancement of the interfacial adhesion between matrix and wood fibre as previously mentioned. Consequently, the fracture toughness by mean of flexural properties would be improved.

Table 5.11 Effect of VTMS on flexural properties.

VTMS (phr)	Flexural strength(MPa)		Flexural modulus(GPa)	
	Original	Cured	Original	Cured
8	32.44 ± 0.38	33.58 ± 0.95	1.37 ± 0.01	1.35 ± 0.95
10	33.00 ± 0.48	33.36 ± 0.69	1.39 ± 0.03	1.38 ± 0.07
15	35.86 ± 0.62	37.08 ± 0.39	1.40 ± 0.06	1.38 ± 0.03
20	37.46 ± 0.23	37.61 ± 0.71	1.43 ± 0.42	1.46 ± 0.05

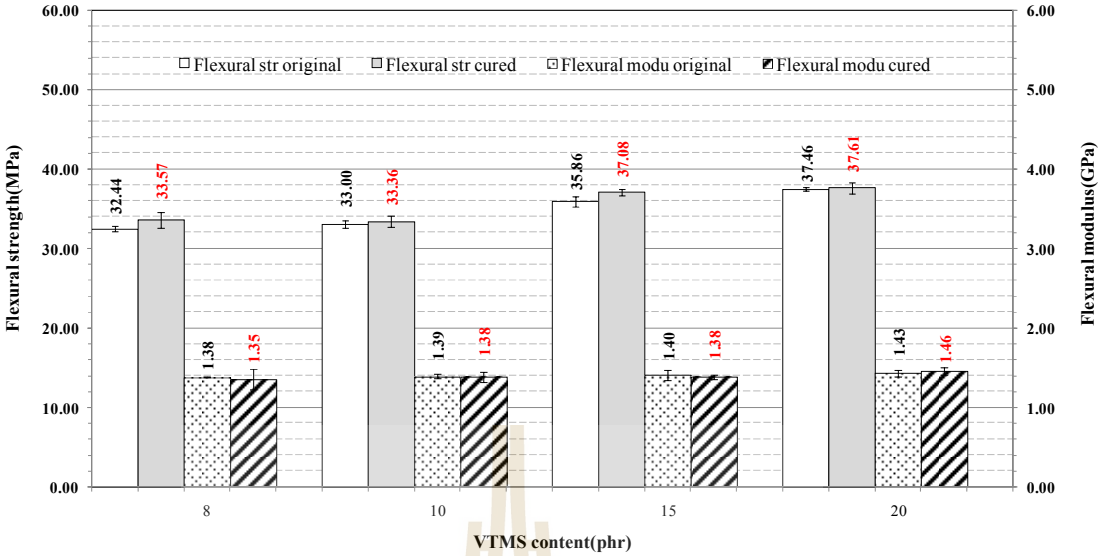

Figure 5.7 Effect of VTMS on flexural properties of the WPC.

5.5.2.4 Impact strengths

Notched and unnotched impact strength of wood composite with the vinyl silane addition are reported in Table 5.12 and they are plotted with the amount of VTMS as shown in Figure 5.8. The result demonstrates that the notched impact strength of wood composites indicate the similar trend to those mechanical properties where it is slightly superior with adding more of VTMS for both with and without sauna treatment. Closer investigation, it seems that the optimal amount of VTMS added is 15 phr. Further increase in the VTMS, for example at 20 phr, the strength of the sample is lowered for both conditioned samples. The exact trend in the strength with the VTMS addition is observed for the unnotched mode of test.

Table 5.12 Effect of VTMS on impact strengths.

VTMS (phr)	Notched impact (kJ/m^2)		Unnotched impact (kJ/m^2)	
	Original	Cured	Original	Cured
8	3.06 ± 0.23	3.71 ± 0.19	10.05 ± 1.66	11.74 ± 1.46
10	3.47 ± 0.01	4.27 ± 0.24	11.22 ± 1.76	11.25 ± 1.01
15	3.79 ± 0.36	4.78 ± 0.09	13.15 ± 1.21	14.23 ± 1.26
20	3.53 ± 0.12	4.52 ± 0.14	12.70 ± 1.84	13.33 ± 0.29

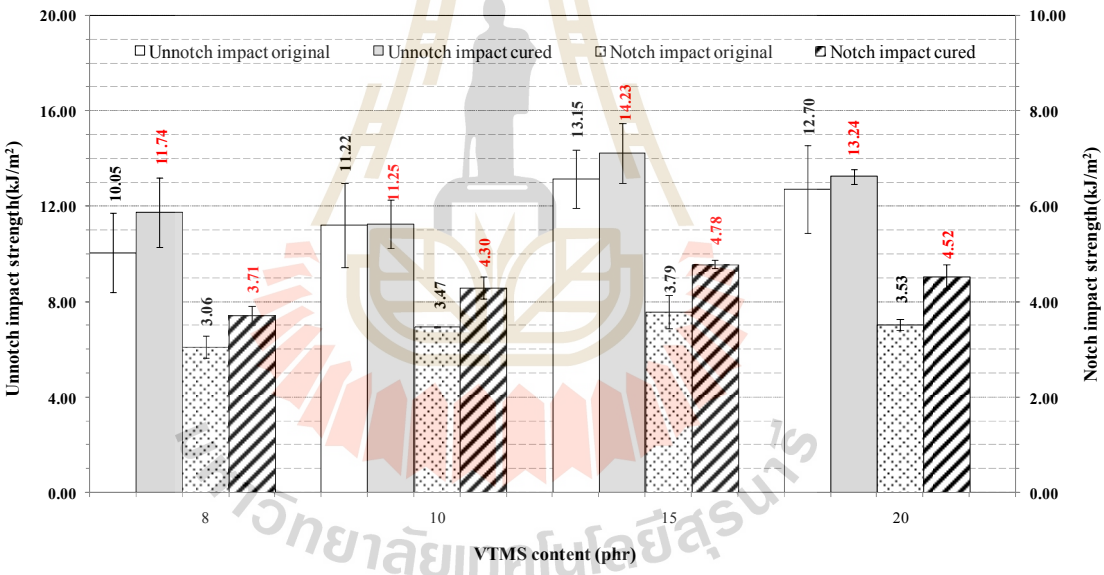

Figure 5.8 Effect of VTMS on the impact strengths of the WPC.

From the impact testing results, it is strengthened the previous statement that increasing in the amount of silane from 8 to 15 phr at constant DCP, 0.10 phr, used the molar mass of the WPC matrix might be increased also the interfacial adhesion between matrix and wood fibre is enhanced. Consequently, the

properties of the WPC, especially the toughness, are improved. The increasing in the molecular chain of the polymer matrix might be via the intermolecular chain crosslink or chain grafting through the peroxide induced silane condensation reaction. Next result, gel determination, will conclude this hypothesis.

5.5.2.5 Gel content

From the above test properties, they are agreed that it is increased with increasing the amount of VTMS addition. The enhancing in the molecular chain of the polymer matrix and also the interfacial adhesion between matrix and wood flour fibre were repeatedly used to explain. The degree of crosslink, gel fraction or *p*-xylene insoluble fraction excluded fibre, of the composites was determined. The test results are summarised in Table 5.13 and graphically shown Figure 5.9. It is seen that the insoluble fraction is rose with the VTMS content. It is almost constant at 15 phr of VTMS. Moreover, gel fraction is obviously increased via the sauna cured process. From this result, it is strongly believed that the crosslinked polymer matrix chain is occurred from the incorporating of peroxide/silane into the WPC formula. It is in agreement with the published research work (Magnus, et al., 2007). At 0.1 phr of DCP, increasing the vinyl silane from 8 to 15 phr, it is found that the gel fraction, believed to be crosslinked matrix chain, is increased. From this gel determination verdict, it can say, with high confident, that raising the amount of VTMS in the WPC formula can enhance the properties of the composite through the matrix crosslink process and also the interfacial adhesion enhancement.

Table 5.13 Effect of VTMS on gel content of wood composites.

VTMS (phr)	Gel content (%)	
	Original	**Cured**
8	22.2 ± 7.0	31.9 ± 28.9
10	19.9 ± 0.8	34.9 ± 20.1
15	23.5 ± 9.9	38.5± 8.5
20	24.6 ± 10.2	38.7 ± 2.2

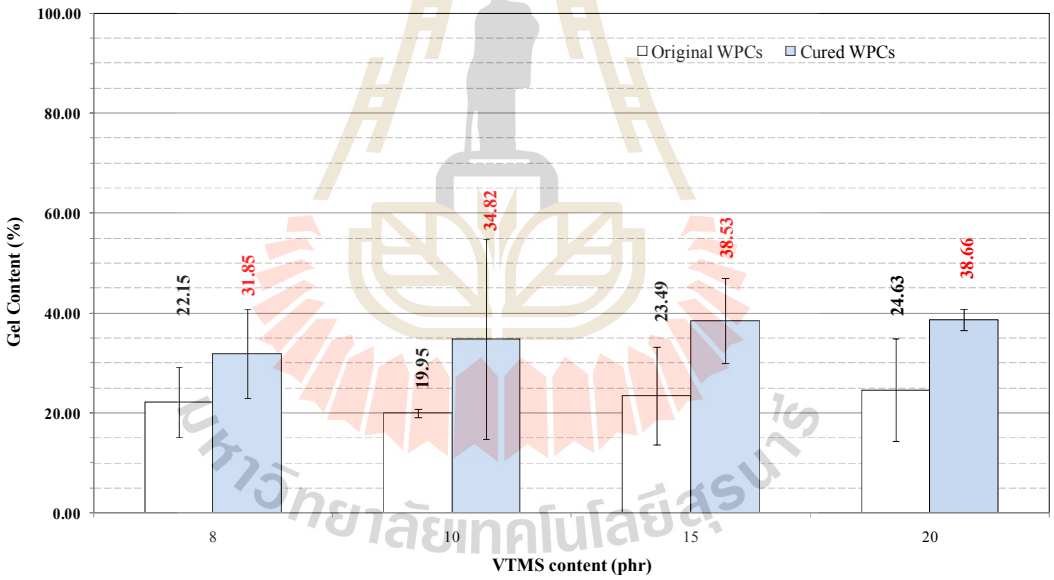

Figure 5.9 Effect of VTMS on the gel content of the WPC.

5.5.2.6 Morphological investigation

The SEM photographs of the fractured surface obtained from the notched impact specimen are presented in Figure 5.10 (***a***) to 5.10 (***f***). Figure 5.10 (***a***) and 5.10 (***b***) are the SEM photographs of the wood composite with 8 phr of VTMS before and after sauna incubation, respectively. Poor interfacial adhesion is obviously observed for the sample without sauna curing because the delamination between fibre and matrix is evidenced. After the sample was sauna cured, Figure 5.10 (***b***), the better interfacial adhesion, no space between fibre and matrix, is significantly improved. When increasing the silane content to 10 phr, it was found that most of the properties were visibly enhanced. Figure 5.10 (***c***) and 5.10 (***d***) are the SEM pictures of the composite with 15 phr of VTMS before and after sauna incubation, respectively. Similar observations to those 8 phr addition are found. The fractured surface of cured composite indicates better adhesion between wood fibre and the matrix.

However, by considering the SEM evidence only, there is not enough clue to gain the differences between adding low and high silane contents from the morphological testing. The certain hint that can be used to support the improvement of the properties by increasing the silane content is than the traces of fibre pull out. Taken from the cured samples, they are noticed that at low VTMS, 8 phr, there are quite a few of left over holes due to the fibre pull out but not too many traces at high VTMS content, 15 phr.

From the results found, increasing of VTMS concentration as crosslink agent was seen that mechanical strength and HDT are improved from 8 to 15 phr of silane. The degree of crosslinking, by mean of gel content, was also increased. There are no significantly improvements in the properties by further raising

the silane content. Therefore, the optimal usage of VTMS derived from this study was at 15 phr with 0.1 phr of DCP. However, in term of the fracture toughness of the wood composite, the test Figures are relative low. Further improvement of this property will be attempted and will be discussed in the next section.

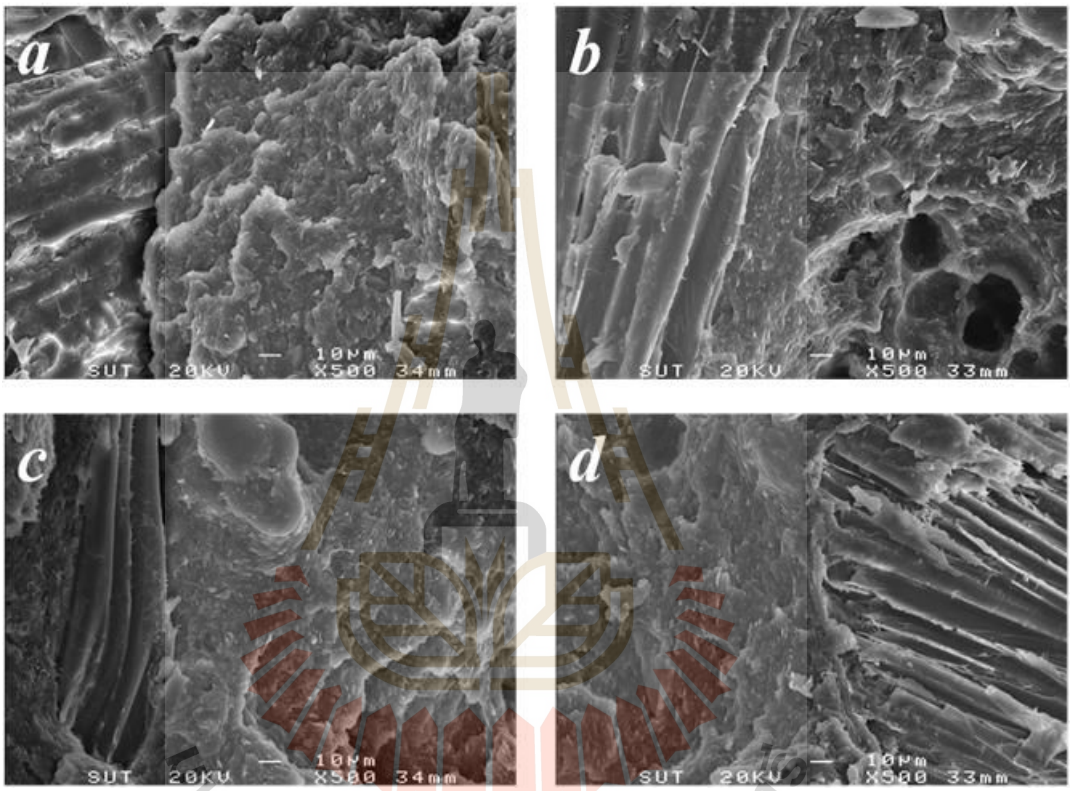

Figure 5.10 SEM of fractured surface of PP wood composite: (***a***) 8 phr of VTMS (original), (***b***) 8 phr of VTMS (cured), (***c***) 15 phr of VTMS (original) and (***e***) 15 phr of VTMS (cured) at X500.

5.5.3 PP copolymer as fracture toughener

From the previous outcome found that increasing silane concentration mechanical properties and HDT were improved. SEM evidenced that adhesion between wood fibre and matrix were increased with increasing VTMS. Propylene-ethylene copolymers are generally used where high fracture toughness applications are needed. Ethylene monomer is copolymerized into PP chain as either block or random manners. In case of block polymer PP, the block chain is dispersed as rubber toughener into the homo polymer matrix or it is normally called impact modifier rubber. In this study, attempting to toughening the WPC by adding PP copolymer, PP 740J, was performed. The designed formula for manufacturing the copolymer PP toughened WPC is shown in Table 5.14. The ratios between homo and copolymer types PP are varied. The rest of the ingredients such as wood flour, tougheners and crosslink system are identical to the previous experiments.

Table 5.14 WPCs formula and PP740J toughening.

Test	PP700J (%)	PP740J (%)	Silane (phr)	Wood (phr)	Talc (phr)	Stabilizer (phr)	UHMWPE (phr)	EPDM (phr)	DCP (phr)
1	100	0	8	35	20	2	10	10	0.10
2	80	20	8	35	20	2	10	10	0.10
3	50	50	8	35	20	2	10	10	0.10
4	20	80	8	35	20	2	10	10	0.10
5	0	100	8	35	20	2	10	10	0.10

5.5.3.1 Melt flow index

Flow ability of WPC samples by mean of MFI are summarized in Table 5.15 and also graphically presented in Figure 5.11. It is found that MFI is raised with increasing the PP copolymer fraction. Regarding to the data sheet of the manufacturer, MFI of copolymer, PP 740J is higher than homopolymer, PP 700J. In according to the rule of mixture shown in equation 5.3, it can be explained that the flow ability of molten composite would be increased with increasing the weight fraction of block copolymer. The calculated MFI of the composites are also included in Table 5.14. It is seen that the measured values are well agreed with the computed Figures. It can conclude that, adding PP copolymer at high fraction will increase the MFI of WPC.

$$\ln \mathrm{MFI}_{\mathrm{blend}} = w_{\mathrm{I}} \ln(\mathrm{MFI}_{\mathrm{I}}) + w_{\mathrm{II}} \ln(\mathrm{MFI}_{\mathrm{II}}) \tag{5.3}$$

where w_{I} = weight fraction of PP homopoymer

w_{II} = weight fraction of PP copolymer

$\mathrm{MFI}_{\mathrm{I}}$ = MFI of PP homopolymer

$\mathrm{MFI}_{\mathrm{II}}$ = MFI of PP copolymer

Table 5.15 Melt flow index of copolymer toughened WPCs.

PP 700J/PP740J (%W/W)	Melt flow index (g/10min)	Calculated MFI (g/10min)
100/0	1.903 ± 0.012	1.903
80/20	1.793 ± 0.023	2.059
50/50	2.220 ± 0.083	2.319
20/80	2.289 ± 0.058	2.612
0/100	2.827 ± 0.022	2.827

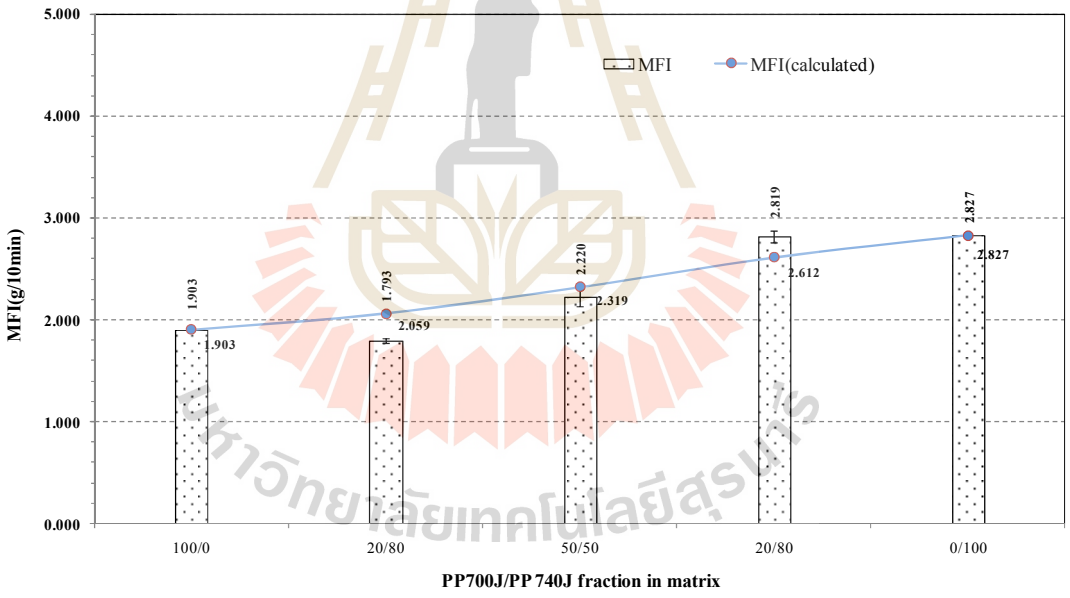

Figure 5.11 Effect of PP740J on MFI of the WPC.

5.5.3.2 Heat deflection temperature

The HDT of wood composites based on homo and copolymer PPs blend matrix is illustrated in Table 5.16 and plotted as shown in Figure 5.12. It is

seen that the HDT of the samples with and without sauna curing are in depended on the fraction of copolymer added. By adopting Fox's equation, as shown below, to calculate the HDT of PPs blend wood composite, the computed values are summarized in the result Table. It is seen that the calculated values are agreed with the measured Figures obtained from the sample without sauna curing.

As seen from the HDT testing result, there is no relationship between the fraction of PP copolymer contents in PPs blend matrix and HDT of the material. Elevation of thermal property of the sample by sauna incubation process would be due to the crosslink reaction and enhancing the interfacial bonding between matrix and wood flour via silane/moisture condensation or increasing in the crystallinity of the PPs matrix by annealing at the temperature above the T_g of polymers.

$$\frac{1}{HDT_{blend}} = \frac{w_I}{HDT_I} + \frac{w_{II}}{HDT_{II}} \qquad (5.4)$$

where HDT_I = HDT of homo PP

HDT_{II} = HDT of copolymer PP

Table 5.16 Effect of PP740J on HDT of wood composites

PP 700J/PP740J (%W/W)	Heat deflection temperature (°C)		
	Original	cured	Calculated
100/0	122.0 ± 0.0	128.0 ± 0.0	122.0
80/20	120.0 ± 0.0	129.0 ± 0.0	121.6
50/50	120.0 ± 0.0	128.0 ± 0.0	120.9
20/80	121.0 ± 0.0	127.0 ± 0.0	120.4
0/100	120.0 ± 0.0	129.0 ± 0.0	120.0

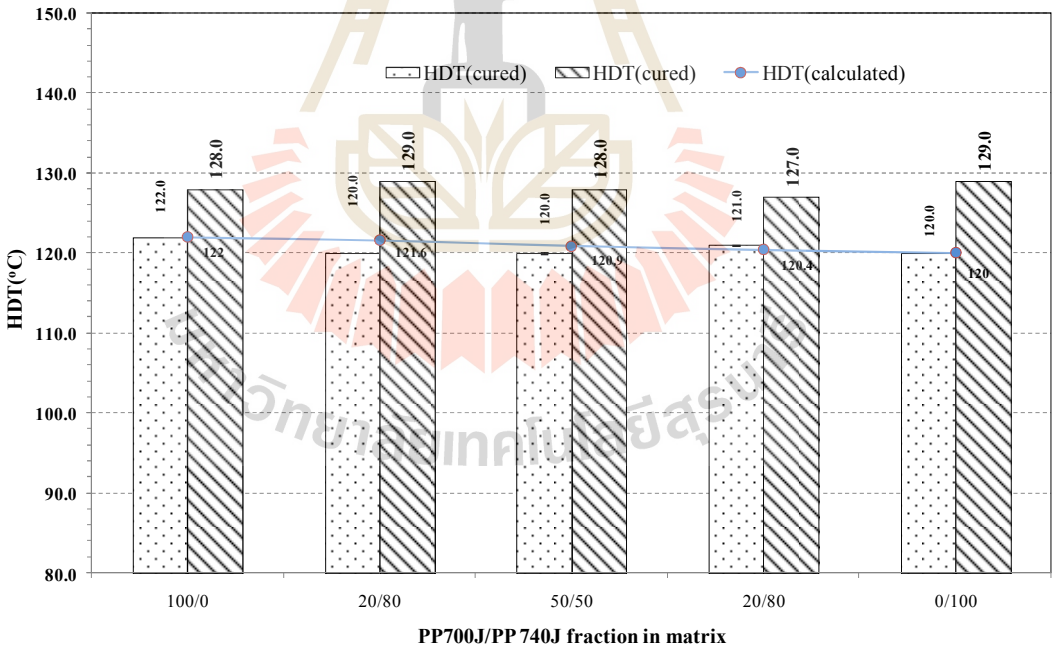

Figure 5.12 Effect of PP740J on HDT of the WPC.

5.5.3.3 Flexural properties

Table 5.17 and Figure 5.13 summary the flexural strength and modulus of the PPs blends wood composites. The results show that flexural strengths of both original and cured samples are slightly decreased with increasing the fraction of PP copolymer in PPs blend matrix. Curing of sample by sauna treatment does fractional increase the strength of the wood specimen. However, with in the standard deviation of error, it is rather hesitate to conclude that the elevation of the strength is due to the sauna treatment. Further loading the copolymer in the blend, the strength become inferior. The depression of the flexural strength with increasing of the copolymer fraction is might be due to the fact that the flexural properties of the copolymer used is lower than the properties of homo polymer.

Table 5.17 Effect of PP740J on flexural properties of composites.

PP 700J/PP740J (%W/W)	Flexural strength (MPa)		Flexural modulus (GPa)	
	Original	Cured	Original	Cured
100/0	31.09 ± 0.74	31.25 ± 1.02	1.25 ± 0.15	1.29 ± 0.08
80/20	31.04 ± 1.32	31.99 ± 0.34	1.36 ± 0.04	1.36 ± 0.08
50/50	30.91 ± 0.39	31.17 ± 0.67	1.27 ± 0.07	1.31 ± 0.09
20/80	27.72 ± 0.48	28.62 ± 0.91	1.23 ± 0.09	1.29 ± 0.03
0/100	28.39 ± 0.86	28.25 ± 0.26	1.28 ± 0.02	1.29 ± 0.01

Similar trend is found for the flexural modulus of the composite samples having the PPs blend as matrix. The test results review that the bending

modulus trend to be lowered by blending more of PP block copolymer. From the manufacturer data, see Table 5.1, the modulus of homo PP used is 1.422 GPa but it is 1.225 GPa for the block copolymer. It means that blending with high copolymer fraction would decreased the modulus of the blend. Sauna incubation had slightly increased the modulus of the WPC specimen.

From the flexural properties testing, blending of block copolymer PP into the homo polymer PP in order to improve the toughness, by mean of the flexural, of the WPC, it was observed that the properties as inferior with increasing the block fraction. Sauna treatment of the copolymer/homo matrix blend to promote the chain crosslink formation was found to be ineffective.

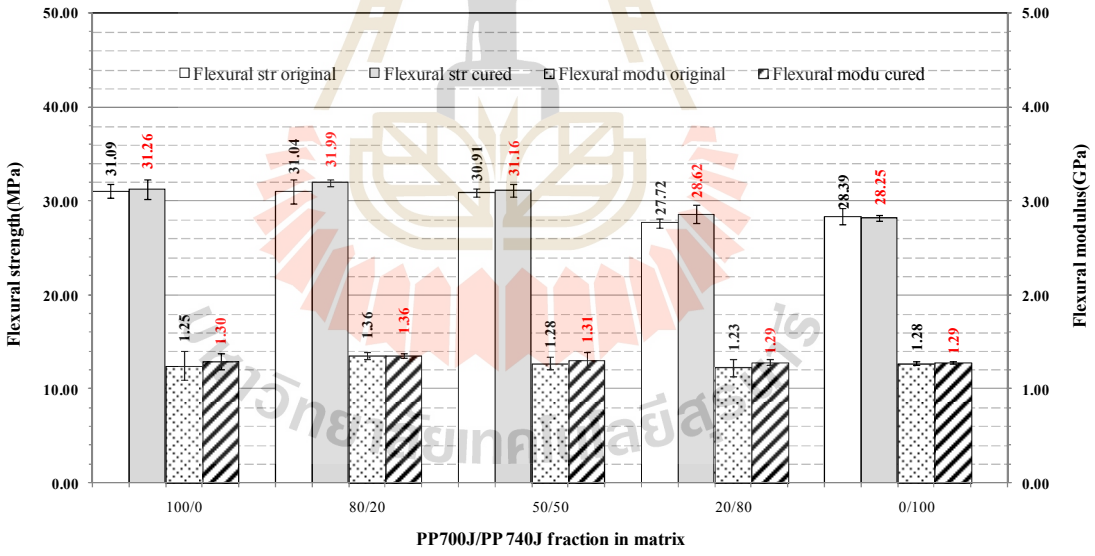

Figure 5.13 Effect of PP740J on flexural properties of the WPC.

5.5.3.4 Impact strength

The toughness of composite with PP copolymer blending in the PPs matrix by mean of the impact strengths of the WPC specimen are shown in Table 5.18 and plotted in corresponding with the of homo/copolymer ratio given in Figure 5.14, respectively. As expected, the test output indicates that the notched impact strength of composite is graduately increased with increasing the copolymer fraction in the blend matrix, for both without and with sauna treatment. Impact strength of cured sample is superior than the original ones.

Table 5.18 Effect of PP740J on impact strengths of wood composites.

PP 700J/PP740J (%W/W)	Notched impact (kJ/m^2)		Unnotched impact (kJ/m^2)	
	Original	Cured	Original	Cured
100/0	3.29 ± 0.16	3.68 ± 0.13	10.70 ± 0.64	10.98 ± 0.74
80/20	3.56 ± 0.11	3.92 ± 0.14	10.38 ± 0.65	10.46 ± 0.52
50/50	3.86 ± 0.24	4.25 ± 0.12	11.95 ± 1.31	12.08 ± 0.69
20/80	4.29 ± 0.05	4.31 ± 0.19	13.88 ± 2.06	12.82 ± 0.54
0/100	4.36 ± 0.16	4.37 ± 0.14	11.05 ± 1.62	10.75 ± 0.28

The similar trend was found for the unnotched impact strength with the optimal fraction of PP copolymer at 80% weight in PPs matrix. Further increase the PP740J fraction, the impact toughness is diminished. Curing of the sample by sauna incubation, it was observed that the unnotched impact does not depend on the copolymer fraction. From the results found it is suggested that the

fractured toughness of the WPC does not influence only from the properties of the matrix but would be also contributed from the adhesion between fibre and matrix. Better matrix toughness but poor in the interfacial adhesion would give rise the inferior fractured strength of the composite. The fluctuation of the unnotched impact strength would be due to the fibre/matrix adhesion. The evidence for the fibre/polymer adhesion will be revealed by the SEM investigation in the next section.

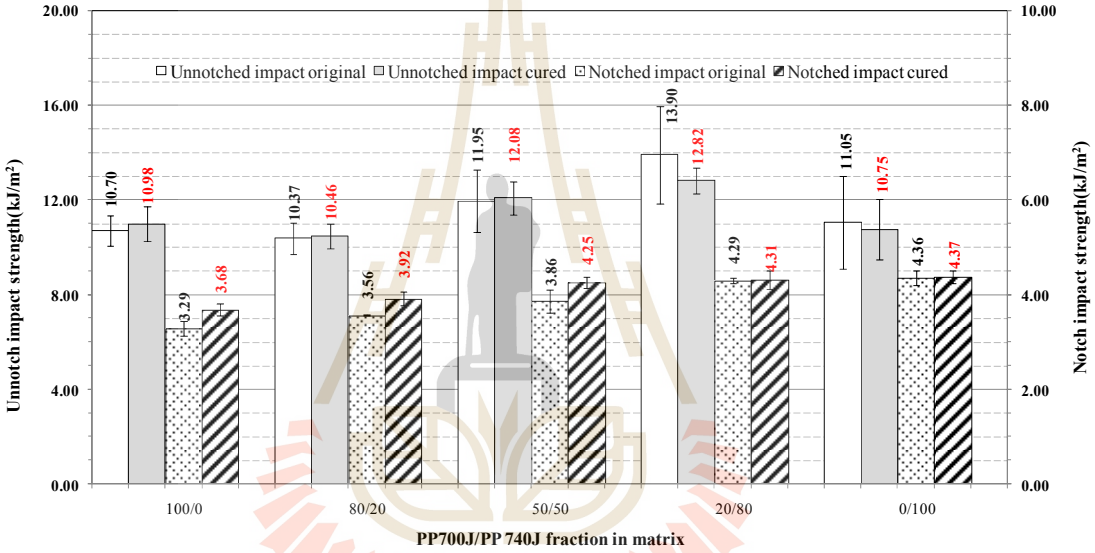

Figure 5.14 Effect of PP740J on impact strength of the WPC.

Blending of the higher toughness copolymer PP into the homo PP matrix of the WPC to improve the fractured strength of the WPC was found to be ineffective. Only notched impact strength of the samples were marginally increased. Other properties were found to be inferior. Within the small fraction of the PP copolymer blended with homo PP, the properties of the WPC were accepTable with easily to process by injection molding.

5.5.3.5 Morphological investigation

From previous mechanical testing results, it was seen that only notched impact strength was improved by blending the PP matrix with copolymer fraction. On the other hand, only copolymer did not show the improvement of the strength either. It was in doubt that not only the blended matrix itself but also the adhesion between the PPs blends matrix with other ingredients would play the important role in the fracture toughness of the composite material. The scanning electron microscopy (SEM) of notched fractured surface of the WPC samples will be used to reveal this hypothesis. Figure 5.15 (***a***) to 5.15 (***f***) are the SEM traces of the WPC base on 100% homo PP, 50% of homo and 100% PP copolymer in the PPs blends matrix, respectively. From the SEM photograph, they are seen that there is no relationship between the wood flour fiber and matrix adhesion with corresponding to the blends fraction. Because the fibre and the PP(s) matrix are in good contact. However, there is obvious different in the adhesion between UHMWPE particle and PP matrix phase. There are distinctive left over holes of UHMWPE on the matrix during the sample fraction of the composite derived from 100% of homo or 100% copolymer as in Figure 5.15 (***a***) and 5.15 (***e***), respectively. Sauna curing of the samples are found to be in succeed as indicated in Figure 5.15 (***b***) and 5.15 (***f***), respectively. Vice versa, the existing of the UHMWPE particle on the composite matrix is seen in Figure 5.15 (***c***) and 5.15 (***d***) when 50% of copolymer PP was blended with the homo type.

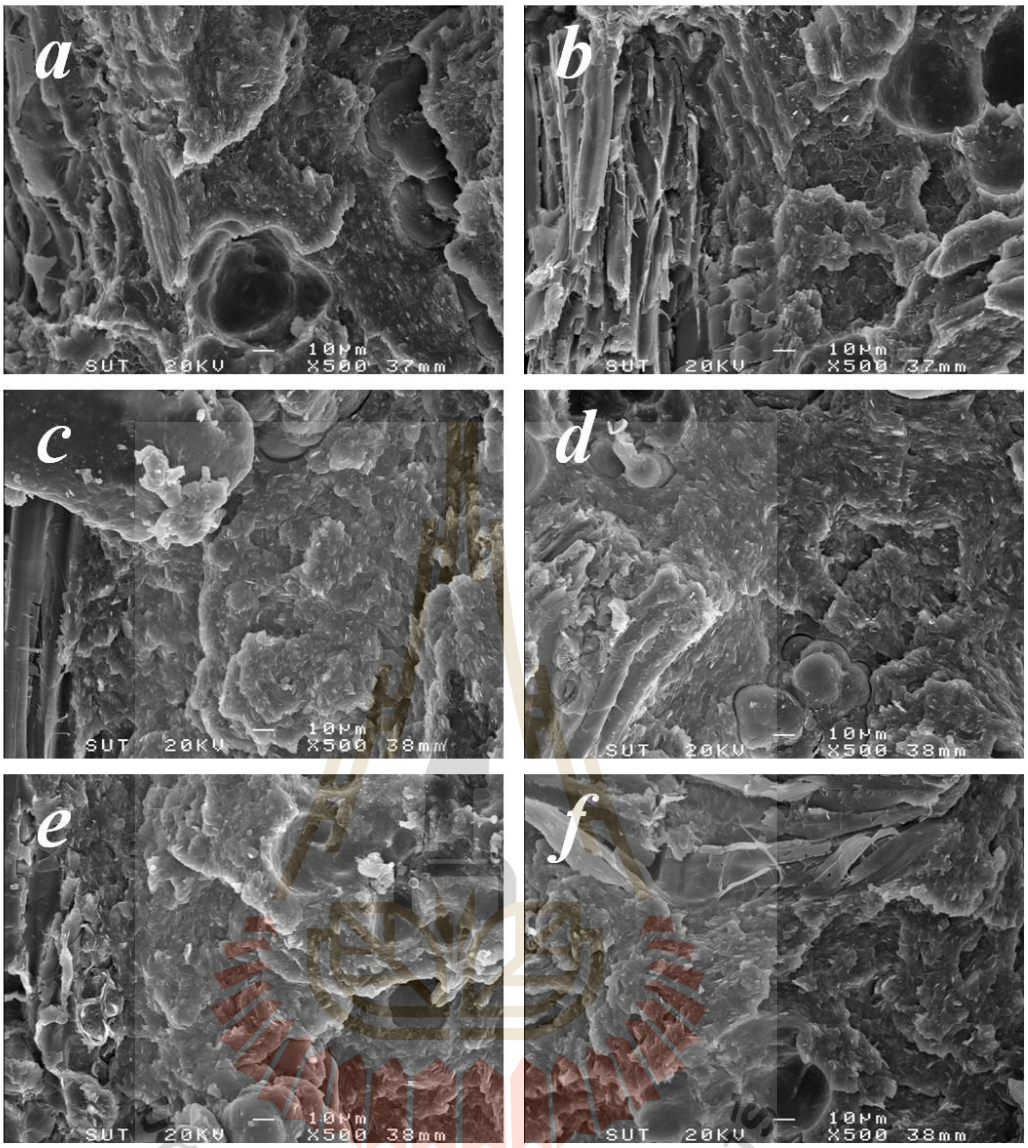

Figure 5.15 SEM of wood composite base on matrix fraction of PP700J/PP740J: (***a***) 0/100 (original), (***b***) 0/100 (cured), (***c***) 50/50 (original) and (***d***) 50/50 (cured), (***e***) 100/0 (original) and (***f***) 100/0 (cured) at **X**500.

It is demonstrated that the better interfacial adhesion between UHMWPE dispersed phase and PPs blend matrix. But there is no further improvement of the adhesion, from the SEM analysis, by sauna treatment the sample.

Taken from SEM study only, good surface contact between UHMWPE particle and 50/50 PPs matrix phase is observed and it might be used to explained the improvement of the notched impact strength of the WPC sample.

5.5.3.6 Termite resistance testing

Durability of wood and wood composite by mean of anti termite attack were tested. Teak and eucalyptus wood were used as referee. Woods mass remaining was calculated as % weight was reported and the results are summarized in Table 5.19. The % weight remained against the buried time is also plotted as shown in Figure 5.16. As expected, from the result illustrates that % weight remain of soft wood, eucalyptus, is rapidly diminished with time. After ten weeks of burying, the wood was ruined and more than 30% of cellulosic of wood was consumed by the insect. Figure 5.17 is evidenced for the termite attraction within ten weeks time. However, when considering the WPC composite specimen for both original and cured sample, it is seen that the % weight remain are almost unchanged within ten weeks of buried time. Exact phenomenon is found for the teak wood. The teak wood is commonly known as highly termite resistance wood. The pictures of WPCs and teak wood after ten weeks of buried time as shown in Figure 5.17 are confirmed that there is no trace of termite attack on the surface of the woods. According to these test result, it is strengthen that WPC derived from wood flour and PP matrix from this study has good resistance from the termite attack. It is ensured that the applications of the WPC based on PP polymer can be used as the construction material without fearing of the termite damaging.

Table 5.19 The termite resistance test result.

specimen	weight%					
	Week 0	Week 2	Week 4	Week 6	Week 8	Week 10
Eucalyptus	100 ± 0.0	89.4 ± 2.4	90.8 ± 2.4	90.8 ± 3.5	83.6.8 ± 9.4	67.3 ± 17.7
Teak	100 ± 0.0	101.6 ± 1.9	105.3 ± 3.9	103.6 ± 3.8	96.2 ± 7.2	102.7 ± 5.7
WPC	100 ± 0.0	100.2 ± 0.5	100.2 ± 0.4	103.3 ± 0.3	103.3 ± 0.3	97.0 ± 1.9
Cured WPC	100 ± 0.0	97.6 ± 0.9	98.2 ± 1.1	98.2 ± 1.1	102.5 ± 4.5	97.6 ± 4.6

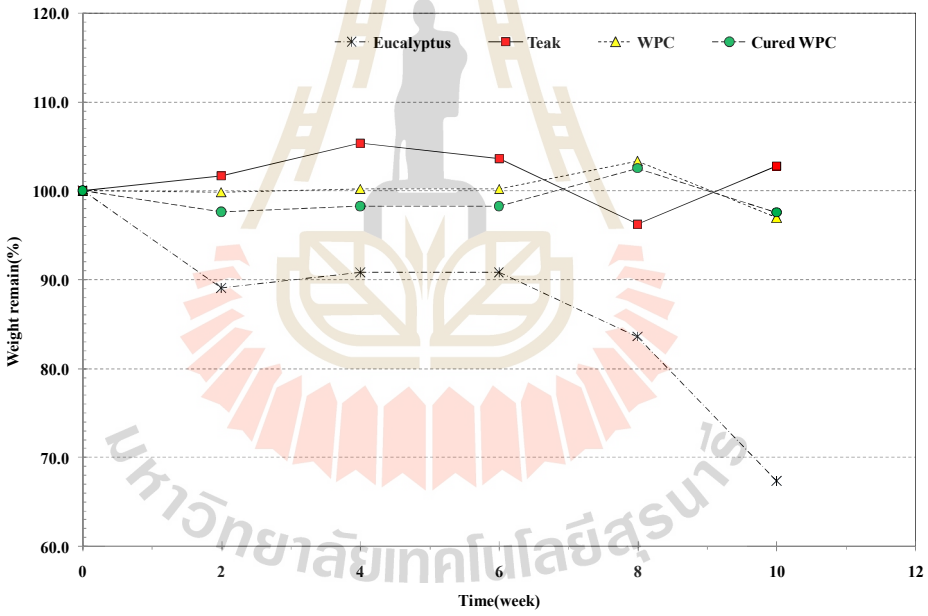

Figure 5.16 Plotted of the remain % weight and buried times.

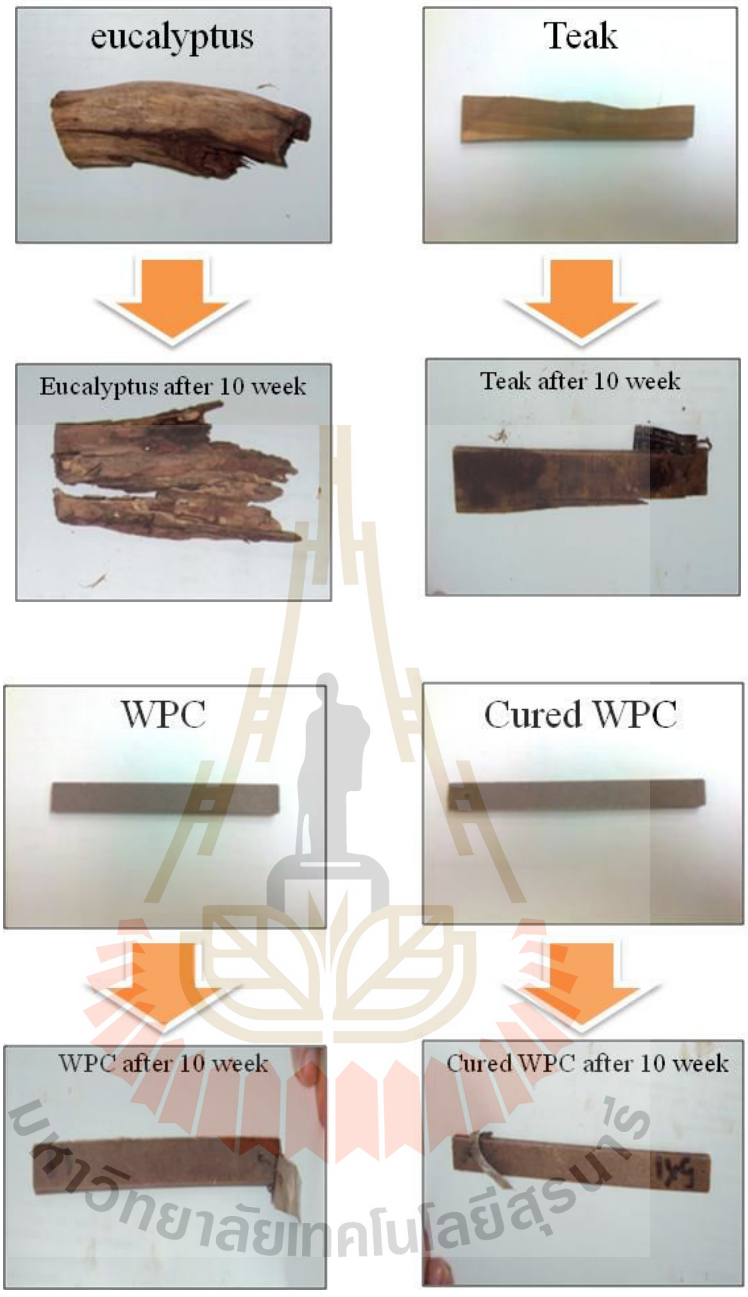

Figure 5.17 Photograph of woods before and after undergoing termite test.

5.6 Conclusions

According to study of effect of DCP, free radical initiator, on the crosslinked PP wood composite, it was found that the MFI was increased and gel content was reduced when increasing the DCP content, respectively. It meant that decomposted free radical induced chain scission of PP. Consequently, addition of excess DCP did not improve neither mechanical properties nor HDT of wood composite. Moreover, it was experienced that the impact strength of the sample was dramatically decreased.

At the given DCP concentration, the further studied concluded that increasing of VTMS as crosslink agent had improved the mechanical strength and HDT of WPC. The degree of crosslinking, by mean of gel content, was also increased. The optimal usage of VTMS was around 15 phr with 0.1 phr of DCP. However, in term of the fracture toughness of the wood composite, the test results were relative low.

PP copolymer as impact improver was attempted. It was found that only impact strength of the WPC based on PP copolymer blend matrix was enhanced but not for flexural properties and HDT. PP copolymer fraction at 80% by weight was recommended. Durability testing by mean of termite resistance exhibited that the WPC derived from this research study had the durability behavior similar to those teak wood which show the excellent termite resistivity.

5. 7 References

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APPENDIX

PUBLICATIONS

List of Publications

Anuchit, K. and Utai, M. (2011). Design of experiment : Wood composite based on crosslinked polypropylene. **The 2nd Research Symposium on Petroleum, Petrochemicals, and Advanced Materials**. 26 April 2011. Bangkok, Thailand

Anuchit, K. and Utai, M. (2011). Design of experiment : Wood composite based on **crosslinked polypropylene.** The 18th International Conference on Composite Materials. 21-26 August 2011. Jeju island, Korea.

DESIGN OF EXPERIMENT : WOOD COMPOSITE BASED ON CROSSLINKED POLYPROPYLENE

Amochit Khongrit[a,*], *Uthai Meeksum*[a,b]

[a] School of Polymer Engineering, Suranaree University of Technology, Nakorn Ratchasima, Thailand
[b] Centre of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok, Thailand

ABSTRACT

Investigation of wood composite based on crosslinked polypropylene was studied. The design of experiment was used to optimize and quantify the amount of the composite constitutes. The 2^k factorial design was conducted to evaluating the statistical effects of material compositions. Three parameters, silane (A), wood flour (B) and talc (C) contents were assigned. Composites were compounded into pellets by co-rotation twin screw extruder at 190°C and test specimens were prepared by injection molding. The measured responds were classified into 2 conditions; original and sauna cured. The original were allowed the samples to anneal at room temperature for approx. a day. The later were achieved by sauna incubation at 105°C for 12 hrs. Impact strength, flexural properties and HDT were tested and obtained as the respond effects. The optimal formulation of WPC was accomplished. Statistical analysis approach using ANOVA testing showed that silane and wood had generally positive effect on the mechanical properties. However talc showed negative effect to properties of WPC. Generally, the mechanical properties were seen to improve after sauna treatment. It evidences that the crosslink bridge between polymer matrix and wood flour via silane/water reaction could enhances the interfacial force. Scanning electron microscopy(SEM) was emphasised the crosslink phenomenon and hence the mechanical competency.

*holly2frozen@hotmail.com

INTRODUCTION

Wood Plastic composites(WPCs) market is going strongly around the world. It is used as substitute or alternate for the natural wood which is wildly prohibited or legally controlled by many countries. Most applications of WPCs are as the building and decorative materials such as outdoor deck, floors, windows and door. The main ingredients of WPC consist of thermoplastic polymer matrix and natural fiber reinforcement. The most common matrices are PVC, PP and PE. The wood flour obtained from timber milling is commonly used. However, the commercially available wood composite has some incompetency such as low mechanical properties compare to those hardwoods. Therefore, the improvements of the long term properties have been explored by many researchers and engineers. The main techniques used for modification of WPCs include grafting, cross linking, matrix blending, and reinforced with other high performance filler(s)[1, 4, 6]. Silane grafting and water crosslinking of polyolefin have received much attention in industrial applications and fundamental research, because of its provide the obvious advantages, such as easy processing, low capital investment, and favorable properties in the processed materials[5].

Silane group was grafted onto the polymer chain by, firstly, adding peroxide to create free radicals that can induce the grafting of a silane group into the polymer backbone. The resultant silane grafted polymer matrices is then hydrolyzed and condense to create –Si–O–Si– bonds between the chains. The bonds between wood and plastic have been suggested to comprise a mix of silane bridges and hydrogen bonds[2]. This network result in the outstanding performance properties. In this studied, WPC based on crosslinked polypropylene and wood flour reinforcement was performed. As the crosslink structure of polymer chain enhances the properties of material such as higher in resistance to heat and light degradation. Accordingly, it will give rise to superior in dimensional stability and durability. The statistical approach by mean of design of experimental(DOE) on the given parameters that effect to the properties of WPC will be the prime interests.

EXPERIMENTAL

A. Materials

Commercial grade isotactic polypropylene homopolymer(PP700J) for injection(MFI = 12g/10min, 230°C/2.16 kg) supplied from SCG Chemical Co., Ltd. was used as composite matrix. Vinyltrimethoxysilane(VTMS), Silquest A 171, as crosslink or coupling agent was purchased from Optimal Tech Co., Ltd. Dicumyl peroxide(DCP) was employed as free radical initiator. Talc(JetFine 3CA) manufactured by Luzenac company with particle size of 1.1 μm was added as filler. Wood flour from timber mill was ground by hammer mill machine into fine powder with particle size, by mean of sieve size, less than 1 mm. Mixture of Irganox 1076 and Irgafos 168 at ratio of 1:1 by weight were used as thermal/processing stabilizer and supplied from Ciba specialty chemicals Co., Ltd.

B. Design of experiment

The 2^k factorial design of experiment was elected to optimize and quantify the amount of the composite constitutes. Three parameters(k=3) were silane(A), wood flour(B) and talc(C) contents. Each parameter was divided into two levels; high(+) and low(-), respectively. In each level, it was also split into two sub levels as shown in table 1. For example, silane content at 3 and 5 phr were assigned as low level, vice versa 8 and 10 phr were assigned as high level, respectively. Eight runs of WPC formula having batch size corresponded to 300 g of PP were constructed as shown in table 2. The statistical analysis were performed by using commercial software, Design Expert™.

Table 1 The parameter and level of DOE

Parameters	High level(+)		Low level(-)	
Silane(phr)	10	8	5	3
Wood (phr)	45	35	25	15
Talc (phr)	40	30	20	10

Table 2 Factorial design matrix

Run	Silane(A) (phr)	Wood(B) (phr)	Talc(C) (phr)	DCP (phr)
1	3(-)	25(-)	20(-)	0.3
2	5(-)	15(-)	40(+)	0.3
3	3(-)	45(+)	10(-)	0.3
4	5(-)	35(+)	30(+)	0.3
5	8(+)	15(-)	10(-)	0.3
6	10(+)	25(-)	40(+)	0.3
7	8(+)	35(+)	20(-)	0.3
8	10(+)	45(+)	30(+)	0.3

C. WPC compounding and test sample preparation

Wood flour was dried in hot oven at 105°C for at least 12 hr to eliminate the trace moisture. Wood flour, VTMS and process stabilizer powder was then mechanically mixed by high speed mixer for 5 minutes. PP pellet and solid DCP in tight seal bag was warmed at approx. 50°C for a few minutes allowing the peroxide to be melted and then, rigorously shake for DCP to be utterly coated on to polymer pellet. Talc and silane treated wood flour were well incorporated with the pellet. The premixed ingredient was kept in the oven 80°C before melt mixing. By using single screw feeder, the dried ingredient was then constantly fed into co-rotation twin screw extruder (Brabender™) with screw diameter of 25 mm., L/D of 20 The temperature profiles on the extruder for melt mixing from feed to die zones were 180, 185, 185, 190 and 190°C, respectively. The extrudate strand was air cooled and granulated in to small pellet using machine crusher. The test specimens were prepared by injection molding machine(Tederic TRX60c) with the barrel temperature of 190°C for all zones. The wood polypropylene composites specimens were separated into 2 sets of samples. One was allowed to anneal at room temperature for at least a day ad called as original sample. The rest was incubated in the oven saturated with water vapour at 105°C for 12 hours. The sauna incubation was used to accelerate the silane/water crosslink reaction. The sample obtained from this process was assigned as sauna cured WPC.

D. Properties measurement and testing

Melt flow index of wood composite was determined according to ASTMD1238. The samples were melted at 170°C under a load of 2.16 kg. Flexural properties of the wood composites was obtained according to ASTM D790 using the Instron universal testing machine(UTM, model 5565). Notched and unnotched impact strength of the composite sample was tested using ASTM D256. Both flexural and impact properties were conducted at room temperature. The ASTM D648 testing with the standard load of 0.455 MPa(66 psi) and heating rate of 2 ±0.2°C/min was followed to measure the heat deflection temperature(HDT) of the sample. Morphology of the fractured surface from the impact test of was examined by scanning electron microscope(SEM). The samples were ionized coating with gold before investigation.

RESULTS AND DISCUSSION

A. DOE Analysis

Notched and unnotched impacts, flexural strength and modulus, HDT and MFI results tested from the standard tests are summarized in table 3. The test values generally review that the sauna incubation has positive effect on the measured properties as they are increased after the incubation process. Using the Design Expert®, statistical analysis of the responds data are performed. For flexural strength respond, the normal probability against the standardized effects plot is shown in Fig 1(*a*) and 1(*b*), for original and sauna cured wood composite, respectively. The plot shows that silane content(*A*) and interaction between silane and talc content(AC) are the greatest effect on flexural strength of WPC. They are positive(+) and negative(-), respectively. Applying the ANOVA testing at 95% of confidential, the result confirms that those two effects are significant effects on the flexural of WPC. The talc content(C) is also the negative effect on the flexural of WPC after sauna curing. However, the ANOVA testing indicates that it is not significantly affected. By applying the rest of the responds, obtained from original and sauna cured sampled, into the

same statistical procedure, it can be summarized that flexural modulus of the annealed samples are also significantly influenced by wood flour(B+), talc(C+) and interaction of wood and talc content(BC-). Flexural mochulus of sauna treated WPC has obviously and positively affected by talc content(C+). Notched impact strength for the original WPCs has significantly positively affect in corresponding with silane(A+), wood flour(B+), interaction between silane and wood flour(AB+) and between silane and talc content(AC+), respectively. Vice versa, silane/water crosslink reaction shows no significant induction on the impact values. Unnotched impact test results for the original sample are revealed that the parameters A+ and AB+ have significantly affect on this respond. On the other hand, the variable A+, ABC+, B- and C- have pronouncingly affected on cured samples. The wood flour(B+) and talc(C+) at high level of contents obviously increase the heat deflection temperature(HDT) for uncured WPC. Moreover, A+, B+, and C+, and the interaction of AB- give rise to higher HDT for post cured WPC. Finally ANOVA analysis found that melt flow index of wood composite is increased by reducing the flour content(B-). The regression model conclusion obtained from the statistical calculation is presented in table 4. The parameters seen in the equations are the significant variable by mean of ANOVA outcome. For example, in the notch impact strength of original sample equation is 1.07+0.04(A)+0.06(B)+0.075(AC) +0.04(AB). It is implied that maximize impact strength of WPC can be achieved if it is compounded in twin screw mixing and injected at 190°C by using silane(A+), wood (B+), interaction between silane and talc(AC+) and between silane and wood(AB+) at high level(= +1). The rest can be estimated as the identical manner.

Table 3. Result data of original and cured samples

Run	MFI g/10min	Flexural strength(MPa)		Flexural modulus(GPa)		Notched impact(kJ/m²)		Unnotched impact(kJ/m²)		HDT(°C)	
		original	cured	original	cured	original	cured	original	cured	original	cured
1	12.27	53.6	53.6	1.84	1.96	1.09	1.34	8.75	9.66	131	136
2	11.63	53.6	54.2	2.04	2.41	0.91	1.27	9.18	7.70	138	138
3	8.61	53.8	53.6	2.16	2.18	1.11	1.32	7.56	8.69	141	141
4	9.02	54.7	56.7	2.34	2.35	0.99	1.35	7.33	6.28	141	143
5	20.40	55.9	57.7	1.84	1.89	0.96	1.35	8.92	11.48	134	140
6	12.54	54.7	54.1	2.43	2.58	1.06	1.41	8.02	9.54	139	142
7	9.95	56.1	57.4	2.29	2.23	1.11	1.45	9.49	8.96	140	139
8	7.24	55.8	56.0	2.47	2.57	1.31	1.12	9.11	9.50	142	142

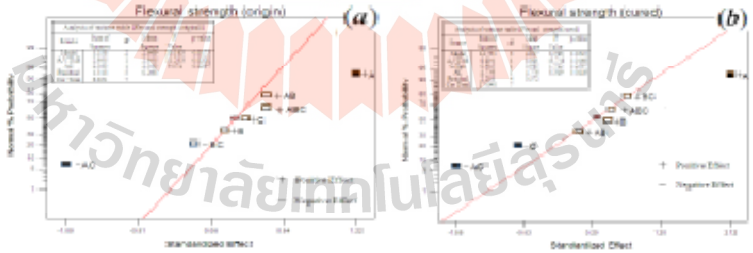

Figure 1. Normal probability and standardized effect plots of flexural strength;(*a*) original, (*b*) cured.

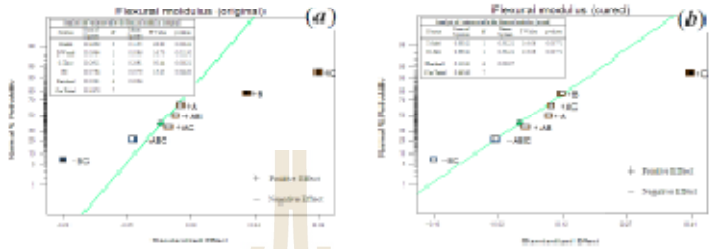

Figure 2. Normal probability and standardized effect plots of flexural modulus;(*a*) original, (*b*) cured.

Table 4. The predicted regression model for the properties of WPCs derived from ANOVA testing

Properties	Regressed models
Melt flow index	11.46-2.75(B)
Flexural strength(origin)	55.01+0.61(A)-0.55(AC)
Flexural modulus(origin)	2.21+0.11(B) +0.19(C)-0.098(BC)
Notch impact(origin)	1.07+0.04(A)+0.06(B)+0.075(AC)+0.04(AB)
Unnotch impact(origin)	8.52+0.37(A) +0.58(AB)
HDT(origin)	138.72+2.81(B)+1.81(C)
Flexural strength(cured)	55.20+1.12(A)-0.41(C)-0.83 (AC)
Flexural modulus(cured)	2.27+0.20(C)
Notch impact(cured)	No significant model
Unnotch impact(cured)	8.64+0.73(A)-0.53(B)-0.88(C)+0.46(ABC)
HDT(cured)	140.67+0.75(A)+1.17(B)+1.42(C)-1.08(AB)

B. Scanning electron microscopy(SEM)

SEM photographs by SEM of the fracture surface of wood polypropylene composites are shown in figure 3(a) -3(f). Figure 3(a) illustrates the surface of WPC before sauna cured and using lowest silane content. The picture shows poor adhesion between wood and matrix indicated by smooth fracture scare and evidence of fiber pull out from PP phase, respectively. Vice versa, figure 3(b), 3(d) and 3(f) are the sauna cured WPC sample with high silane levels(A+). The results evoke good adhesion between wood flour and PP phase. This observation can be supported by the value of impact test. They suggest that sauna treatment on WPC compounded using high silane level is achieved through silane/water macro crosslink reaction. Hence, the crosslink bridge between polymer matrix and wood flour could play the important role for enhance the surface interaction and bonding strength between matrix and reinforcement, accordingly. Increasing in silane content would increase the mechanical properties, especially toughness, of WPC. The SEM of run 8 show in figure 3(e) and 3(f) for original and sauna cured WPC, respectively. The sample was prepared by mixing the flour and talc at high levels and it is shown the relative superior in all properties. However, the test values are slightly declined after silane/water crosslinked. This can be explained that as increasing the fiber/filler loading, they tendency to be agglomerated. Also

as adhesion between the fiber/filler cluster particle increased through the silane/water reaction, the particle become too dense. Therefore, stress transfer from matrix to filler and flexibility of chain is inferior. As the result, the impact toughness is decreased [2].

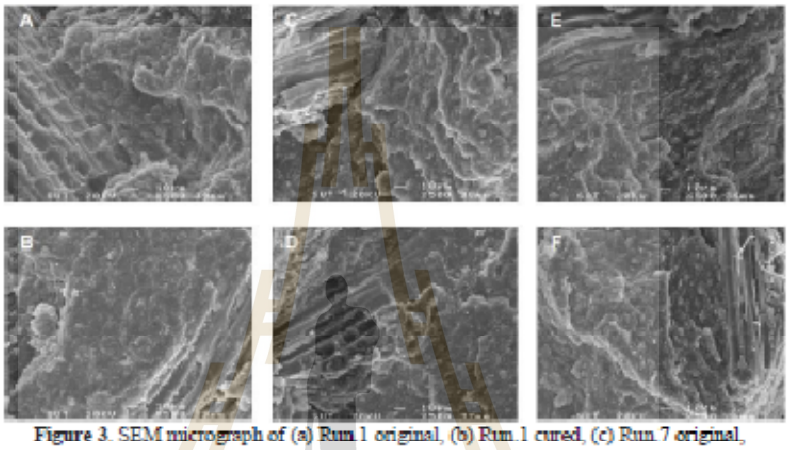

Figure 3. SEM micrograph of (a) Run.1 original, (b) Run.1 cured, (c) Run.7 original, (d) Run.7 cured (e) Run.8 original and (f) Run.8 cured(X500).

CONCLUSIONS

From the design of experiment approach to validate the optimal contents of WPC based on crosslinked PP, it was found that compounding of WPC at high level(+) of silane, wood flour and talc content produced the composite with generally good mechanical and thermal properties. Sauna cured via silane/water macro crosslinked reaction facilitated the interfacial adhesion between fibre and matrix and hence enhanced the mechanical properties. Further increased in the constituent portion will diminish the toughness of the sample as fibre/filler become aggregate into bigger particle and too dense. Moreover, incorporating the fibre/filler at high load gives rise to the lower in melt index that make the WPC difficult to flow during processing.

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18TH INTERNATIONAL CONFERENCE ON COMPOSITE MATERIALS

DESIGN OF EXPERIMENT: WOOD COMPOSITES BASED ON CROSSLINKED POLYPROPYLENE

A. Khongrit[1,2]*, U. Meekum[1,2]
[1] School of Polymer Engineering, Suranaree University of Technology, NakornRatchasima, Thailand
[2] Centre of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok, Thailand
*holly2frozen@hotmail.com

Keywords: *Wood polypropylene composites, Crosslinked polypropylene, Design of experiment, sauna treatment*

1 General Introduction

Wood Plastic composites (WPCs) market is going strongly around the world. It is used as substitute or alternative for the natural wood which it prohibited or legally controlled by some countries. The main matrix of WPC is thermoplastic polymers and reinforced with natural fibers. The most common matrices are PVC, PP and PE. The wood flour obtained from timber milling is commonly used. However, the commercially available wood composite has some incompetency such as mechanical properties. Therefore, the improvement of the properties is main interest by many researchers. The main techniques used for enriching the WPCs include grafting, cross linking, matrix blending, and reinforced with other filler [1-3]. In this work, WPC based on crosslinked polypropylene reinforced with wood flour was performed. The crosslinked structure of polymer would enhance the properties of material such as higher in heat resistant and UV-light. Accordingly, it will give rise to superior in dimensional stability, durability. The statistical approaches by mean of design of experimental (DOE) on the parameters that effect the properties of WPC will be the prime interests.

2 Experimental and sample preparation

The 2^3 factorial design of experiment, which k = 3, were silane(A), wood flour(B) and talc(C) contents. Each parameter was divided into two levels; high(+1) and low(-1), respectively. In each level, it is also split into two sub levels as shown in table 1. According to the parameters, the design matrix is constructed in table 2. Each row was assigned as compound ingredient for WPC. Dicumyl peroxide(DCP) was added into the formulation as free radical initiator. The measured responds were MFI, HDT, impacts and flexural properties. Eight runs of WPC having batch size corresponding to 300 g of PP was mixed and pelletised by co-rotation twin screw extruder at 190°C. Test specimens were injected at 180°C. The measured responds were classified into 2 conditions; original and cured. The originals were allowed the samples to anneal at room temperature for approx. a day. The later were achieved by sauna incubation at 105°C for 12 hrs. Sauna incubation was used to accelerate the completion of silane condensation/water crosslink reaction. The Design Expert™ was statistically used to analyze the results.

3 Result and discussion

The responds obtained from standard tests were summarized in table 3. The test values review that there are increasing in the figures by sauna incubation. Showing only flexural strength and analyzed by the design of experimental, the result of normal probability and the effects plot is shown in Fig 1(*a*) and 1(*b*), respectively. From the plot shows that silane(A) and the interaction between silane and talc(C) are and the greatest effect on the flexural strength of WPC with no sauna treatment. They are positive(+) and negative(-) effects on the strength, respectively. According to ANOVA testing at 95% of confidential confirms that those two effects are the significant on the flexural. For the cured sample by sauna incubation shown in fig 1(b), the similar consequences are observed. The wood flour(C) content is also the negative effect on the flexural property. The statistical conclusion by ANOVA examination are also manifested. The rest of the

responds were analyzed by ANOVA and the results are summarized in table 4. The SEM of fractured surfaces of WPC for Run 1 (all low levels) and Run 8(high levels) before and after post cured process are illustrated in fig. 2, respectively. It is obviously confirmed the improvement of surface adhesion between polymer matrix and wood fiber by sauna incubation. It indicates that the crosslink reaction through silane/water reaction could play the important role for enhance the surface interaction. Hence, increasing in silane content would increase the interfacial bonding and hence the mechanical properties, especially toughness.

4 Conclusion:

By using the DOE approach, the optimal formulation of WPC from crosslinked PP is accomplished. Silane has generally positive effect on the mechanical properties. It delivers the crosslink bridge between polymer matrix and wood fiber via silane/water reaction and enhances the adhesion of the composite. Consequently, the mechanical properties are improved.

Parameter	High level(+1)		Low level(-1)	
Silane(phr)	12	8	5	3
Wood Flour (phr)	45	35	25	15
Talc (phr)	40	30	20	10

Table 1. The parameter and level of DOE

Test	Silane(A) (phr)	Wood(B) (phr)	Talc(C) (phr)	DCP (phr)
1	8(-1)	25(-1)	20(-1)	0.3
2	5(-1)	15(-1)	40(+1)	0.3
3	12(+1)	45(+1)	40(+1)	0.3
4	5(-1)	35(+1)	30(+1)	0.3
5	8(+1)	15(-1)	10(-1)	0.3
6	12(+1)	25(-1)	40(+1)	0.3
7	8(+1)	35(+1)	20(-1)	0.3
8	12(+1)	45(+1)	30(+1)	0.3

Table 2. Factorial design matrix in terms of both actual and coded factor levels.

Run	Flexural strength(MPa)		Flexural modulus(GPa)		Notched impact(kJ/m²)		Unnotched impact(kJ/m²)		HDT(°C)	
	origin	cured	origin	cured	origin	cured	origin	cured	origin	cured
1	33.6	33.6	1.84	1.86	1.09	1.24	8.75	8.66	131	136
2	35.6	36.2	2.04	2.41	0.91	1.27	9.18	7.78	138	139
3	33.8	33.6	2.16	2.18	1.11	1.22	7.56	8.69	141	141
4	34.7	35.7	2.04	2.35	0.99	1.26	7.33	6.28	141	143
5	35.9	35.7	1.84	1.89	0.96	1.26	8.92	11.48	134	140
6	34.7	36.1	2.41	2.88	1.06	1.41	8.02	8.04	139	142
7	36.1	37.6	2.29	2.23	1.11	1.43	9.49	8.96	140	139
8	35.8	36.0	2.47	2.87	1.01	1.12	9.11	8.59	142	142

Table 3.Result data of original and cured samples

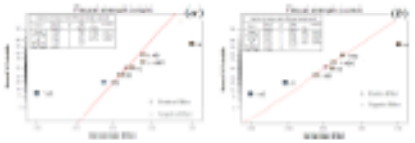

Fig 1. Normal probability plots of Flexural strength (*a*) original, (*b*) cured.

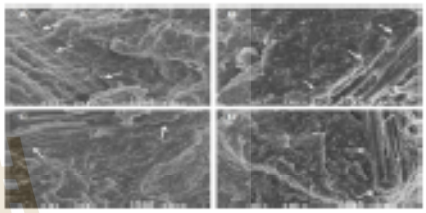

Fig.2. The SEM micrograph of (*a*) Run No.1 (origin), (*b*) Run No.1(cured), (*c*) Run No.8(origin) and (*d*) Run No.8(cured).

Test	Regressed models
MFI	11.46-2.75(B)
Flexure strength (origin)	55.01+0.61(A)-0.55(AC)
Flexure modulus (origin)	2.21+0.11(B)+0.19(C)-0.09B(BC)
Notch impact (origin)	1.07+0.04(A)+0.06(B)+0.07S(AC)+0.04(AB)
Unnotch impact (origin)	8.52+0.37(A)+0.58(AB)
HDT (origin)	138.52+2.81(B)+1.81(C)
Flexure strength (cured)	55.30+1.12(A)-0.61(C)-0.88 (AC)
Flexure modulus (cured)	2.27+0.20(C)
Notch impact (cured)	No significant model
Unnotch impact (cured)	8.64+0.75(A)-0.58(B-0.88(C)+0.46(ABC)
HDT (cured)	140.63+0.75(A)+1.13(B)+1.63(C)-1.08(AB)

Table 4. The predicted regression model for properties of WPCs derived from ANOVA testing

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BIOGRAPHY

Mr. Anuchit Khongrit was born on April 9, 1985 in Bangkok, Thailand. He earned his Bachelor's Degree in Industrials Engineering from Rajamangala University of Technology Isan (RMUTI) in 2010. During his bachelor's degree study, he presented papers, "*Cotton dying development process from the natural color*" at the IE Network Conference, Khon Kaen, Thailand. He then continued his Master's degree in Polymer Engineering at School of Polymer Engineering, Institute of Engineering at Suranaree University of Technology. During his master's degree study, he presented papers, "*Design of experiment: wood composite based on crosslinked polypropylene*" at the 2nd International Conference on Advances in Petrochemicals and Polymers, Bangkok, Thailand. And the 18th International Conference on Composite Materials, Jeju island, Korea in the same topic.