HIGH HEAT DISTORTION TEMPERATURE PP COMPOUND

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พอลิโพรพิลีนผสมที่มีค่าอุณหภูมิการบิดงอสูง

นายอนุชา คงฤทธิ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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HIGH HEAT DISTORTION TEMPERATURE PP COMPOUND

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

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อนุชา คงฤทธิ์ : พอลิโพรพิลีนผสมที่มีค่าอุณหภูมิการบิดงอสูง (HIGH HEAT DISTORTION TEMPERATURE PP COMPOUND) อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.อุทัย มีคำ, 178 หน้า.

พอลิโพรพิลีนผสมเป็นโครงสร้างร่างแหเมทริกซ์โดยเปอร์ออกไซด์/ไซเลนโดยวิธีการเชิงสถิติแบบการทดลองแบบพหุคูณ (2^K) จากการวิเคราะห์ทางสถิติพบว่าโฮโมพอลิโพรพิลีนให้ผลค่าอุณหภูมิการบิดงอและคุณสมบัติการรับแรงดัดในเชิงบวก ในทางตรงกันข้ามให้ค่าดัชนีการไหลลดลง การใช้ปริมาณโฮโมพอลิโพรพิลีนที่ปริมาณต่ำและพอลิโพรพิลีนชนิดโคพอลิเมอร์ปริมาณสูงทำให้ผลในเชิงบวกต่อค่าแรงต้านการตกกระแทก จากการสรุปโดยทางสถิติให้ข้อเสนอแนะว่าค่าดัชนีการไหล ค่าอุณหภูมิการบิดงอ คุณสมบัติการรับแรงดัดมีค่าสูง เมื่อใช้ปริมาณของโฮโมพอลิโพรพิลีนที่ระดับสูง

ผลกระทบของปริมาณไดคิวมิลเปอร์ออกไซด์ในปฏิกิริยาการเกิดโครงสร้างร่างแห และการศึกษาการผสมพอลิโพรพิลีนชนิดโคพอลิเมอร์ผสมกับโฮโมพอลิโพรพิลีน พอลีเอทธิลีนที่มีค่าน้ำหนักโมเลกุลสูงยิ่งยวด(UHMWPE) ถูกนำมาผสมเพื่อเพิ่มความเหนียวของพอลิโพรพิลีนผสม จากผลพบว่าพอลีเอทธิลีนที่มีค่าน้ำหนักโมเลกุลสูงยิ่งยวดไม่สามารถทำให้เกิดความเหนียวได้ การเพิ่มปริมาณของไดคิวมิลเปอร์ออกไซด์ทำให้คุณสมบัติลดลง ซึ่งปริมาณที่เหมาะสมคือ 0.1 ส่วน และหากปริมาณของพอลิโพรพิลีนชนิดโคพอลิเมอร์มีสัดส่วนเพิ่มมากขึ้นวัสดุจะมีความเปราะ

ตัวเติมและตัวเสริมแรงถูกนำมาใช้ยกระดับคุณสมบัติทางความร้อนและคุณสมบัติทางกลซึ่งพบว่าทาล์คัมสามารถยกระดับคุณสมบัติทั้งทางความร้อนและทางกลให้กับพอลิโพรพิลีนกับพอลีเอทธิลีนที่มีค่าน้ำหนักโมเลกุลสูงยิ่งยวดผสม ปริมาณของทาล์คัมที่ใช้คือ 20 ส่วน การศึกษาการผสมผสานของสารตัวเติมจากผงแกลบข้าวและเขม่าดำ ซึ่งผลค่าอุณหภูมิการบิดงอลดลงเมื่ออัตราส่วนน้ำหนักของเขม่าดำเพิ่มขึ้น เขม่าดำสามารถเพิ่มความต้านทานการแตกหักได้ แต่ทำให้ค่าอุณหภูมิการบิดงอลดลง ไฟเบอร์กลาสถูกใช้เป็นตัวเติมชนิดเสริมแรง จากผลแสดงให้เห็นว่าไฟเบอร์กลาสสามารถยกระดับคุณสมบัติทั้งทางความร้อนและทางกลได้ อย่างไรก็ตามเป้าหมายของค่าอุณหภูมิการบิดงอที่ 150 องศาเซลเซียส ไม่สามารถเป็นได้จากเทคนิคการผสมดังกล่าว

สาขาวิชา วิศวกรรมพอลิเมอร์ ลายมือชื่อนักศึกษา______________________
ปีการศึกษา 2555 ลายมือชื่ออาจารย์ที่ปรึกษา________________

ANUCHA KHONGRIT : HIGH HEAT DISTORTION TEMPERATURE PP COMPOUND. THESIS ADVISOR : ASST. PROF. UTAI MEEKUM, Ph.D., 178 PP.

DESIGN OF XPERIMENT/CROSSLINKED PP/PP COMPOUND/TALC/CB/RHA FIBRE GLASS REINFORECD PP AND HEAT DISTORTION TEMPERATURE

Polypropylenes(PPs) blends with addition of peroxide/silane induce condensation were studied by the design of experiment approach using the 2^k design method. The statistical results showed that homo type PP was positive effect on HDT and flexural properties. In contrast, homo type PP had negative effect on MFI. The lower of homo and high of block PP had the positive effect on the notched impact strength. The statistic conclusion suggested that the higher in MFI, HDT and flexural properties were attained when the high level of content of homo PP was employed.

Effect of DCP concentration in silane/peroxide crosslink system and also blending the homo PP with its block copolymer was also studied. For the sake of the bending toughness of the PP compound, the UHMWPE was used as toughener. The results found that the UHMWPE as toughener was ineffective. The property of the PP blends were decreased with increase content of DCP, the optimal of peroxide content was 0.1 phr. The material became more brittle with increasing the copolymer fraction.

The fillers and reinforcement were used to enhance thermal and mechanical properties. It found that talc enhanced the thermal and mechanical properties of the compound having PP/UHMWPE blend as matrix. The 20 phr of talc was used. Addition of the hybrid fillers derived from carbonized rice husk ash(RHA) and carbon black(CB) was studied. It resulted that the HDT decreased when the weight ratio of CB was increased. The carbon black fraction increased the fracture toughness but lower the HDT. The fiber glass was used as reinforcement. The result exhibited that the fiber glass enhanced the thermal and mechanical properties. However, the target value of HDT at 150°C has not been obtained by the above compound techniques.

School of Polymer Engineering Student’s Signature_____________

Academic Year 2012 Advisor’s Signature_____________

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Anucha Khongrit

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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

SYMBOLS AND ABBREVIATIONS (Continued)

kN = Kilonewton

mm = Milliliter

mm/min = Milliliter per Minute

min = Minute

m^2/g = Square meter per gram

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 Basic Background

Polymer is large molecules composed of repeating units and having very high molecular weight. It normally consists of hundreds, thousands, or even millions of repeating unit of monomer joined together, typically by covalent bond, to form the macro chain. The detail fundamental of polymer characteristics are being discussed as follow;

1.1.1 Chain Structure of polymers

1.1.1.1 Homo polymer

A homo polymer contains only a single type of repeat unit, or derived from a monomer, on chain connected to from the linear homo polymer. The common different possible within the homo polymer chain is spatial arrangements or so call stereo tacticity. Typically, there are three types of the chain tacticity; isotactic, syndiotactic and atactic. Isotactic polymer is composed of isotactic macromolecules. In isotactic macromolecules, all the substituent(**R**) is located on the same side of the macromolecular backbone. In syndiotactic or syntactic macromolecules, the substituent has alternate positions along the polymer chain. Finally, in the atactic macromolecules, the substituent of the repeated unit is placed randomly along the polymer chain. The structural tacticities are illustrated in Figure 1.1

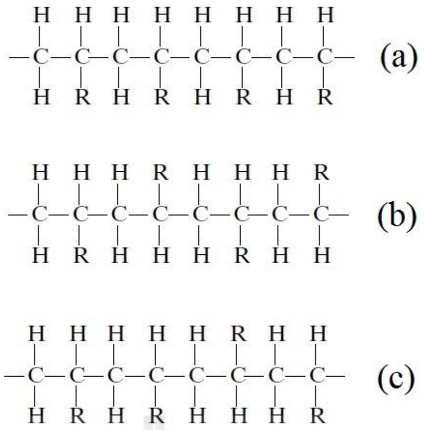


Figure 1.1 Tacticity of the polymer, (a) isotactic, (b) syndiotactic and (c) atactic

1.1.1.2 Block copolymers

Copolymer means the chain structure constructed from two or more monomer repeating units. Block copolymer is one type of copolymer chains. It contains a linear arrangement of the monomer blocks which commonly combines from two or more blocks. For example of the di-block copolymer is shown in Figure 1.2

-A-A-A-A-A-B-B-B-B-B-

Figure 1.2 Structure of the di-block copolymer

The blocks are linked as tail to head. Since the individual blocks are usually long enough to be considered as polymers in their own right. It typically manifests its own characteristic on the blocks chain. Block copolymer is generally used as chain compatibilizer in the blend or it is added into homo polymer to modify the properties that is specifically needed. For example, higher impact strength polypropylene/ethylene copolymer is blended with homo PP. The copolymer chain acts as impact modified rubber phase within the continuous homo polymer phase. The blend is commercially called as copolymer type polypropylene.

1.1.1.3 Random copolymers

A random copolymer is a statistically scattered of the second monomer on the copolymer chain. Therefore, it is sometime called statistical copolymer. Outstanding characteristic of the random polymer is similar to those block copolymer. But, in the PP analogous, it gives the superior optical properties; glossy, clarity and brightness. The schematic arrangement of monomers in random polymer is given in Figure 1.3

-A-A-B-A-B-A-B-B-A-A-

Figure 1.3 Structure of random polymers

1.1.1.4 Grafted copolymers

A grafted copolymer comprises of backbone species, poly A, and a side-chain species or grafted chain, poly B. Combination of two or more chains of constitutionally or configurationally different features, one of which serves as a backbone main chain, and at least one of which is bonded at some point(s) along the backbone and it is constituted as side chain. The side chain(s) comprises of the units of monomers that differ from the backbone chain. However, if the two monomers in backbone and side chains are the same, the polymer is said to be branched homo polymer. Grafted copolymer is typically used as impact resistant materials and also the compatibilizers for the preparation of stable blend or alloy polymeric materials. It is also used in the manufacturing the thermoplastic elastomers (TPEs) and primer for coatings and adhesives. The structure of grafted copolymer chain is shown in Figure 1.4.

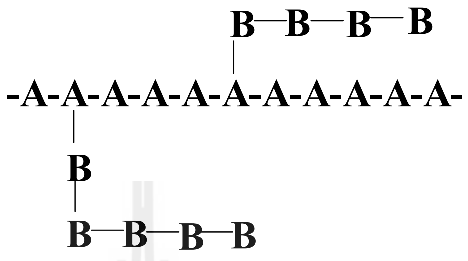


Figure 1.4 Structure of grafted polymers

1.1.1.5 Branch chain polymer

Branch chain polymer consists of main macromolecule backbone having a number of side chains or branches attached along the main chain. Main long chains comprise of the identical repeat units as the side chain(s). Properties of branch polymer depend on number of branch chains and also the length of side chains. For the longer branch chain, it is normally very flexible. It could be used in applications such as plastic films. The most common example of branch polymer having long side chain is low density polyethylene (LDPE). And for the shorter branch chain, it is quite rigid and stiff. Sometimes, it could be used as the structural engineer. High density polyethylene (HDPE) is the most common example of short chain branch polymer. Structure of branch polymer show as Figure 1.5

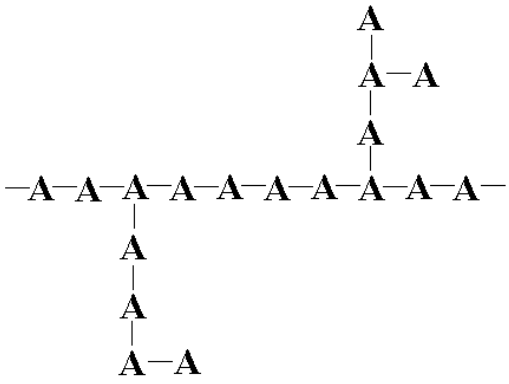


Figure 1.5 Structure of branch polymers

1.1.2 Polymeric materials and modifications

1.1.2.1 Polymeric materials

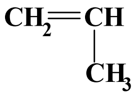
Polymeric material is a wide range of synthetic or semi-synthetic organic solids that is typically used for the manufacturing of industrial products. As polymeric material is typically high molecular mass, and may contain other external substances to improve performance and/or reduce production costs. Monomers of polymer are either natural or synthetic organic compounds. There are two types of polymeric materials; thermoplastics and thermosetting polymers. Thermoplastics are the polymer that does not undergo chemical change in their composition when heated and can be repeatedly molded without the significantly deteriorate in the properties. Examples of thermoplastics are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polytetrafluoroethylene (PTFE). But thermosets or thermosetting, once they are formed and shaped into the final product, they cannot be molten by heat or any mean. They would stay in the solid form. The final chain structures of the thermosets are network like. The common thermosets polymers are melamine, epoxy, unsaturated polyester and vulcanized rubber.

1.1.2.2 Polymer blends and compounds

The polymer compound has been the major contributor in the development of new formulations for the polymeric material. A virtually endless array of additives, modifiers, colorants, fillers, and reinforcements permits polymer resin suppliers to impart specific properties of the basic polymers resulting in the expanding opportunities for new applications and cost reductions. Compounding relies on polymer chemistry to combine base polymer with modifiers, additives, fillers, reinforcements, and other polymers to create new compounds or alloys polymer. Compounded polymers can offer better performance, greater strength and smoother processing at a competitive cost.

1.2 Polypropylene and Properties Enhancement

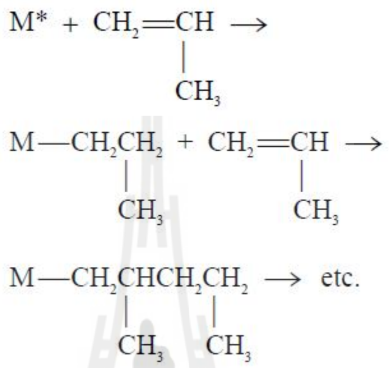
Polypropylene (PP) is a thermoplastic polymer. It is one of the polyolefin type polymers. PP is prepared from polymerization of propylene monomer (Figure 1.6) to form large molecule. Typically, propylene is reacted with organometallic, transition metal catalyst, to provide a site for the reaction to occur, and then propylene molecules are added sequentially through a reaction between metallic functional group on the growing polymer chain and unsaturated bound of propylene monomer.



$$CH_2{=}CH(CH_3)$$

Figure 1.6 Propylene monomer

One of the double bond carbon atoms of the incoming propylene molecule inserts itself into the bond between the metal catalyst and the last carbon atom of the polypropylene chain. The linear polymer chain of carbon atoms is formed with methyl groups (CH_3) attached to every other carbon of chain shown in figure 1.7.



$$M^* + CH_2{=}\underset{CH_3}{\underset{|}{CH}} \rightarrow$$

$$M{-}CH_2\underset{CH_3}{\underset{|}{CH_2}} + CH_2{=}\underset{CH_3}{\underset{|}{CH}} \rightarrow$$

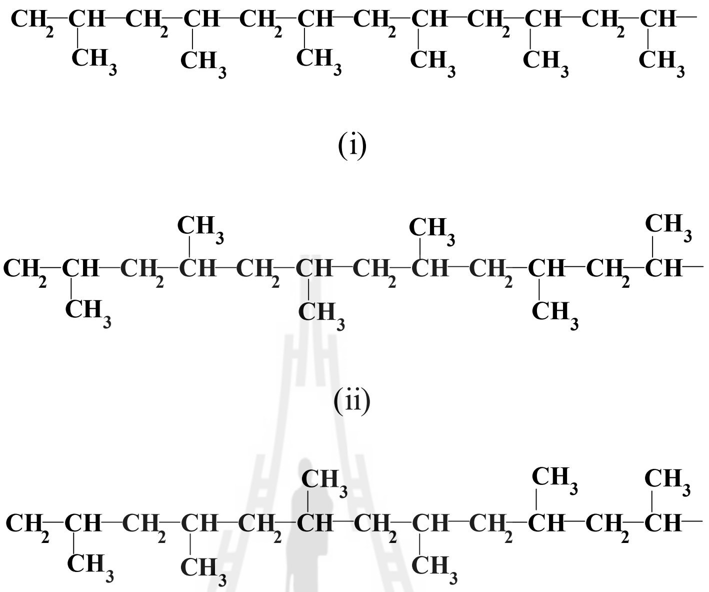
$$M{-}CH_2\underset{CH_3}{\underset{|}{CH}}CH_2\underset{CH_3}{\underset{|}{CH_2}} \rightarrow \text{etc.}$$

Figure 1.7 Polymerization reaction propylene monomers

In polypropylene polymerization, catalysts are organometallic transition metal complexes. They provide active sites or polymerization sites where the polymerization reaction occurs, by holding the growing polymer chain and the propylene monomer in close proximity to each other so that they can react. With commercial catalysts, a high yield of stereospecific polypropylene is produced. Ziegler-Natta catalysts is a complex of transition metal halides, usually titanium trichloride ($TiCl_3$), with an organometallic compound, typically triethylaluminum, as cocatalyst to initiate the polymerization. Afterward heterogeneous Ziegler-Natta catalysts were developed with magnesium chloride ($MgCl_2$) used as the inert support material. Zeigler-Natta catalysts are multi-sited catalysts, containing several reactive sites. As a result, the polypropylene produced can include polymer molecules with a broad range of molecular weights and some branching off from the main polymer chain. For film and fiber applications and for injection molding of thin walls or parts with intricate structures, a narrower molecular weight distribution and increased melt flow rate may be required. For these applications, the polypropylene produced must be chemically or thermally broken down in post-reactor extrusion.

Metallocene catalysts have recently been developed for industrial used, and metallocene produced polypropylene is now available. Metallocenes are organometallic compounds with a sandwich-like spatial arrangement, consisting of a transition metal; such as iron, titanium and zirconium, situated between two cyclic organic compounds. Current metallocene catalyst systems commonly used is the zirconium chloride ($ZrCl_2$) as the transition metal complex, with a cyclopendadiene as the organic compound and an aluminoxane as cocatalyst. Polypropylenes made using metallocene catalysts exhibit superior in rigidity and transparency, higher heat distortion temperatures, improved impact strength and toughness even at subambient temperatures, and low extractable traces (Maier, C. and Calafut, T., 1998)

Polypropylene can be (i) isotactic, (ii) syndiotactic and (iii) atactic as indicated in Figure 1.8. It is depended on the orientation of methyl groups. In isotactic polypropylene is the most common commercial form. The methyl groups are all in same side of polymer chain. In syndiotactic PP, methyl groups are alternate on opposite sides of the polymer backbone. Atactic polypropylene, methyl groups are randomly orientated with respect to the polymer backbone. The average molecular weight of polypropylene is generally ranges from 220,000–700,000 g/mol. It is long chain lengths result in a higher molecular weight for the polymer. The isotactic form shows high degree of crystallinity, because the structure of the isotactic has the highest crystallinity resulting in good mechanical properties such as stiffness and tensile strength.



$CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-$

(i)

$CH_2-\underset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-$

(ii)

$CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-CH_2-\overset{CH_3}{CH}-$

(iii)

Figure 1.8 Stereo chemical configurations of polypropylene; (i) isotactic PP, (ii) syndiotactic PP and (iii) atactic PP.

For syndiotactic polypropylene, it is less in stiffness than isotactic but better in impact strength and clarity. Because of the irregular structure, the atactic form has low crystallinity, resulting in the rubber like and amorphous material. Increasing the amount of atactic polypropylene in a predominantly isotactic formulation will increase the room temperature impact resistance and stretch ability but decreases the stiffness, haze, and color quality (Maier, C. and Calafut, T., 1998).

Outstanding characteristics of polypropylene are generally higher in tensile, flexural, and compressive strength and higher in modulus than polyethylenes. It is caused by the steric interaction of the methyl groups, which result in a more rigid and stiff polymer chain than in polyethylene. Polypropylenes manufactured from metallocene catalysts exhibit excellent rigidity and transparency, higher heat distortion temperatures, improved impact strength and toughness. Because the metallocene catalyzed PP has a very narrow molecular weight distribution compared to conventional polypropylene (Maier, C. and Calafut, T., 1998).

Polypropylene is widely used in many sectors of industry because it is easy to process, light weight, high strength, and low price. It various applications used such as packing and automotive parts. However, some of its properties still need to be improved. There are several approaches to improve the drawback properties of PP that includes; blending, compounding with filler and/or additives, and crosslinking. Blending is the most common routine to combine outstanding properties of the two or more polymers together. The blending with thermoplastics such as polyethylene is of great interest as it does not significant lowers its tensile strength. PP/Ultra high molecular weight polyethylene (UHMWPE) blended has unique properties such as high impact strength, high wear strength, high abrasion resistance, as well as lightweight. Blending with copolymer to meet specific needs or improve properties. The fillers are important roles to modify the properties of polymers and beneficial in reducing the unit cost of the material. In general polymer industries, packaging materials, household, automotive parts, there are many type of fillers used, such as calcium carbonate, carbon black, fibrous and talc. They have generally been used to enhance the mechanical properties of polymers. For the crosslinked PP, it is normally used to improve the environmental degradation, especially the UV-resistance. The common commercially applications of the crosslinked PP is packaging, container, automotive interior/exterior part.

In this research work, improvement of thermal properties, especially service temperature, by mean of heat distortion temperature (HDT) is the prime interest. Blending, compounding and crosslinking were attempted to succeed the research goal.

1.3 Research objectives

The main objectives of this research study to improve the thermal properties of the polypropylene include;

(i) To verify the main effect of homo and copolymer types PP on the thermal properties of the PPs blends in the present of silane/peroxide crosslink system.

(ii) To investigate the effect of fillers for enhancing the HDT of the PP compound.

1.4 Scope and limitation of the study

In this work, the PP compound having the HDT higher than 150^{o}C was the prime target. It would be used for the oil cooking grade microwave ware and others appropriate high temperature applications. The blend of three typical PP molecular architectures namely, homo polymer, block and random copolymers was statistically investigated by the 2^{k} design of experimental approach. The peroxide/silane crosslink system using dicumyl peroxide (DCP) and vinyl trimethoxyl silane (VTMS) was supplementary employed. The compounding of the PP blends with the various fillers such as talc, low carbon rice husk ash, carbon black and glass fiber, were attempted to reach the main goal, HDT higher than 150°C. The blending and compounding processes was performed by the continuous process through the twin screw extruder. Not only the HDT testing was analyzed but also the retaining the decent mechanical properties by mean of tensile, flexural and impact testing, and process ability of the materials by melt flow rate was closely monitored. The test specimens were prepared by injection molding. The standardized testing methods were followed. Morphological of the blends and compounds were also observed by scanning electron microscopy (SEM).

1.5 References

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CHAPTER II

LITERATURE REVIEW

2.1 Poly(propylene) Blends

A polymeric alloy has been increasing interest because blending is an important route for preparation of materials with synergistic and tailored properties. Developments of polymer blends have been mainly focused on two component systems such systems typically have a matrix and dispersed morphology (Hemmati, M. 2001). Blending of different plastic resins has long been practiced in the manufacturing industry for various reasons including: (i) tailor made blends to meet specific processing and performance requirements that cannot be satisfied by a single component; (ii) blending of polymers can be used in the field of recycling post consumer wastes to upgrade their properties, (iii) scientific interests; and (iv) financial incentives (Hamid, A. and Mourad I. 2010).

2.1.1 Polymer blends of PP

Abdel H. and the team (2009) studies isotactic polypropylene (iPP) blended with very low-density polyethylene (v-LDPE). The main objectives of investigating are impact, thermal aging/treatment. Samples of PE/PP blends containing 100/00, 75/25, 50/50, 25/75 and 0/100 wt% were prepared via injection molding technique. The tensile measurements indicated that the yield strength and the modulus decreased with increasing the PE content. The strain to break for pure PE was found to be much higher than that for pure PP and for their blends the intermediate values were observed. The hardness measurements also revealed that increasing in the PE content in PE/PP blends reduced the hardness value of PP.

Team of Wang, X. (1995) studied the blend systems based on polypropylene(PP) and ultrahigh molecular weight polyethylene (UHMWPE). The mechanical evaluation demonstrated that the synchronous toughening and reinforcing effects was achieved from the combination of the PP and the UHMWPE. In which the toughness and the tensile properties was improved with increasing the UHMWPE content.

Jose, S. and his workers(2004) published the different in the compositions of blends between isotactic polypropylene (iPP) and high density polyethylene (HDPE) blends containing 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10 wt.%. The observed young’s modulus with the compositions showed a positive synergism with maximum corresponding to 80% PP. The notched Izod impact strength upon composition of the blends indicated that higher amount of HDPE increased the impact strength.

Dı´az, M.F. et al. (2009) investigated the effect of the in situ compatibilization on the mechanical properties of PP/PS blends. Styrene/AlCl3 was used as catalyst system. The graft copolymer (PP-g-PS) formed at the interphase showed relatively high emulsifying strength. Scission reactions, occurring in parallel with grafting, were verified for PP and PS at high catalyst concentration, but no crosslinking reactions were detected. The tensile strength did not change with the catalyst concentration. The in situ compatibilized blends showed considerable improvement in mechanical properties, but were adversely affected by chain scissions at high catalyst contents.

Zhang, X. and co-workers (2005) reported the effect of interfacial adhesion on the impact strength of the immiscible PP/PET-g blends compatibilized with triblock copolymers. It was used to enhance the properties and lower the cost of polypropylene (PP). The ratio of PP to PET-g was fixed at 70/30 and compatibilized, namely, with styrene–ethylene/butylene–styrene (SEBS), styrene–butadiene–styrene (SBS) and styrene–isoprene–styrene (SIS). The addition of SIS caused a considerable increase in the impact toughness, but only slightly improved toughness was observed for blends compatibilized with SEBS. The effect of SBS on improving the impact toughness lied in between that of SIS and SEBS.

Bertin, S. and Robin, J-J. (2002) reported the recycling of mixed plastic wastes composed of low density polyethylene (LDPE) matrix and polypropylene(PP). Blends of virgin polymers have been prepared to compare the mechanical properties of both virgin and regenerated materials. By adding compatibilizing agents such as ethylene–propylene–diene monomer(EPDM), ethylene–propylene monomer, or PE-g-(2-methyl-1,3-butadiene) graft copolymer, the elongation at break and impact strength were improved for all blends. The effect of these various copolymers was quite different and was in relation with their chemical structure. The recycled blends exhibited suitable properties leading to applications that require good mechanical properties.

2.1.2 Polymer and rubber blends of PP

Polypropylene based blends containing waste tire dust (WTD) with trans-polyoctylene rubber (TOR) and dynamic vulcanization was investigated by Awang, M., Ismail H. and Hazizan, M.A. (2007). The results indicated that the incorporation of TOR and dynamic vulcanization improved the tensile properties of

PP/WTD blends. Chemical and oil resistance of the PP/WTD blends with TOR and dynamic vulcanization was also enhanced.

Ismail, H. (2002) studied the thermoplastic elastomers based on polypropylene/natural rubber (PP/NR) and polypropylene/recycle rubber (PP/RR) blends. They used fine rubber powder obtained from the sanding process of polishing rubber balls and artificial eggs. Polypropylene/recycled rubber blends was prepared. The results indicated that at similar rubber content, PP/RR blends offered higher, tensile strength and Young’s modulus but lower elongation at break and stabilization torque than PP/NR blends.

Van der wal, A. and co-worker (1999) studied the effect of the rubber content on the deformation and impact behaviour of polypropylene/EPDM rubber blends. The rubber content ranged from 0 to 40 % by volume were investigated. The results showed that tensile modulus and the yield stress linearly decreased with increasing the rubber content. The impact strength at low temperatures was relatively low and the fracture was brittle. At high temperatures, the impact strength was very high and the fracture was ductile.

Ma, L. F. and the research team (2012) studied toughening of polyamide 6 (PA-6) with the b-nucleated thermoplastic vulcanizates (TPVs) based on polypropylene (PP)/ethylene–propylene–diene rubber grafted with maleic anhydride (EPDM-g-MAH) blends. A series of TPVs without and with different dosage of b-nucleating agent (b-NA) were prepared and used to toughen PA-6 at the same proportion. The PA-6 blends toughened with b-nucleated TPVs (b-TPVs) exhibited significantly enhanced the toughness, balanced mechanical properties and thermal properties compared with PA-6 toughened by TPV without b-NA or only by EPDM-g-MAH.

Rheological properties of the maleated natural rubber/polypropylene (MNR/PP) blends with phenolic modified polypropylene(Ph-PP) and polypropylene-g-maleic anhydride (PP-g-MA) compatibilizers were investigated by Charoen, N. and co-worker(2006). The 60/40 MNR/PP blends were later prepared by a melt mixing process using PP-g-MA and Ph-PP at various loading levels of 3, 5, 10, 15 and 20 wt % of PP. They found that the apparent shear stress and shear viscosity increased with an increase in apparent shear rate over a range of loading levels of compatibilizers of 0–5%. Increasing loading level of compatibilizers higher than 5 wt% caused a decreasing trend of the flow properties.

2.2 PP Compounds

The compounding process has been the major contributor in the development of new formulations for the plastics industry. A virtually endless array of additives, modifiers, colorants, fillers, and reinforcements permits resin suppliers to impart specific properties to the basic polymers, resulting in expanding opportunities for new applications and cost reductions. Fillers and reinforcements are commonly used to improve the mechanical properties, temperature resistance, environmental resistance, and to reduce the cost of the plastic materials (Campo, E.A., 2008).

Virgin polymer is mean polymer pellet without any additive or filler added. Sometimes, a few stabilizers such as UV-stabilizer or thermal/processing stabilizer are allowed in the virgin polymer. Filler in polymer industrial aim to reduce the product cost or sometime improve mechanical properties, heat resistance and hardness. The filler can be categorized as inorganic and organic. In terms of inorganic fillers such as silica, calcium carbonate (CC) and talc are also the main materials used in PP compounds. At the present global warming crisis, the organic fiber, or natural fiber, is most important resources for polymer/fiber composites. Several academic research attempts to establish the technologies to produce the polymer/natural fiber composite for the industrial applications. However, very few works have been adopted or scale up for the commercial manufacturing.

2.2.1 PP and organic fillers

Carbon black (CB) is a material produced by the incomplete combustion of heavy petroleum products such as FCC tar, coal tar, ethylene cracking tar, and a small amount from vegetable oil. The use of CB as a filler in thermoplastic polymers is not only limited to use as a pigment but it is also used to prolong the life time of plastics used for outdoor purposes. This is due to the features which can be found in modified materials and generally seen in composite materials with CB filler.

Chiu, H.-T. and Chiu, W.-M. (2009) studied the effect of carbon black (CB) as filler on mechanical properties of filled isotactic polypropylene (iPP) and propylene-ethylene block copolymer (Co-PP). The mixing of appropriate amounts of the two components were melt blended in a twin screw extruder. The blended pellets were used to prepare a series of test specimens by injection molding. The blending of CB in Co-PP improved the impact strength, and also improves the flexural modulus and tensile strength; however, the heat distortion temperature (HDT) of the Co-PP/CB blends was decreased with greater filler content. Furthermore, the filler of CB improved the tensile yield strength only at low filler content of iPP/CB blends, and the heat distortion temperature(HDT) and flexural modulus of the iPP/CB blends increased with greater filler content.

Qi, D. and co-worker (2008) presented the blend between phenolic rigid organic filler/isotactic polypropylene. The influence of phenolic particles on the tensile properties of the micro composites was studied by uniaxial tensile test. They found that the Young's modulus of the blend specimens increased with filler content, while the yield and break of the specimens were related to the filler particles size. The yield stress, the breaking stress and the ultimate elongation of the specimens were close to those of unfilled iPP.

Zhu, S. and team (2011) studied the modified montmorillonite polypropylene nano composites. The montmorillonite/polypropylene (Mt/PP) nano composites were prepared by a melt blending technique using different contents of modified Mt with and without maleic anhydride grafted polypropylene (PP-g). The mechanical properties of Mt/PP nano composites were improved significantly. The modified Mt in a PP matrix led to a significant reduction of melt viscosity and enhancement in the Izod notched impact strength. The Izod notched impact strength and elongation at break of Mt/PP nano composites were 1.95 and 2.77 times as high as those of pure PP. The tensile strength of Mt/PP nano composites was also improved in the presence of PP-g, the same as the elongation at break.

2.2.2 PP and inorganic fillers

Lapcik Jr, L. et al. (2009) studied the effect of talc filler on the physic chemical and mechanical properties of the filled polypropylene matrix. A range of mechanical properties were measured on tensile test, bending test, fracture toughness and notched impact strength. It was found that increasing talc content lead to a concomitant increase mechanical strength and toughness.

Abu Bakar, M.B. and team (2006) studied the mechanical, flow and morphological properties of talc and kaolin filled copolymer polypropylene hybrid composites. PP copolymer and filler was compounded in twin screw extruder. The result illustrated that most of the hybrid composites showed a significant decrease in flow, tensile, flexural, and impact properties compared with the single filler of filled PP composites. This hybrid formulation from 20 wt% of talc and 10 wt% of kaolin had given an economically advantageous material with the mechanical properties; tensile, flexural and impact, comparable to those of the talc filled PP composites.

Wang, T. and co-worker (2007) investigated an alternative method to modify talc for use in the fabrication of composites of polypropylene (PP) and talc. Grinding pulverization was employed to prepare talc fillers; referred to hereafter as *p*-talc. The properties of the composites made with *p*-talc compared favorably with composites made with *p*-talc that was further treated with a silane coupling agent; referred to as *s*-talc. The mechanical properties, dynamic modulus, tensile strength, and impact resistance of the PP/*p*-talc composites were very similar to the PP/*s*-talc composites. The modification of talc by grinding was thus a highly effective alternative method to prepare PP/talc composites that did not required the chemical treatment.

Wu, C.L. et al (2005) presented the mechanical performance of nano silica/polypropylene composites, effects of particle surface treatment, matrix ductility and particle species on mechanical performance of the composites. The results indicated that graft polymerization onto the precipitated nano silica was still an effective method to pretreat the particles, which led to an overall improvement of the composites properties. In addition to the grafting polymers covalently attached to the nanoparticles, matrix ductility and nanoparticles size were important factors that influence the extent of performance enhancement of the composites.

2.2.3 PP and fibrous materials

In general, high fiber content is required in order to achieve a high performance of fiber reinforced polymer. Therefore, the effect of fiber content on the mechanical properties of fiber reinforced polymer is of particular interest and significance to the material science. It is often observed that the increase in fiber content leads to the increase in the strength and modulus and also in the toughness if the matrix has a low toughness (Fu, S.-Y. 2000).

2.2.3.1 Synthetic fibers

Lee, N. J. and Jang, J. (1999) published their work on the effect of fiber content on the mechanical properties of glass fiber mat/polypropylene composites. Glass fiber mat was prepared by the fiber mat manufacturing machine developed in laboratory. The tensile and flexural modulus increased with the increment of glass fiber content. However, the tensile and flexural strengths exhibited maximum values and showed a decreasing at the higher glass fiber content. The impact absorption energy also exhibited a similar result with the tensile and flexural properties.

The influence of fiber length and concentration on the properties of glass fiber reinforced polypropylene was investigated by Thomason, J.L. (2002). He presented the results of a step by step comparison of the mechanical performance of injection molded ‘long’ (LF-PP) and ‘short’ (SF-PP) glass fiber polypropylene compounds. The comparison of these the systems had been made over the 0 – 40 wt% of fiber content range. At the same fiber diameter and fiber content LF-PP gave the significant improvements in room temperature tensile and flexural strength, notched and unnotched impact resistance. The improvement in impact resistance was also higher at lower test temperature. LF-PP also gave the increasingly higher modulus over SF-PP as the strain was increased. The effect of lowering the fiber diameter in SF-PP had been shown to increase both strength and the unnotched impact. But not to the levels obtained with LF-PP at higher fiber diameter. Notched impact and modulus of SF-PP were relatively unaffected by reduction of the fiber diameter.

Akonda, M.H. and co-worker (2012) worked on the recycled carbon fibre reinforced polypropylene thermoplastic composites. The carbon fiber (CF)/polypropylene (PP) were produced from chopped recycled carbon fibers (reCF). Thermoplastic composite test specimens fabricated from the wrap spun yarns having 15 – 27.7 % of reCF volume content. The average values obtained for tensile, and flexural strengths were 160 MPa and 154 MPa, respectively for composite specimens containing 27.7 % reCF.

2.2.3.2 Natural fiber

La Mantia, F. P. and co-workers (2004) investigated the processing and mechanical properties of organic fiber/polypropylene composites. The organic fibers came from natural sources, wood, kenaf, and sago. They were used to compare with short glass fibers, as widely used inorganic filler. The organic fibers caused the enhancements in the rigidity and thermo mechanical resistance of the matrix in a way that was rather similar to the one observed for the inorganic filler.

The reduction in impact strength was observed for both types of fillers. The use of an adhesion promoter could improve their behavior.

Mohd. Ishak, Z.A. et al.(2001) studied the effect of the fiber volume fraction on the tensile behavior of injection molded rice husk filled polypropylene (RH–PP) composites. It was found that the diffusion coefficient and the maximum moisture content were depended on the filler volume fraction and the immersion temperatures. Incorporation of RH into the PP matrix had led to a significant improvement in the tensile modulus and a moderate improvement in the tensile strength.

Khalid, M. and co-worker (2008) published the comparative study of polypropylene composites reinforced with oil palm empty fruit bunch fiber and oil palm derived cellulose. The cellulose was derived from oil palm empty fruit bunch fiber (EFBF). The cellulose is potentially attractive thermoplastic filler compared to traditional oil palm fibers filled polypropylene. The tensile strength and flexural modulus of cellulose is higher than the EFBF composite. The PP filled cellulose composite gave better results in comparison with PP-EFBF composite.

Flexural and impact properties of oil palm empty fruit bunch (EFB)/polypropylene composites, the effect of maleicanhydride chemical modification of EFB was studied by Rozman, H.D. and team (2003). EFB filler was chemically modified with maleic anhydride (MAH). The composites with MAH-treated EFB showed higher flexural and impact strength than those with untreated EFB. The modification had significantly improved the flexural modulus and toughness of the composites.

Kim, S. J. and co-workers (2008) investigated the mechanical properties of polypropylene/natural fiber composites, comparison of wood fiber and cotton fiber. The tensile strength of the PP/wood fiber composites decreases with increasing wt % of the wood fibers, whereas that of the PP/cotton fiber composites displays different behavior. With the addition of 10 wt % of cotton fiber, the tensile strength was decreased. But with the addition of 20 and 30 wt % cotton fiber, it increased the strength because of the entanglement of the cotton fibers.

Preparation and characterization of polypropylene wheat straw clay composites was investigated by Reddy, C.R. and team (2010). The composite samples were prepared through melt blending method using a co-rotating twin-screw extruder. The composition of constituents of hybrid composite such as percentages of wheat straw, clay and maleic anhydride grafted polypropylene as a coupling agent was varied in order to investigate their influence on flexural properties. The increase in PP-MA coupling agent also increased the flexural modulus. The addition of clay as additional filler had no significant role on flexural properties of the composite.

Nano SiO_2 filled rice husk/polypropylene composites on physical and mechanical properties was investigate by Nourbakhsh, A. and co-worker (2011). The reinforcing effect of hybrid filler including rice husk (RH), beech bark(BB) and nano SiO_2, in polypropylene were studied. In the sample preparation, four levels of filler loading; the used waste of the lignocellulosic materials(55 – 58 wt.%) and nano SiO_2 (0 – 4 wt.%) were manufactured. The results showed that while flexural properties and elongation at break were moderately improved by the increasing in the amount of filler in the matrix. However, tensile and Izod impact strengths decreased dramatically. But, the composites showed the acceptable mechanical strength levels. The mechanical properties of composites filled with RH were generally greater than the BB composites. Nano SiO_2 addition showed little positive effect on the mechanical properties. It concluded from this study that the used waste lignocellulosic materials were attractive reinforcements from the standpoint of their physic mechanical properties.

2.3 Crosslinked Polyolefins

Polyolefins are the largest volume family of commercially important high-tonnage thermoplastic polymers. Crosslinking of polyolefin such as high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP) can improve their high temperature properties and extend their applications. Radiation crosslinking, peroxide crosslinking, silane crosslinking and peroxide/silane crosslinking are the four main manners of crosslinking that is industrially employed. The detail of the networking formations are discussed as following.

2.3.1 Radiation induce crosslink

Radiation crosslink is typically carried out on products produced by conventional processors. The crosslink step is affected by high energy radiation; electron beams or gamma rays. The crosslink technique produced free radicals by radiation. This method uses high energy radiation to achieve crosslink. After which, the product is subjected to radiation. The hydrogen atoms originally present in the molecules of chain are “knocked off” from the carbon atom by the high energy radiation, leaving behind a free radical on the polymeric chain. This generated free radical is unstable and will seek for another free radical carbon adjacent to it to form a stable covalent bond. As the irradiation progress, bonds are formed. Hence, crosslink structure is created (Hashim, S. 2003).

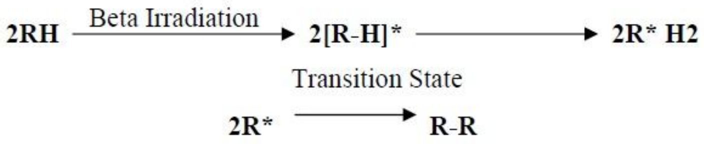

Figure 2.1 Beta irradiation crosslink techniques (Hashim, S. 2003).

Matjaz D, et al. (2003) researched on the effects of talc and low dose gramma irradiation on mechanical properties and morphology of iPP and iPP/talc composites. Gramma irradiation from Co-60 panoramic radiation source, irradiation induced the chain scission and crosslink. The iPP and iPP/talc composites were characterized by tensile testing, measurements of notched impact strength and scanning electron microscopy. The role of untreated talc or talc surface treated with aminosilanes as well as the influence of g irradiation on mechanical properties and the morphology of modified *i*-PP.

Gao, J and team (2002) studied the effects of radiation on the crosslinking and branching of PP. Crosslinked and branched behavior of homopolypropylene (HPP), impact modified copolypropylene (IPP), and random copolypropylene (RPP) were resolved. Using of the Charlesby–Pinner equation for some parameter calculations was performed. It was found that IPP had the highest gel dose value, crosslinking G value/scission G value, and gel fraction after irradiation among HPP, RPP. Therefore, IPP is the best material for making radiation crosslinking and radiation branching PP among HPP and RPP.

Khan, M.A. et al. (1999) studied the radiation effect on the physical, thermal, mechanical and degradable properties of biodegradable polymer. The bionolle films prepared by compression molding process and it was irradiated with electron beam (EB) radiation of different doses. It observed that the tensile strength of bionolle was enhanced when bionolle film was exposed under 20 kGy radiations. Both irradiated and non-irradiated of the bionolle films were subjected to different degradation test in outdoor and indoor conditions. Loss of tensile strength of irradiated bionolle due to storage degradation like in roof, ground and indoors were minimum compared to those non-irradiated bionolle.

Stephen, R and coworker (2006) studied the thermal stability and ageing properties of sulphur and gamma radiation of vulcanized natural rubber (NR) and carboxylated styrene butadiene rubber (XSBR) latices and their blends. Thermal degradation and ageing properties of these individual lattices and their blends were investigated with special reference to the blend ratio and vulcanization techniques. As the XSBR content in the blends were increased, their thermal stability were found to increase. Among sulphur and radiation vulcanized samples, radiation cured possesses higher thermal stability due to the higher thermal stability of carbon/carbon crosslink. The properties of aged samples were found to decrease due to chain depletion. However, the moduli of XSBR and NR/XSBR blends were found to increase owing to the formation of crosslinks upon ageing.

2.3.2 Peroxide crosslink

Peroxide crosslink is the process used peroxide agents to initiate the reaction of hydrogen atom. In the system, the polymer chain is crosslinked in the presence of peroxides at high temperature. Peroxides are heat activated chemicals that generate free radicals. Radicals are carbon based entities and capture a hydrogen atom from one of the carbon atoms in the polymer chain, leaving localized polymer radical or reactive species (Kircher, K. 1987). This reactive species can then form a crosslink bond with other polymer radical or hydrogen from another polymer strand creating another free radical. Two adjacent carbon atoms of such condition will form a carbon/carbon bond to achieve stability. And then a crosslink is formed. These chain termination and propagation reactions appear in a simplified form as seen in Figure 2.2 (Nobel, A. 2000).

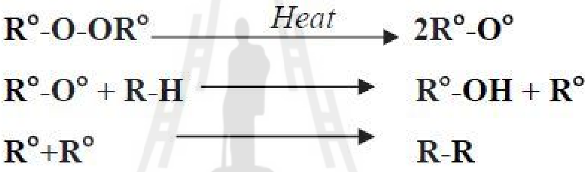

Figure 2.2 Peroxide crosslink techniques (Nobel, A. 2000)

Babu, R.R. et al. (2009) investigated the influence of different mixing protocols, at a fixed blend ratio of polypropylene/ethylene octene copolymer thermoplastic vulcanizates, on the morphology, mechanical properties of peroxide cured. The best balance of properties was observed at 3 milliequivalents (2 phr) concentration of peroxide. Tensile failure surface analyses of the thermoplastic vulcanizates prepared was employed to gain an insight into the mechanism of failure and to correlate the mechanical properties. The SEM analyses revealed that the phase morphology of the blend components in the TPVs depended very strongly on the route employed for preparation. TPVs prepared by adding EOC curative master batch to the molten PP; phase mixing method, exhibited better mechanical properties and the finer phase morphology than those prepared by preblending and split addition method. In conventional method, the decreasing in the mechanical properties at high concentration of peroxide might be attributed due to the severe degradation in the PP matrix phase.

Effect of different types of peroxides on rheological, mechanical, and morphological properties of thermoplastic vulcanizates based on natural rubber/polypropylene blends was investigated by Anoma, T. and cowork (2007) to find a proper balance between the influences of degree of crosslinking of the rubber and degradation of the PP phase. Also, relative amounts of decomposition products of each peroxide played an important role in the properties of the thermoplastic vulcanizates (TPVs). The main factors that influenced the properties of the TPVs were; the typical crosslinking temperature, the crosslink efficiency and the relative amounts of decomposition products of each peroxide in combination with the degradation of PP. DCP and DTBPIB indicated typical crosslinking temperatures close to the mixing temperature provided high crosslink efficiency and highly reactive radicals. They provided high amounts of crosslinks in the rubber molecules. Moreover, in relation to decreasing viscosity of the PP via the PP degradation mechanism, the TPVs with DCP or DTBPIB give superior overall properties relative to DTBPH or DTBPHY as curative agents.

Lai, S.M. et al (2005) investigated the fracture behaviors of polypropylene and metallocene polyethylene(PP/m) thermoplastic vulcanizate via peroxide crosslinking. The mixing of mPE (40 wt%) and PP (60 wt%) containing various dosages of peroxide was performed to activate dynamic cure using an internal mixer. Tensile strength was firstly decreased with increasing the levels of peroxide concentrations but yet increased again at higher level of peroxide concentrations at all test temperatures. Tear strength generally decreases with reduced energy dissipation and tends to level off at higher degree of cure.

2.3.3 Peroxide/silane crosslink

Vinyl based silanes can be used to induce the crosslinking of polyolefin chain. They have received much attention in recent years not only for industrial applications but also in fundamental research. Because of, their various advantages, such as easy processing, low capital investment, and favorable properties in the processed materials. The typical vinyl terminated silane, vinyl trimethoxy silane (VTMS), reagent employed both research and industrial works is shown in figure 2.3. The usual procedure for silane crosslink process is through the preparation of a silane grafted polymer using free radical reaction step through the peroxide initiation of the vinyl alkoxysilane. After shaping into products, the alkoxilated silane graft polymer is crosslinked by exposure to the humid environment. The crosslink reaction involves hydrolysation of the hydrolysable alkoxy groups with moisture, followed by condensation of the formed hydroxyl groups to form stable siloxane linkages. The schematic diagram of the peroxide/silane crosslinking reaction mechanism is also summarized in figure 2.3 (Kalyanee S.and Keskanok K., 2005).

Crosslinking of polyolefin can applied to all polyolefin types; however, the vast majority of the publications are concerned with polyethylenes. Few studies concerning the crosslinking of polypropylene (PP) has been reported. Crosslinking of PP gained no practical importance. This is most likely a consequence of the nature of the PP chain structure. During the crosslinking process, PP chain scission is accompanied as a side reaction. This would negatively influence the properties of the crosslinked product. Crosslinking provides an important method to improve the mechanical properties, thermal and chemical resistance of polyolefin (Wang, Z. 2005).

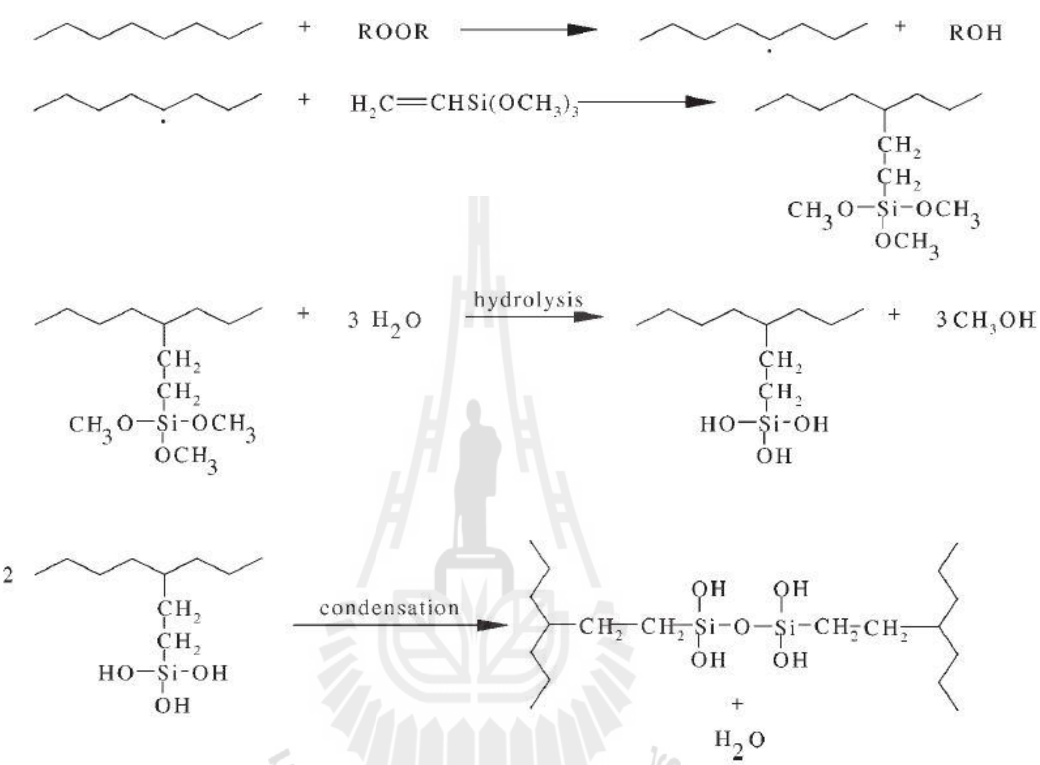

Figure 2.3 Peroxide/Silane crosslink process (Kalyanee S.and Keskanok K., 2005).

Wang, Z., Wu, X., Gui, Z., Hu, Y., and Fan, W (2005) studed the silane crosslinked polypropylene (PP). It was prepared first by the grafting of silane onto the backbone of PP in a melt process and then by crosslinking in warm water. The silane used was vinyl trimethoxysilane (VTMS) and vinyl triethoxysilane (VTES). For peroxides used were Dicumyl peroxide (DCP) and Di-*tert*-butyl-peroxide (TBP). The effects of type and concentration of silanes and peroxides on the silane grafting on PP chain were investigated. It was found that type and concentration of silane and/or peroxide had a great influence on silane crosslinked PP.

Kalyanee S.and Keskanok K. (2005) studied silane grafting and water crosslinking of polypropylene (PP) and its compound with calcium carbonate. Silane grafting of the polymers was performed in the melt by the use of vinyltrimethoxysilane (VTMS) and dicumyl peroxide (DCP). The results showed that during the grafting process, PP chain scission was accompanied as a side reaction. Peroxide concentration was found to be a major factor in determining the extents of grafting and PP degradation. After conducting a crosslinking reaction a combined effect of filler and silane crosslink network in enhancing composite modulus, tensile stress, heat distortion, and decomposition temperatures was evidenced.

Liu, N.C. and coworker (1999) studied the melt grafting of unsaturated silanes onto the powdered polypropylene (PP) in a Haake Rheocord RC90 batch mixer and cured in hot water. The influences of grafting formulations and processing conditions on the equilibrium torque during processing and the gel percentage of crosslinked PP were investigated. The gel percentages for grafted PP by type of silane, methacryloylpropyltrimethoxysilane (VMMS) grafted PP were markedly higher than those of vinyltriethoxysilane (VTES). While, significantly less degradation of PP during grafting was observed for VMMS grafted PP. When benzoyl peroxide(BPO) was used as initiator, only a minor degradation of PP during grafting was observed. Whereas, the use of dicumyl peroxide(DCP) as initiator resulted in severe degradation of PP, especially at high DCP concentrations.

Song, G. (2006) investigated the polypropylene foam prepared by the novel one step silane grafting and crosslinking method. High melt strength polypropylene (HMSPP) used for the foaming was prepared in a twin screw extruder. Benzoyl peroxide (BPO) was used as an initiator. The results indicated that all of the agents were effective and necessary, and the proportions of the components, especially BPO, highly influenced the melt flow rate (MFR) of the HMSPP. With the decrement of the MFR of the HMSPP, the average size of the cells and the number of the unclosed cells decreased while the density of the cells increasesed.

Vapour phase grafting of vinyltrimethoxysilane and water crosslinking of polypropylene was investigated by Hu, M. and his team (2006). Free radical grafting of vinyltrimethoxysilane (VTMS) onto isotatic polypropylene (PP) in vapour phase. VTMS can be grafted onto PP in vapour phase. Its observe that, grafting degree increases with increasing DCP and monomer concentration. The grafting of VTMS can inhibit the degradation of PP to some extent in comparison with the DCP modified PP. But when the initiator concentration is high, the inhibition becomes minor. The TG results show that the thermal stability of the silane crosslinked PP increases and the stability of the DCP modified PP decreases compared with that of the pure PP.

2.4 Flash Point and Cooking Temperature of Oils

The flash point of a volatile material is the lowest temperature at which it can vaporize to form an ignitable mixture in air. Table 2.1 summarizes the typical flash point for oils that are typically used for cooking. In the cooking oil, the flash point is determined the ability of oil temperature in the deep fry cooking. The higher in the point, mean that, cooking at higher temperature without reaching the smoking point is allowed. Deep frying is normally controlled at between 180 and 190°C. In microwave cooking, streaming process with heat generation by water molecule rotation is commonly achieved.

Table 2.1 Typical flash point for cooking oils

Cooking oils	**Flash point (^oC)**
Coconut oil	216
Corn oil	277
Cottonseed oil	234
Olive oil	225
Grape seed oil	200
Peanut oil	271
Safflower oil	260
Sesame oil	260
Soybean oil	254
Sunflower oil	274

However, deep fry cooking can be also performed in the microwave oven with slightly lower in oil temperature, 150-160^{o}C. Microwave ware is very crucial for oil cooking in microwave. At present, ceramic ware is normally used for this purpose. PP is the most commonly used for microwave cooking via the stream process. It can withstand the cooking temperature not more than 100^{o}C which is the typical streaming temperature. Therefore, only food warming or defrosting of ready meal can be done on the PP packaging. It would a great challenge for innovating the polymer packaging that can be used at oil cooking temperature in microwave. This is one of our goal applications for this study.

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CHAPTER III

DESIGN OF EXPERIMENT: PEROXIDE/SILANE CROSSLINKED POLYPROPYLENE BLENDS

3.1 Abstract

Polypropylenes (PPs) blends with addition of peroxide/silane induce condensation were studied by the design of experiment approach using the 2^k design method. Three types of PP were used and assigned as the design parameters. They were homo polymer PP (**A**), ethylene block (**B**) and random (**C**) copolymers. Each parameter was divided into two levels; high (+) and low (-). Dicumyl peroxide (DCP) and vinyl trimethoxyl silane (VTMS) was employed as crosslink system. Polymer compounding was performed in the continuous process using co-rotation twin screw extruder. The test specimen was prepared by injection molding and divided into two sets of samples; original and sauna cured. The properties of the blends by mean of HDT, impact strengths and flexural properties were tested and used as the designed responds. The results concluded that homo type PP showed the positive effect on HDT and flexural properties. In contrast, homo type PP had negative effect on MFI. It was also the positive effect on the HDT of the sample after sauna curing. Homo and block PP had the positive effect on notched impact strength of the sample without sauna treatment but no effect to the cured. The interacted parameters between block random PP (**BC**) had the negative effect on the unnotched impact strength for both original and cured specimen. Vice versa, the homo polymer indicated the explicit

result to the flexural properties. The properties prediction models derived from the statistical design were obtained. The morphological traces by scanning electron microscopy (SEM) revealed that the compounds were miscible and there was no trace of phase separation.

3.2 Introduction

Blending of polymers is one of the processes to utilize the polymeric materials that manifest the drawback properties. The process will combine outstanding properties of one polymer to another. However, the compatibility of the blended polymers is very important. Generally, addition of compatibilizing agents such as copolymer or grafted copolymer is required. There are so many blended polymers that have been commercialized and vastly research works have been gathered to explore the newly blend system. Polypropylene homo polymer (Homo PP) is the most widely material employed by the industries. Homo PP features such significant properties as high strength to weight ratio, high stiffness and high heat distortion temperature. This combined with good chemical resistance and weld ability allows this material to be used in many corrosion resistant structures. Polypropylene block copolymer (block PP) includes a linear arrangement of ethylene monomer blocks are combination of polymer chains. Block PP is high impact strength at low temperature. Polypropylene random polymer (Random PP) is propylene with randomly linked with ethylene units. Random PP is similar to block copolymer but give a better optical properties, gloss, clarity and brightness. Homo PP is stiffer and stronger than block PP. But, block PP tends to have better stress crack resistance and low temperature toughness than homo type at the expense of quite small reductions in other properties (E. Alfredo Campo, 2008). Copolymer is typically tougher and more durable than homo PP. Random PP is as highest transparency of all type. Study the effects of three types of polypropylene; homo polymer, block copolymer and random copolymer, on the properties of the blends; heat distortion temperature, impact strengths and flexural properties, by the statistical approach namely design of experimental (DOE) is the prime concern of this chapter. The optimal contents of those polymers in the peroxide/silane crosslinked blends that manifest the outstanding properties, especially high in HDT, it is the principal interest. However, if the research need does not recover in this statistical approach study, the result will be used as the fundamental knowledge for further investigation.

3.3 Research methodology

3.3.1. Materials

Three types of PPs were used in this study. There are PP homo polymer (PP 700J), PP block copolymer (PP 740J) and PP random copolymer (PP 750J). They were kindly supplied from SCG Chemical Co., Ltd. The chemical structure and properties of the polymers supplied by the manufacture are summarized in Table 3.1 and 3.2, respectively. The free radical initiator was dicumyl peroxide (DCP). The decomposed and generated radical from this initiator is relative stable at as high temperature as above 120^{o}C. The silane coupling agent was vinyl trimethoxy silane (VTMS), Silquest$^{®}$ A 171. It was used as complementary crosslink agent. The chemical was purchased from Optimal Tech. Co., Ltd. The peroxide/silane crosslinking process is commonly undergone by the condensation reaction via siloxyl/water condensation through the sauna incubation or moisture curing.

Table 3.1 Chemical structure of PPs

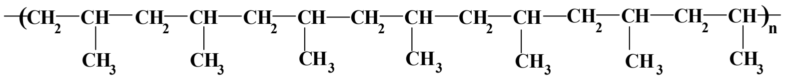
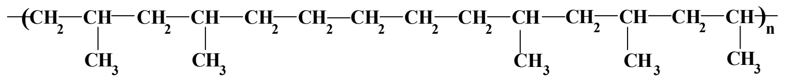
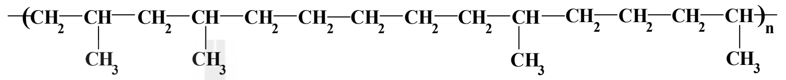
PPs	Chemical structure
Homo PP	 $\left(CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH} \right)_n$
Block PP	 $\left(CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-CH_2-CH_2-CH_2-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH} \right)_n$
Random PP	 $\left(CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-CH_2-CH_2-CH_2-CH_2-\underset{CH_3}{CH}-CH_2-CH_2-CH_2-\underset{CH_3}{CH} \right)_n$

Table 3.2 Physical properties of the PPs

Physical Properties	**Homo PP (PP 700J)**	**Block PP (PP 740J)**	**Random PP (PP 750J)**
Melt Flow Rate(230/2.16), g/10 min	12	27	12
Density, g/cm^3	0.91	0.91	0.91
Melting Point, ^{o}C	163	163	150
Heat deflection temperature (@0.455MPa), ^{o}C	110	110	90
Flexural Modulus, MPa	1422	1225	1176
Notched Impact, kJ/m^2	3.8	10.0	8.8
Ethylene Content(%)	0	1	1

3.3.2 The design Matrix

The 2^k factorial design of experiment with k = 3 was erected in order to optimizing and quantifying type and also amount of polypropylenes, in the blends, on the designed responds; mainly on thermal and mechanical properties. Three parameters were PP homo polymer (**A**), PP block copolymer (**B**) and PP random polymer (**C**) contents. According to the rule of design, the parameter must be divided into two levels; high (+1) and low (-1), respectively. In this research study, each level was again further divided into two sub levels as shown in Table 3.3.

Table 3.3 The parameter and level of DOE

Parameters	**High level(+)**		**Low level(-)**	
(**A**) P700J(Homo PP)(g)	+70	+60	-40	-30
(**B**) P740J(Block PP)(g)	+70	+60	-40	-30
(**C**) P750J(Random PP)(g)	+70	+60	-40	-30

Each parameter, the polymer content at 30 and 40 phr were assigned as low levels. Vice versa, at 60 and 70 phr were assigned as high levels, respectively. According to the rule of design at k = 3, therefore eight, $2^3 = 8$, experimental runs of polypropylene blending formula were constructed. The design matrix of all eight combinations is given in Table 3.4. The crosslinking agents, DCP and VTMS, were constantly added at 0.1 and 1.0 phr, with respect to the total amount of PPs used, into each formula, respectively.

Table 3.4 Design matrix and compound formula for peroxide/silane crosslinked polypropylene.

Run	P700J(A) (g)	P740J(B) (g)	P750J(C) (g)	DCP (g)(phr)	Silane (g)(phr)
1	60(+)	70(+)	70(+)	(**0.20**)(0.1)	(**20**)(1.0)
2	70(+)	60(+)	40(-)	(**0.17**)(0.1)	(**17**)(1.0)
3	60(+)	40(-)	60(+)	(**0.16**)(0.1)	(**16**)(1.0)
4	70(+)	30(-)	30(-)	(**0.13**)(0.1)	(**13**)(1.0)
5	30(-)	60(+)	60(+)	(**0.15**)(0.1)	(**15**)(1.0)
6	40(-)	70(+)	40(-)	(**0.15**)(0.1)	(**15**)(1.0)
7	30(-)	30(-)	70(+)	(**0.13**)(0.1)	(**13**)(1.0)
8	40(-)	40(-)	40(-)	(**0.12**)(0.1)	(**12**)(1.0)

3.3.3 Specimen preparation

Method to prepare the blending sample in this study is schematically summarized in Figure 3.1. First step, all polypropylene pellets (P700J, P740 and P750J) was cooperated in plastic bag and vigorously shaken. After that, amount of the calculated 0.1 phr of solid dicumyl peroxide (DCP) was incorporated with the solid pellet polymers and the ingredient was placed in warm oven at 80^{o}C for at least 5 min to allow DCP to liquidize. The ingredient was removed from the heat and again vigorously shaken for the liquidized DCP completely coating on the surface of the solid pellets. Then, 1.0 phr of liquid vinyl trimethoxy silane (VTMS) was added into the ingredient and well shaken. The melt compounding of the PPs blend was performed in closely intermeshing co-rotation twin screw extruder, with L/D ratio and screw diameter of 20/1 and 25 mm, respectively. The extruder barrel temperature profile from feed to die zone is equally controlled at 170°C. The screw speed of 10 rpm was electronically monitored, giving an approximate residence time of 6 minutes. The extruded strand was then air cooled and granulated in to pellet using mechanical jaw crusher. The compound pellet was dried in oven at 80°C for at least 2 hours to dispose the residual moisture prior to do the injection molding. Samples are injected on Tederic TRX60c injection molding machine at barrel temperature of 160, 165, 170, 170 and 170°C from feed to nozzle tip, gradually. The mold temperature was set at 40°C at the cooling time of 30 seconds. The molded specimens were dividing into 2 sets of samples. One was allowed to anneal at room temperature for at least a day before testing, and it was assigned as "**original**" sample. The other set was incubated in moisture vapor saturated oven at 105°C for at least 12 hours to ensure the competition of crosslink reaction via the siloxane/moisture condensation reaction. Finally, the incubated sample was allowed to cool down to room temperature for a day priority to conduct the test. This type of sample was, now on, called "**sauna cured or cured**" sample.

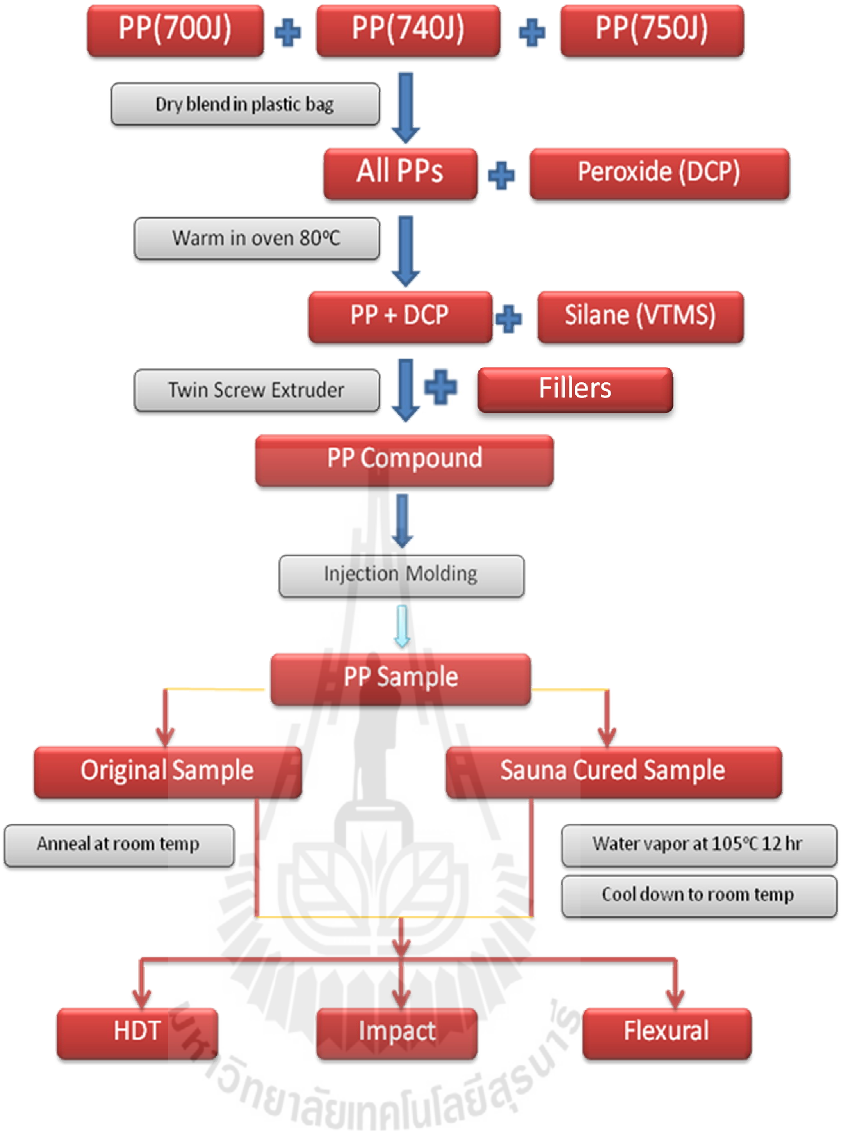


Figure 3.1 Schematic diagrams for the sample preparation of peroxide/silane crosslinked polypropylene blends

3.3.4 Properties measurement and analysis

3.3.4.1 Rheological testing

The rheological property of the polypropylene blends by mean of melt flow index (MFI) was perform and test in accordance with ASTM D 1238 by using the Kayeness melt flow indexer (model 4004). The pellet sample obtained was dried at 80°C for at least 2 hrs. Testing samples was allowed to melt at 170°C and driven through the capillary die (Ø 1 mm.) using the piston load of 2.16 kg. The melting time was set at 360 seconds. Three cuts of extrudate were performed with the cut times of 15 second. The weight of the extrudate was computed into the melt flow index (MFI) figure in the standard unit of g/10min.

3.3.4.2 Heat deflection temperature

Heat deflection temperature (HDT) of the polypropylene blends for the original and sauna cured sample was obtained in accordance with ASTM D 648. The standard testing machine from Atlas, model HDV 1, was employed. Samples was tested in the edgewise position, with the support span length of 100 mm, a simple beam with the load applied at its center of the spanned sample to give standardized stress of 0.455 MPa (66 psi). The raising temperature at a uniform rate of 2±0.2°C/min was assigned. Liquid silicone oil was used as heating transfer media. The HDT value is reported in degree Celsius (°C). It was recorded as soon as the specimen had been deflected to 0.25 mm or 0.01 inches that monitored by dial gauge. This temperature was recorded as the deflection temperature under flexural load of the test specimen. Three samples were examined and the average value was reported.

3.3.4.3 Impact testing

Unnotched and Notched impact strengths, in Izod mode, of the polypropylene for the original and sauna cured sample was tested using ASTM D 256. The injection molded specimen the with the dimension of 4x13x63 mm (WxLxH) was notched by the notching machine. The identical injected samples were also tested without notching. 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 Atlas impact testing machine, model BPI, was employed. The impact strength values were reported in kJ/m^2 that was calculated from lost impact energy divided by the cross section area at the fractured point.

3.3.4.4 Flexural testing

Flexural properties by mean of the strength and modulus of the polypropylene for both original and sauna cured sample were examined in accordance with ASTM D 790. The testing machine, 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 computerized control. The test specimens were placed plat wise to the bending load. The test was conducted at room temperature in normal atmospheric condition. At least five piece of specimen were tested. The flexural properties both strength and modulus was averaged and recorded.

3.3.4.5 Morphological investigation

Morphology of the fractured surface of the polypropylene was examined using scanning electron microscope (SEM). The fractured specimen from notched impact testing was cut in to small piece. It was then attached onto the SEM 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 JSM 6400 at the accelerating voltage of 20 keV.

3.4 Design of Experiment

Analysis of variance (ANOVA) and regression techniques are useful to determine if there is a statistically significant difference between treatments and levels of variables. DOE techniques offer a structured approach to change many factor settings within a process at once and observe the data collectively for improvements or degradations. DOE analyses not only yield a significance test of the factor levels but also give a prediction model for the response. These experiments can address all possible combinations of a set of inputs factor or a subset of all combinations. There are many advantages of the DOE that include;

1) Separating true effects from noise.
2) Solve problems that cannot be solved by common methods.
3) Wide variety of fields and applications.
4) Reducing product and process variation.

and 5) Save time and reduce cost of the run through single parameter experiment.

3.4.1 Interpretation of DOE

According to the 2^k factorial by *k* is the parameters to study approach, for example with k = 3, eight runs are constructed as the experimental matrix to evaluating the statistical effects of the recipe composition factor on the given respond(s). The effect of the factor is defined as the change in response produced (Y_i) by a change in the level of the factor such high (+) and low (-) level. It is called main effect (E_f) and mathematically calculated as follow (Forrest W. Breyfogle III, 1999).

$$E_f = \frac{\Sigma Y_{iE+}}{n/2} - \frac{\Sigma Y_{iE-}}{n/2} \tag{3.1}$$

where E_f = main effect of factor

y_{iE+} = the response of high level factor

y_{iE-} = the response of low level factor

After calculating the main effect and interaction effect of factors then the calculated value is ranked. The Z-value and then *p*-value are resolved as the following procedure;

The ***p***-value is calculated from equation 3.2

$$p = \frac{i - 0.5}{2^k - 1} \tag{3.2}$$

where i = Rank number of the effect, that order by followed effect value

k = Number of factor are used design

Accordingly, Z-value as cumulative probability, as shown in Figure 3.2 is obtained from the conversion of ***p***-value as from the Standardized Normal Curve Table. Summary method to calculated Z-value and *p*-value is shown in Table 3.5

Table 3.5 Statistical values of parameter and their interaction.

Effect value ($E_{f,i}$)	**Rank (*i*)**	***p*-value**	**Z-value**
$E_{f,1}$	1	$\frac{1-0.5}{2^k-1}$	$\frac{x-\mu}{\sigma}$
$E_{f,2}$	2	$\frac{2-0.5}{2^k-1}$	$\frac{x-\mu}{\sigma}$
$E_{f,3}$	3	$\frac{3-0.5}{2^k-1}$	$\frac{x-\mu}{\sigma}$
...	...	...	...
...	...	...	...
...	...	...	...
$E_{f,2^k-1}$	2^k-1	$\frac{(2^k-1)-0.5}{2^k-1}$	$\frac{x-\mu}{\sigma}$

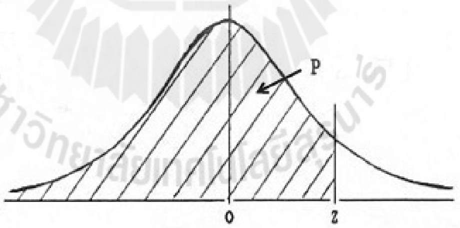


Figure 3.2 Standardized normal curves

The obtained *p*-value together with the standardized effect is either half normal or normal plotted. The significant effect from the plot is again evaluation by ANOVA testing at the given degree of confidential, for example at 95% ($\alpha = 0.05$) and so on.

3.5 Results and discussions

3.5.1 Analysis of MFI

Melt flow index obtained at melt temperature of 170 ^{o}C and piston load of 2.16 kg for all polymer blends formula are summarized in Table 3.6. The test values are much higher than the MFI of the virgin polymers that were tested at the higher melt temperature, 190^{o}C, as given in Table 3.2. It indicates that blending of PPs in the presence of DCP/silane might, somehow, undergo chain degradation rather than crosslinking.

Table 3.6 MFI of the polypropylenes blend

Run	P700J(A) (g)	P740J(B) (g)	P750J(C) (g)	DCP (phr)	Silane (phr)	MFI@170/2.16
1	60(+)	70(+)	70(+)	0.1	1.0	20.72
2	70(+)	60(+)	40(-)	0.1	1.0	17.95
3	60(+)	40(-)	60(+)	0.1	1.0	18.26
4	70(+)	30(-)	30(-)	0.1	1.0	19.51
5	30(-)	60(+)	60(+)	0.1	1.0	22.29
6	40(-)	70(+)	40(-)	0.1	1.0	23.87
7	30(-)	30(-)	70(+)	0.1	1.0	20.48
8	40(-)	40(-)	40(-)	0.1	1.0	23.19

The calculation of the standardized effects of the individual parameter and also the interacted parameters with assisting of Design Expert^{TM} was performed and they were converted into the standardized probability, *p*. The plot of the normal probability against the standardized effects and also the pareto chart between *t*-value and their ranks are plotted and shown in Figure 3.3 and 3.4, respectively. From the standard effects plot, Figure 3.3, it is seen that only homo polymer (PP 700J) which is negative effect (-**A**) to the MFI illustrates the tendency to be the significant effected to the melt index of the PP blends because it is located outside the regressed linear trend line. It is also indicated the greatest negative effect value. To strengthen this statement, the pareto chart is taken into consideration, Figure 3.4. The chart reviews that homo polymer has the calculated *t*-value above the given critical value. The rest are not. From this preliminary observation, it is strongly suggested that the parameter, homo PP, is significant effect on the MFI of the blends. Furthermore, the statistical testing using the ANOVA will finalize the conclusion of the test. The analyzed test results are concluded in Table 3.7. At 95% degree of confidential, the statistical outcomes reveal that *p*-value of the designed model and the parameter **A,** homo PP, are 0.0136. The number is less than the assigned critical value, at 0.05. The ANOVA analysis concludes that the homo polymer, PP 700J, has the significant and negative influence on the MFI of the blends. It means that blending the PPs form those three type of PP polymers with high level of loading homo type polymer will give rise the blend with low flow ability, lower MFI.

3.5.2 Analysis of HDT

The service temperature of the polymer blends by mean of heat deflection temperature (HDT) measured at heating rate at 2±0.2^{o}C/min was tested and the test results are reported in Table 3.8 for both original and sauna cured samples.

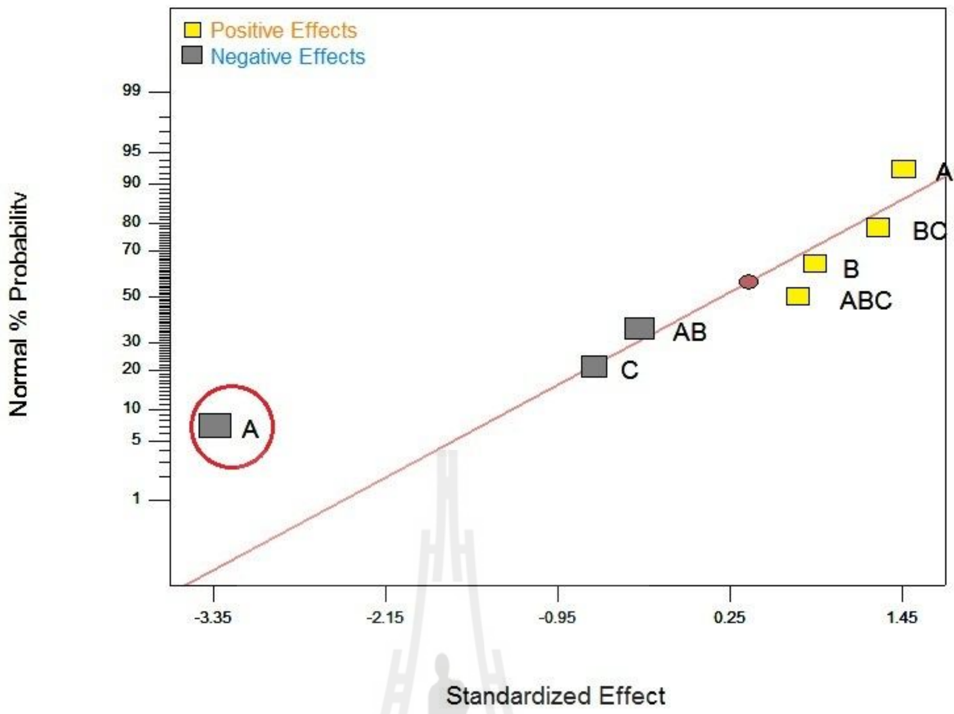


Figure 3.3 Normal probability plot of MFI

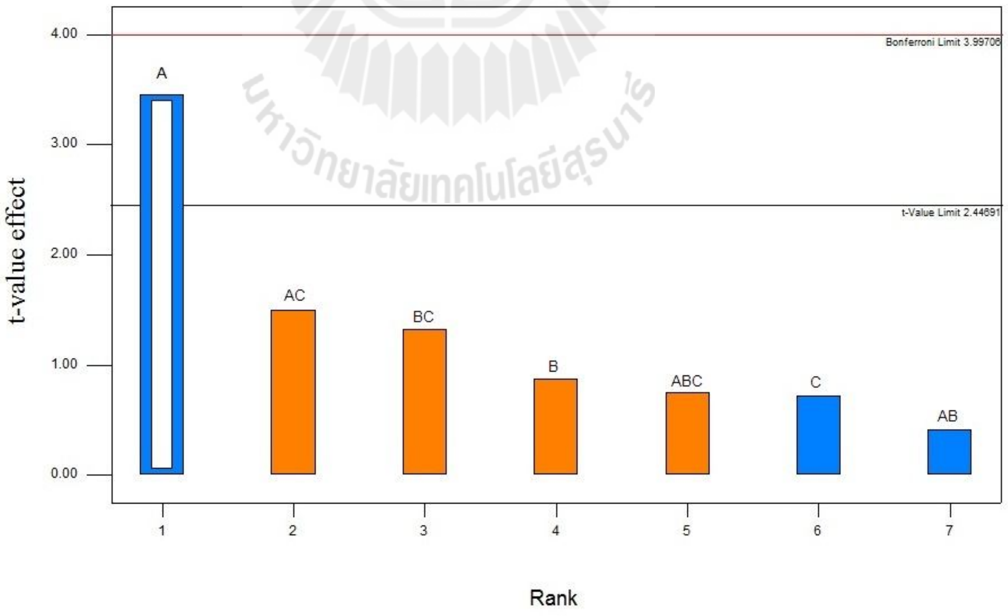


Figure 3.4 Pareto chart analysis of MFI

Table 3.7 ANOVA conclusion for MFI

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	22.41	1	22.41	11.91	0.0136
A-P700J	22.41	1	22.41	11.91	0.0136
Residual	11.29	6	1.88		
Cor Total	33.7	7			

The HDT of the PPs blend before undergo sauna incubation is slightly lower that the HDT of the virgin PPs. It is obviously seen that the HDT of cured sample are raised about 20 – 30°C after sauna incubation process comparing with the sample without the curing process. There are two possibilities to explain this phenomenon. One is the increasing in the crystallinity of the PPs during prolong incubation at temperature, 105°C, higher than the T_g of the blended polymer for more than 12 hours. Generally, the more increasing in the crystallinity of the semicrystalline polymer, the higher in HDT. However, chain condensation via silane/moisture to form the tighter chain network can also elevate the service temperature of polymer. However, from the MFI test result the crosslinking of the PP chain via DCP/silane induction is beyond the possibility. Vice versa, chains degradation is highly possible. Therefore, the former hypothesis would be the best to support the superb of HDT via the sauna treatment. From the previous research works, it found that annealing the PP at 105°C for more than 6 hours, the crystallinity fraction analyzed by differential scanning calorimetry (DSC) of this polymer was evidently increased (Thanatiwat N. 2011).

Table.3.8 Heat deflection temperature of the polypropylene blends

Run	**Heat deflection temperature(^{o}C)**	
	original	**cured**
1 (+,+,+)	90.5 ± 1.8	122.4 ± 0.6
2 (+,+,-)	92.4 ± 3.6	122.9 ± 0.8
3 (+,-,+)	92.3 ± 2.9	123.3 ± 0.1
4 (+,-,-)	89.9 ± 1.8	123.7 ± 0.7
5 (-,+,+)	89.7 ± 0.8	115.8 ± 0.5
6 (-,+,-)	88.5 ± 2.5	116.6 ± 1.0
7 (-,-,+)	92.3 ± 2.0	114.7 ± 0.9
8 (-,-,-)	90.7 ± 0.8	117.1 ± 1.3

For the statistical analysis of the HDT of the PP blends, Figure 3.5 and 3.6 are the normal plot and pareto chart for the sample without sauna curing, respectively. The standard normal plot suggests that interaction parameters between block copolymer, PP (740J) and random copolymer, PP (750J), (-**BC**) and also between homo polymer, PP (700J), and the block, PP (740J), (+**AB**), are out of the linear trend line. These two interacted parameters are negative and positive effect on the HDT of the original sample, respectively. They are suspected to be the real effect on the HDT of the blends. With the assisting of the pareto chart shown in Figure 3.6, it manifests that the calculated *t*-values of those two interacted parameters are far below the critical limit line. The chart suggests that the parameters do not have the significant effect on the HDT of the PP blends before undergo sauna treatment. To strengthen the statement, the ANOVA testing conclusion given in Table 3.9 confirms that the *p*-values of the designed model and the suspected parameters are below the given critical figure. It is finally concluded that the designed experiment; type and quantity of PPs used, do not have the significant effect on the HDT of the PP blends.

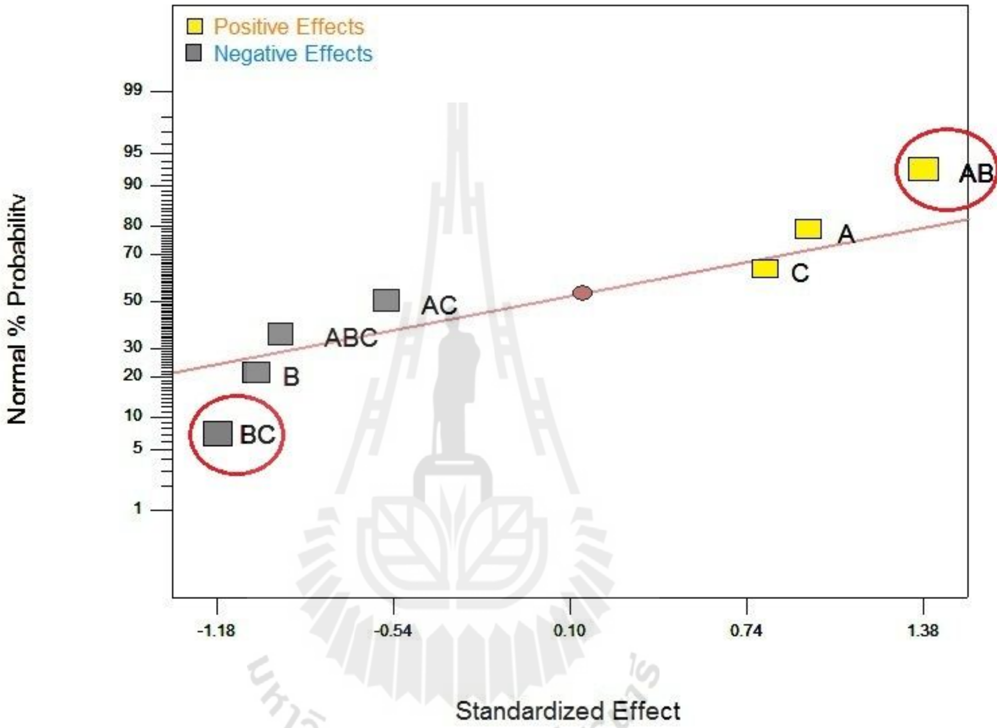


Figure 3.5 Normal probability plot of HDT original sample.

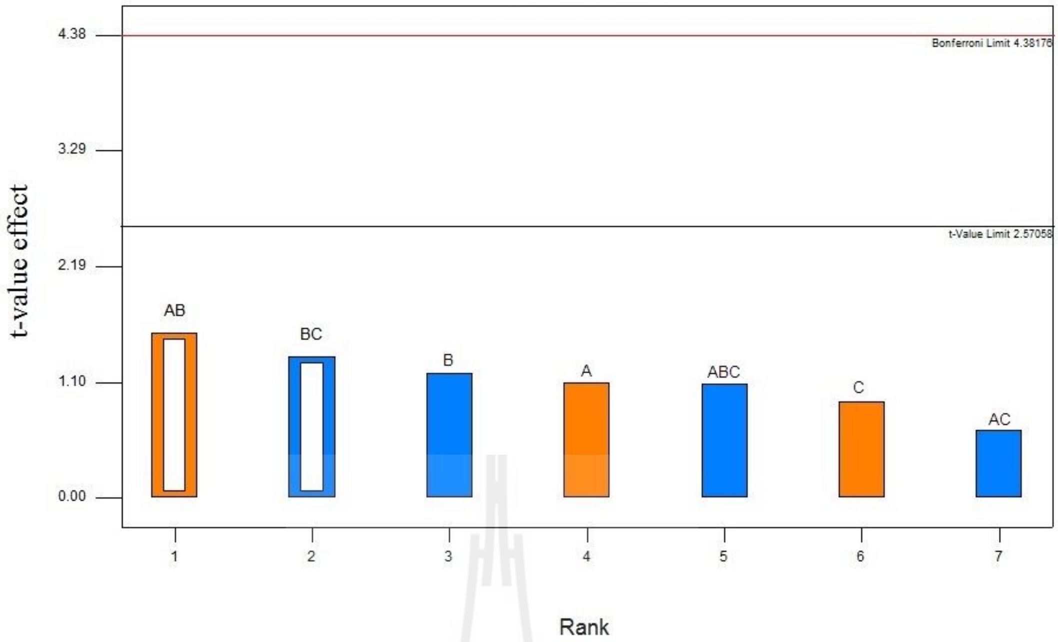


Figure 3.6 Pareto chart analysis of HDT original sample.

Table.3.9 ANOVA test for HDT original sample.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	6.62	2	3.31	2.12	0.2156
AB	3.82	1	3.82	2.45	0.1786
BC	2.8	1	2.8	1.79	0.2386
Residual	7.81	5	1.56		
Cor Total	14.43	7			

However when the blends was undergone sauna treatment in moisture saturated oven at 105°C for at least 12 hours, the standardized effect plot and the pareto chart of the HDT obtained from those specimen are shown in Figure 3.7 and 3.8, respectively. It is seen that PP 700J (+**A**) are obviously out of the linear trend line of the normal plot. It shows the great tendency to be significant and positive effect parameter on HDT of cured polymer blends. Similarly, the calculated *t*-value of +**A** on the pareto chart is also far above limit boundary line. The result found emphasis the previous observation that the homo polymer does has the significant effect on the HDT of the blends after undergo sauna curing. Nevertheless, the statistical ANOVA analysis given in Table 3.10 is finally used to conclude that the designed model and homo PP are real significant and positive effect on the HDT of the sauna cured PP blend. Blending of PPs using high levels of PP (700J) and sauna treatment would generate the material with higher HDT. From this result, it could verify the previous hypothesis that whether crystallinity or chain bonding through the silane/moisture linkage plays the major role for increasing the HDT of the blends. It could say that the increasing in the crystallinity through sample annealing at above T_g of the polymer hurdle the HDT of the PP blends.

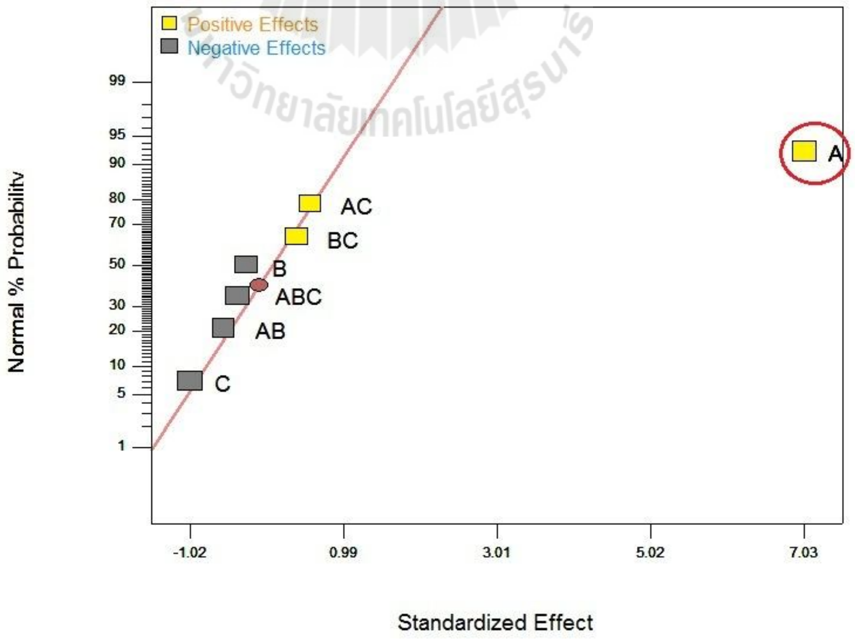


Figure 3.7 Normal probability plot of HDT cured sample.

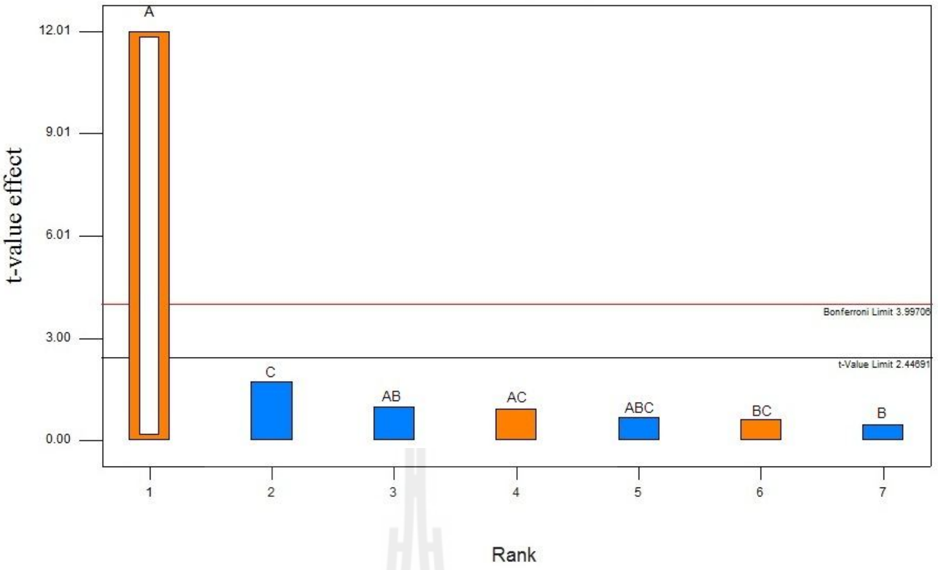


Figure 3.8 Pareto chart analysis of HDT cured sample.

Table.3.10 ANOVA test for HDT cured sample.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	98.91	1	98.91	144.28	< 0.0001
A-P700J	98.91	1	98.91	144.28	< 0.0001
Residual	4.11	6	0.69		
Cor Total	103.03	7			

3.5.3 Analysis effect of impact strengths

Notched and unnotched impact strengths for the original and cured blends samples are present in Table 3.11. The results show that notched impact strength of cured sample is higher than the original sample for all blends but for the unnotched test mode, the difference between two treatments cannot be simplified. Taking the notched respond for the original sample into the statistical analysis by looking at the standard normal plot and pareto chart, the evaluation outcome are illustrated in Figure 3.9 and 3.10, respectively.

Table.3.11 Impact strengths (kJ/m^2) of polypropylene blend

Run	**Notched Impact Strength (kJ/m^2)**		**Unnotched Impact Strength (kJ/m^2)**	
	Original	**Cured**	**Original**	**Cured**
1 (+,+,+)	2.37 ± 0.21	3.83 ± 0.40	48.71 ± 12.55	43.77 ± 6.52
2 (+,+,-)	2.34 ± 0.22	3.76 ± 0.61	57.53 ± 2.94	68.95 ± 6.76
3 (+,-,+)	1.96 ± 0.25	3.39 ± 0.62	67.30 ± 5.33	67.21 ± 5.56
4 (+,-,-)	1.59 ± 0.28	2.76 ± 0.26	47.41 ± 8.65	47.41 ± 22.84
5 (-,+,+)	3.47 ± 0.30	4.33 ± 0.12	62.53 ± 8.43	64.65 ± 13.31
6 (-,+,-)	2.93 ± 0.31	3.83 ± 0.18	62.78 ± 2.92	56.83 ± 11.64
7 (-,-,+)	2.51 ± 0.32	4.04 ± 0.78	68.32 ± 3.95	78.54 ± 10.78
8 (-,-,-)	2.52 ± 0.11	3.58 ± 0.15	51.18 ± 10.12	48.76 ± 15.15

The plot shows that there are two parameters, PP (700)(-**A**) and PP (740J)(+**B**), are out of the linear trend line which are suspected to be the significant effect to the notched impact strength. Confirmation by the pareto chart, it is strengthen that these negative and positive effects are the significant effect to the given test respond because their *t*-values are obviously above the critical limit value. Moreover, the conclusion obtained from the ANOVA testing as shown in Table 3.12, also confirm that *p*-values of the designed model, parameter A and parameter B are, 0.0029, 0.0031 and 0.0080, consequently. They are below the given degree of confidential, 0.05. It means that the parameters and levels of parameters used for designing the experiment have the significant effect to the notched impact strength of the PPs blend. Blending the PPs with low level content of homo polymer, P 700J, and high level of block copolymer, P 740J, would result in high impact strength for the original blend sample.

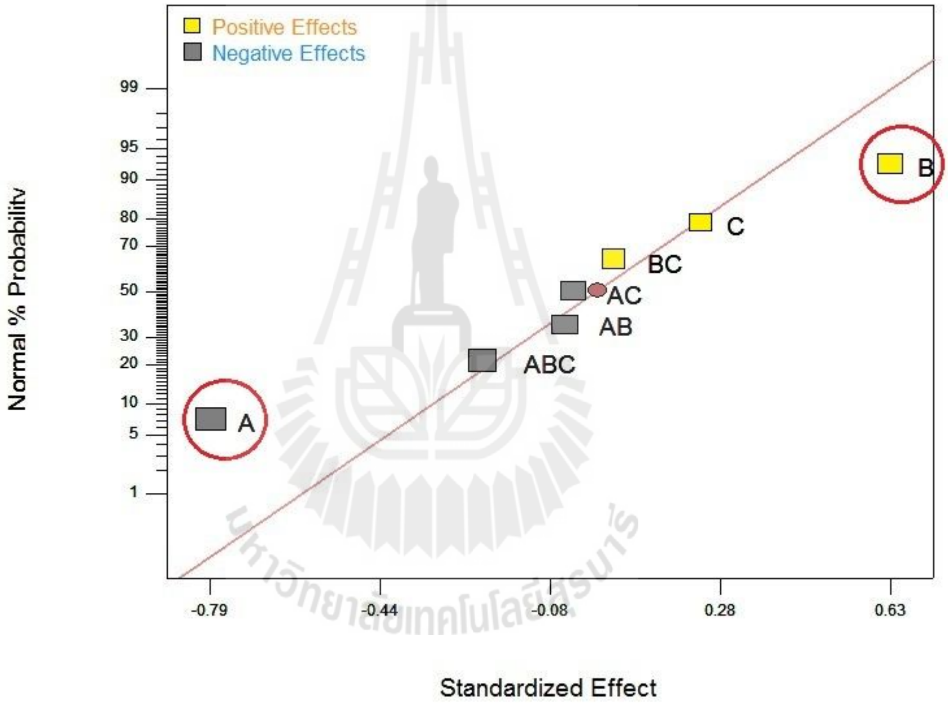


Figure 3.9 Normal probability plot of notched impact original sample.

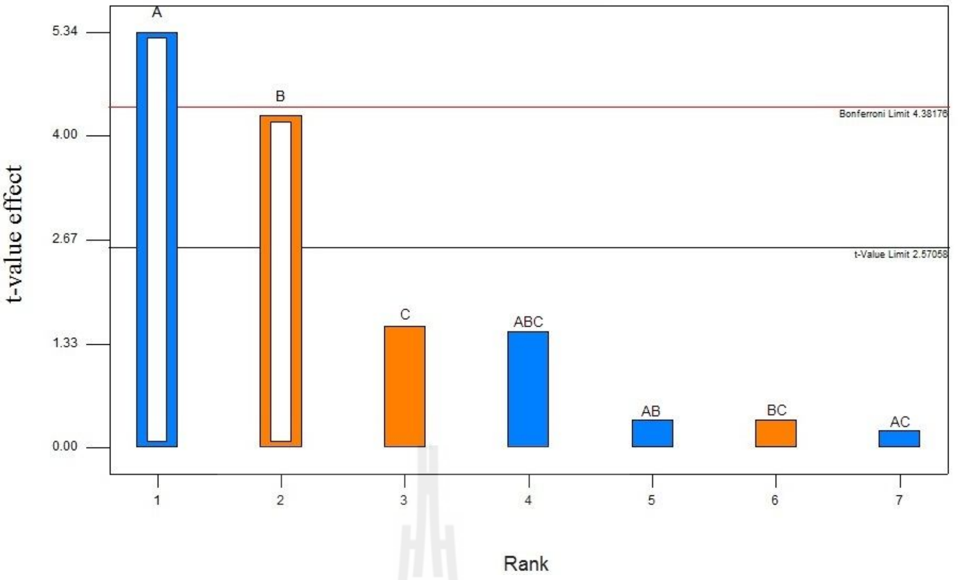


Figure 3.10 Pareto chart analysis of notched impact original sample.

Table.3.12 ANOVA test for Notched impact original sample.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	2.06	2	1.03	23.34	0.0029
A-P700J	1.26	1	1.26	28.51	0.0031
B-P740J	0.8	1	0.8	18.16	0.0080
Residual	0.22	5	0.044		
Cor Total	2.28	7			

In case of sample with sauna treatment, the normal plot of the notched impact respond is show in Figure 3.11. There are two parameters located outside the regressed line, PP (700J)(-**A**) and PP (740J)(+B), which are negative and positive effects, respectively. According to the DOE rule of analysis, these two parameters were suspected to be the significant parameters that have the real effect to the notched impact strength of sauna cured specimen. However, the test result from the pareto chart given in Figure 3.12 shows that the calculated *t*-values of those two parameters are below the critical limit value. It suggests that the parameters do not have the significant effect to the impact strength. Also, the ANOVA conclusion given in Table 3.13 confirms that the *p*-value of the designed model and of those suspected parameters are higher than the critical value at 0.05. It means that the either type of PPs or the amount of homo-PP and block-PP in the blends do not have great influence on the notched impact strength of the blends after undergo sauna incubation.

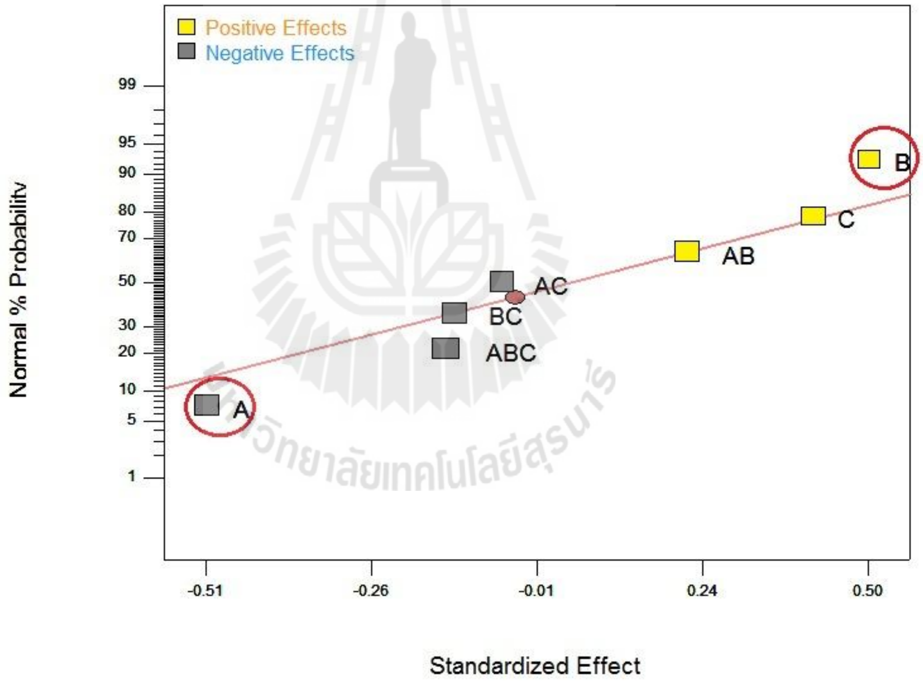


Figure 3.11 Normal probability plot of notched impact cured sample.

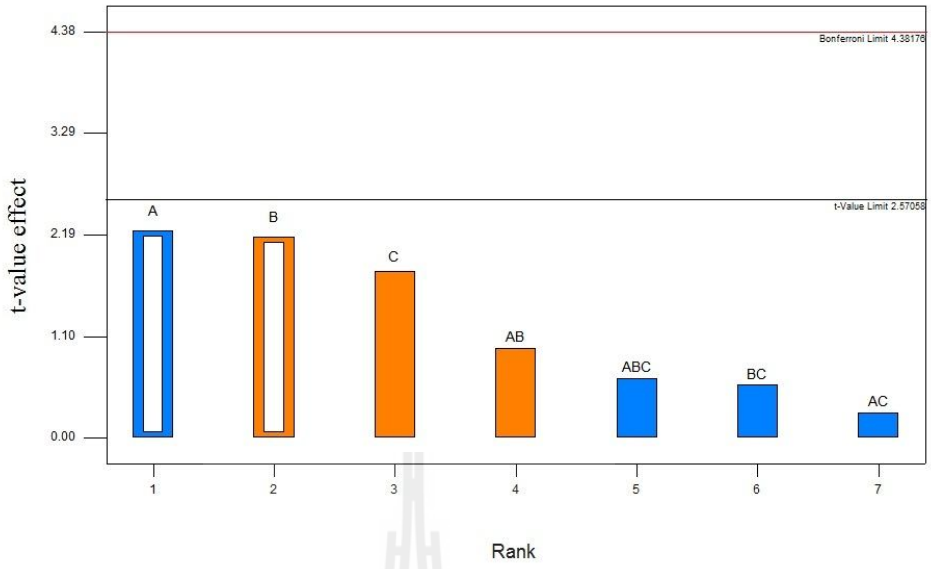


Figure 3.12 Pareto chart analysis of notched impact cured sample**.**

Table.3.13 ANOVA test for notched impact of cured sample.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	1.02	2	0.51	4.85	0.0674
A-P700J	0.53	1	0.53	5	0.0757
B-P740J	0.5	1	0.5	4.71	0.0822
Residual	0.53	5	0.11		
Cor Total	1.55	7			

Figure 3.13 and 3.14 illustrate the normal and pareto plots for the unnotched impact for the sample without sauna curing, respectively. It is seen that random-PP (750J)(+C) and interaction between block-PP (740J) and rondom-PP (750J)(-BC) are alighted outside the linear regressed line. These two parameters were selected and supposed to be the significant variables for the statistical analysis

Preliminary, the pareto chart reveals that only the interacted parameter is lined beyond the critical boundary. The statistical ANOVA conclusion given in Table 3.14, finally, strengthen that the interaction between block and random PPs(-BC) has the significant effect to the unnotched impact of the PPs blends. Because, both *t* and *p*-values of BC are beyond the designed critical values.

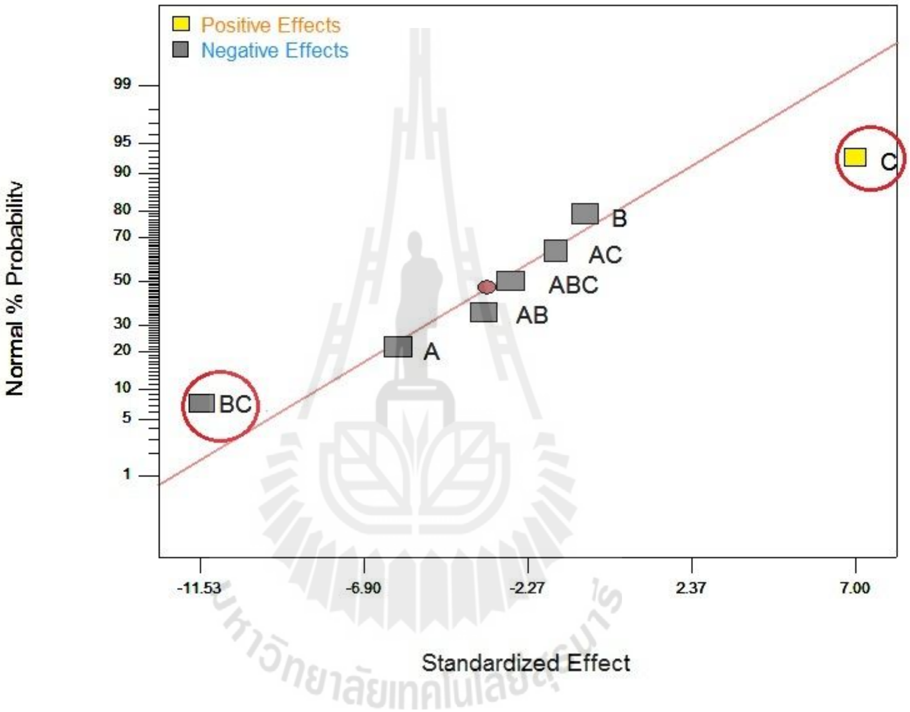


Figure 3.13 Normal probability plot of unnotched impact original sample.

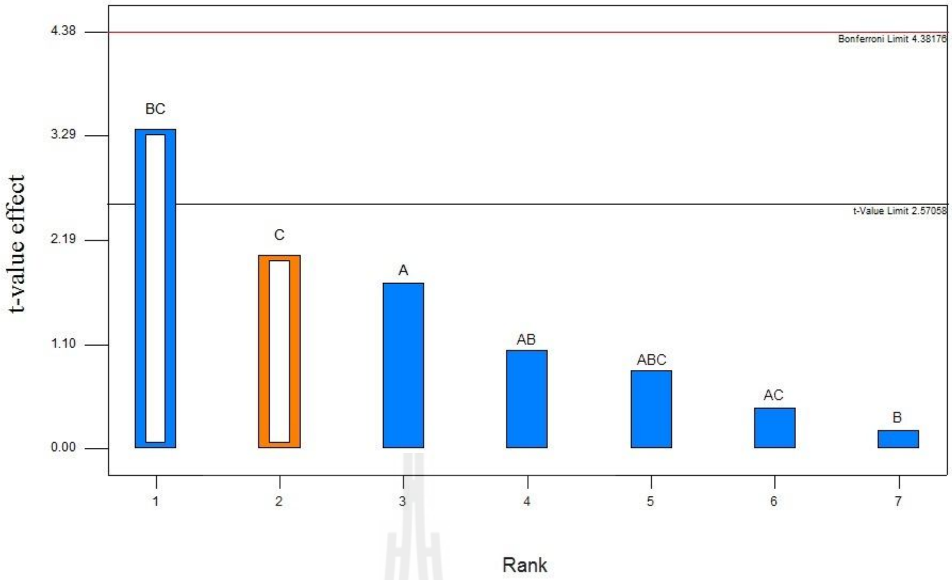


Figure 3.14 Pareto chart analysis of unnotched impact original sample**.**

Table.3.14 ANOVA test for Unnotched impact original sample.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	404.56	1	404.56	16.98	0.0062
BC	404.56	1	404.56	16.98	0.0062
Residual	142.96	6	23.83		
Cor Total	547.52	7			

The material toughness by mean of unnotched impact testing of cured PPs blends was also analyzed. The normal and pareto results are presented in Figure 3.15 and Figure 2.16, respectively. It is noticed that all the calculated standardized effect values are perfectly linear lined, except only the interaction of –BC which is slightly excluded from the group and it is the highest negative standardized effect. However, the pareto picture indicates that this interacted parameter is significant effect to the unnotched impact of the blends. Because, its calculated *t*-value is marginally higher than the critical value, $t_{\text{crit.}}$ = 2.44691. Therefore, the conclusion is verified by the ANOVA testing reported in Table 3.15. It is seen that the calculated *p*-value of BC is less than 0.05. Meaning that, the designed experiment and the amount of block and random PPs used in the blends had negative and significant effect to the unnotched impact strength of the sample with sauna curing treatment. The sauna cured blend derived from either high level of block (+B) but low level of random (-C) polymer or vice versa, -B and +C, would has the lower in the unnotched impact strength.

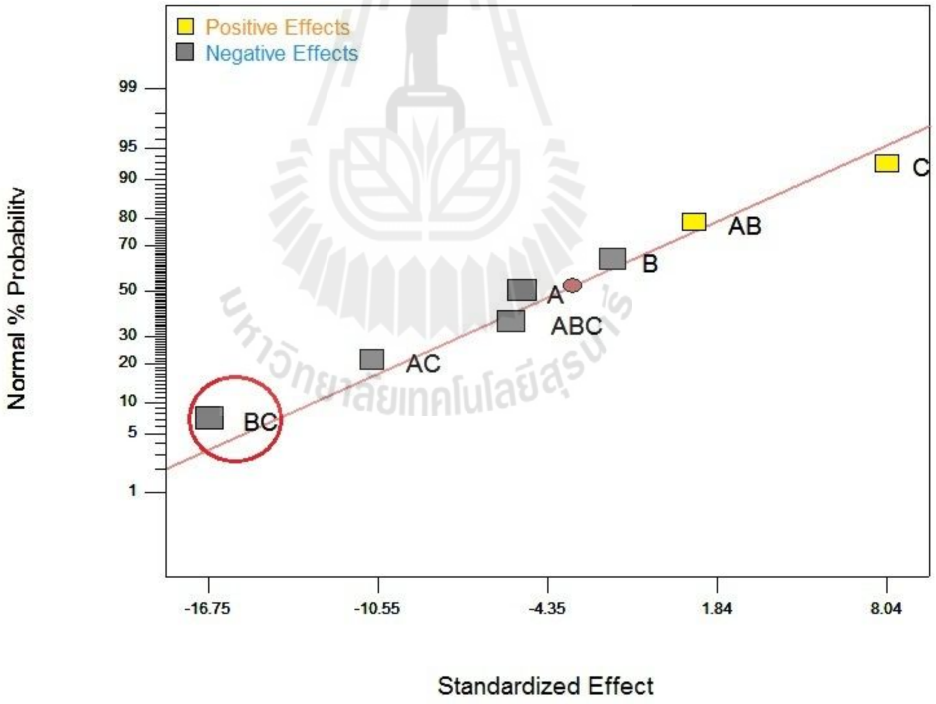


Figure 3.15 Normal probability plot of unnotched impact cured sample.

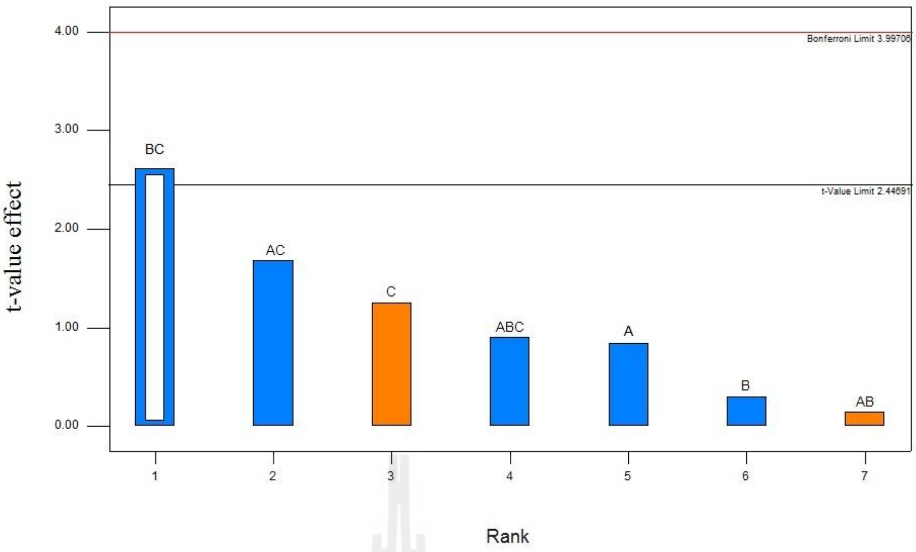


Figure 3.16 Pareto chart analysis of unnotched impact cured sample**.**

Table.3.15 ANOVA test for Unnotched impact cured sample.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	490.63	1	490.63	9.12	0.0234
BC	490.63	1	490.63	9.12	0.0234
Residual	322.91	6	53.82		
Cor Total	813.54	7			

3.5.4 Analysis of flexural properties

Flexural properties both the strength and modulus obtained by the standard testing method of the PPs blends are summarized in Table 3.16 for the samples with and without sauna curing, respectively. Typically, It seen that sauna cured has superior the flexural properties, especially the strength, of the blends.

Table.3.16 Flexural properties of PPs blends

Run	Flexural Strength(MPa)		Flexural Modulus(GPa)	
	Original	Cured	Original	Cured
1 (+,+,+)	47.54 ± 0.46	53.73 ± 0.34	0.90 ± 0.02	0.98 ± 0.01
2 (+,+,-)	47.06 ± 1.79	54.10 ± 0.50	0.93 ± 0.01	0.98 ± 0.03
3 (+,-,+)	47.75 ± 0.69	52.89 ± 0.35	0.91 ± 0.01	0.97 ± 0.04
4 (+,-,-)	49.58 ± 0.49	56.30 ± 0.59	0.95 ± 0.01	1.04 ± 0.01
5 (-,+,+)	45.82 ± 0.44	51.02 ± 0.78	0.87 ± 0.03	0.90 ± 0.00
6 (-,+,-)	45.90 ± 0.22	51.20 ± 0.47	0.88 ± 0.02	0.95 ± 0.01
7 (-,-,+)	47.65 ± 0.32	51.69 ± 0.37	0.90 ± 0.02	0.91 ± 0.02
8 (-,-,-)	47.01 ± 0.56	52.46 ± 0.76	0.88 ± 0.03	0.95 ± 0.02

The DOE analysis of the flexural strength respond on the effect of the PP homologous in the blend by mean of the normal plot for the original sample is given in Figure 3.17. The plot clearly indicates that PP (740J)(-**B**) and PP (700J)(+**A**) which show the negative and positive standardized effect, respectively, are beyond the linear trend line. Therefore, they are suspected for being the main significant effect to the flexural strength. In accordingly, from the pareto chart obtained in Figure 3.18, it is found that *t*-values for both parameters are higher than the critical value ($t_{\text{crit.}}$ = 2.57058). It means that PP (740J)(-**B**) and PP(700J)(+**A**) are the significant parameters for the flexural strength of the original blend sample. The concluded statement is confirmed by the ANOVA testing result given in Table 3.17. It is seen that the *p*-value of the experimental designed, A and B are 0.0185, 0.0269 and 0.0249, respectively. They are less than the given critical value at 0.05.

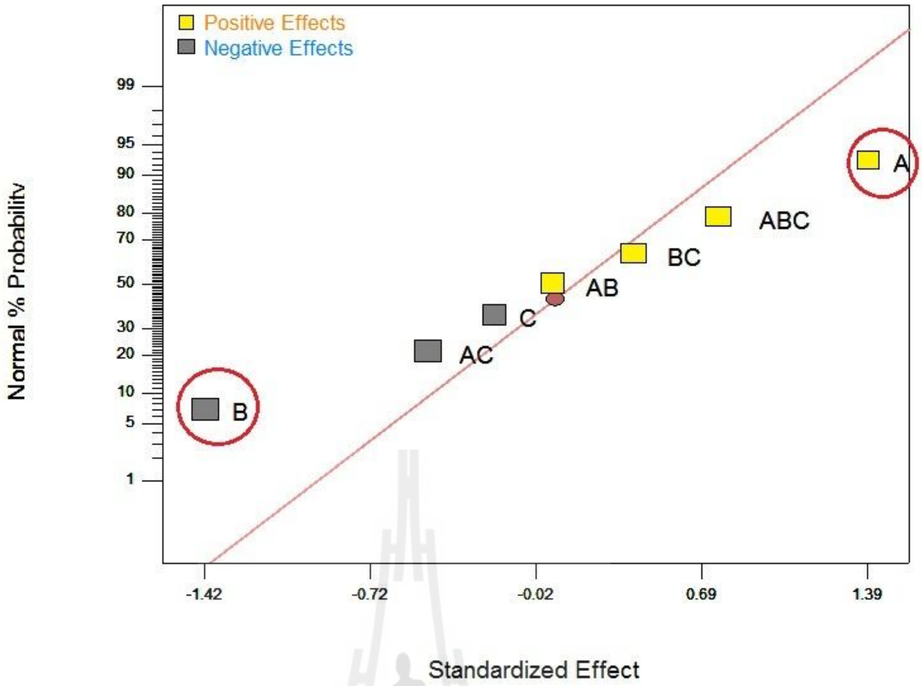


Figure 3.17 Normal probability plot of Flexural strength original sample.

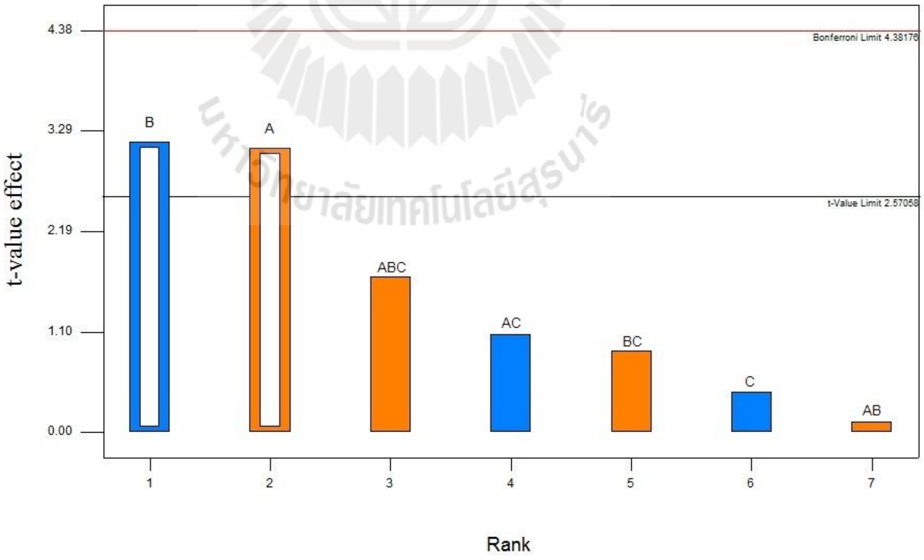


Figure 3.18 Pareto chart analysis of Flexural Strength original sample.

Taken these statistical conclusion, it can say that block copolymer, PP (740J)(-**B**), and homo polymer, PP (700J)(+**A**), have the significant effect on the flexural strength the PPs blend samples without sauna cured. It is statistically meant that, increasing the content of PP (740J) in the blend would decrease in flexural strength and, on the contrary, increasing content of PP (700J) would increase the flexural strength of the blend.

Table.3.17 ANOVA test for Flexural Strength original sample.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	7.87	2	3.93	9.82	0.0185
A-P700J	3.85	1	3.85	9.61	0.0269
B-P740J	4.02	1	4.02	10.03	0.0249
Residual	2	5	0.4		
Cor Total	9.87	7			

For the sample with sauna cured, Figure 3.19 shows the standard normal plot of the standardized effect. It is observed that only PP (700J)(+**A**) is obviously excluded from the linear points. Also, the pareto chart, Figure 3.20, indicates that *t*-value of parameter A is above the critical value. It means that this parameter is significant effect to the flexural strength of the blend. The ANOVA conclusion in Table 3.18 also reinforces that the designed model less and the parameter A are the significant effect on the flexural strength of the blend sample after sauna curing. It is meant that higher in the content of PP (700J) in the blending will superior in the flexural strength of the cured specimen.

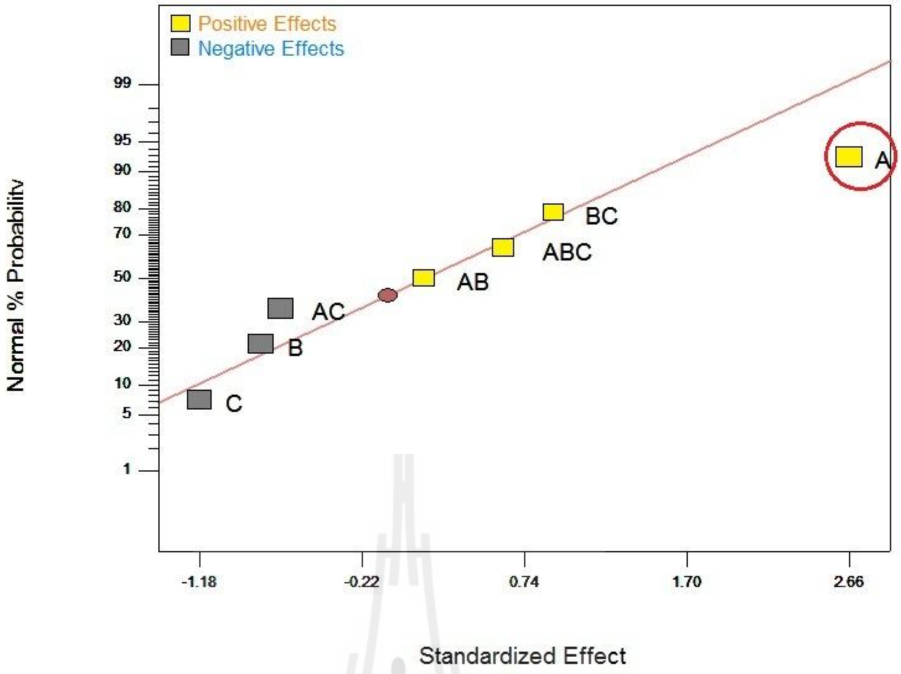


Figure 3.19 Normal probability plot of Flexural Strength cured sample.

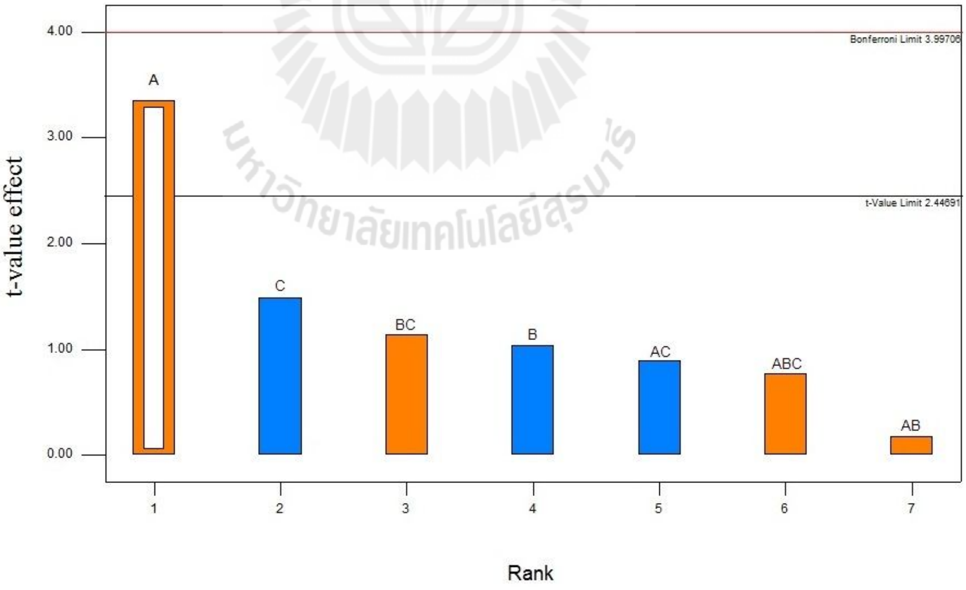
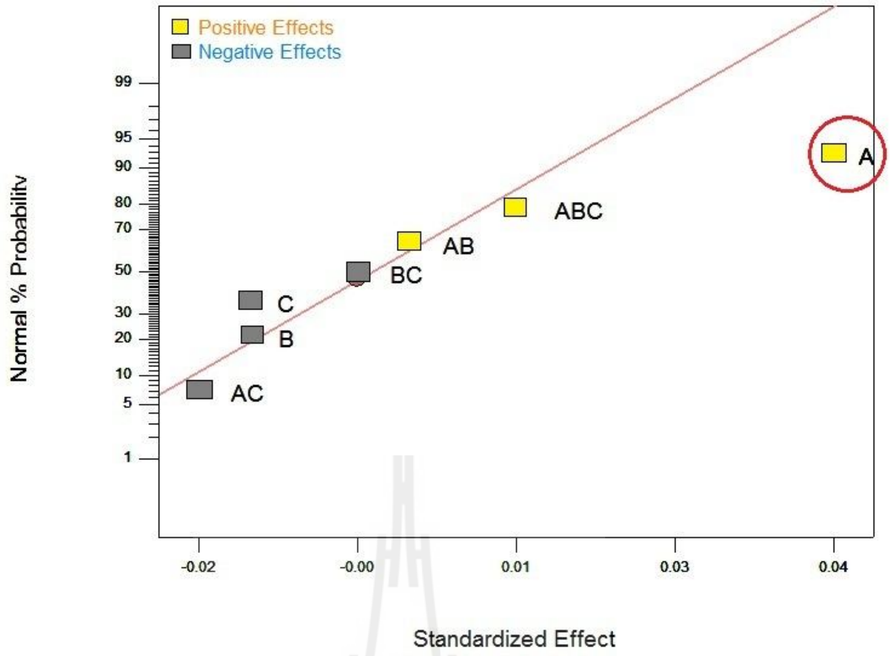


Figure 3.20 Pareto chart analysis of Flexural Strength cured sample.

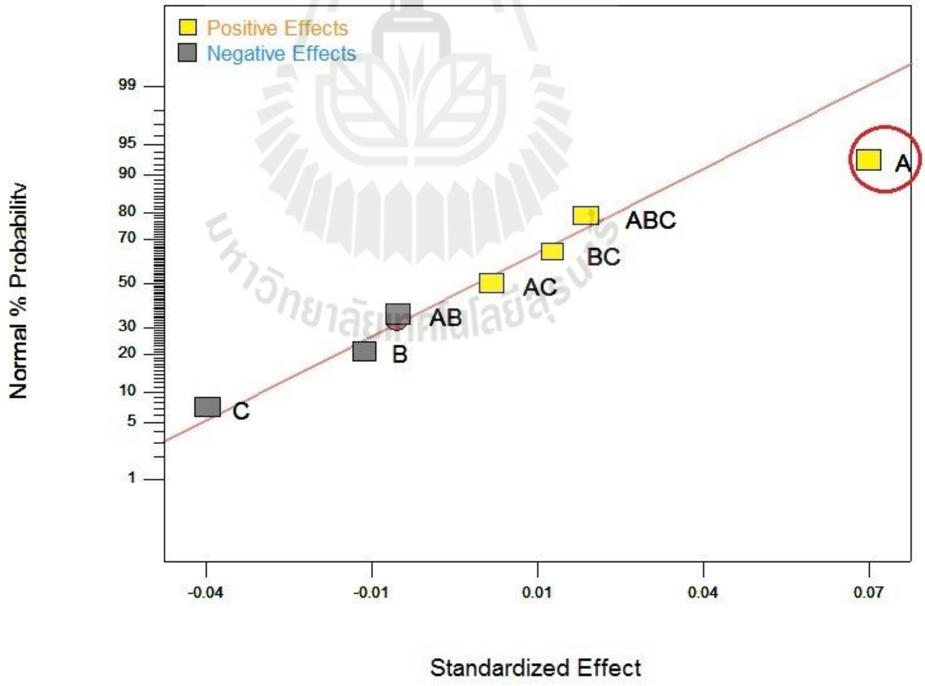
Table.3.18 ANOVA test for Flexural Strength cured sample.

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	14.18	1	14.18	11.21	0.0155
A-P700J	14.18	1	14.18	11.21	0.0155
Residual	7.59	6	1.26		
Cor Total	21.77	7			

The standard normal plots of the flexural modulus obtained from the original and cured specimen are illustrated in Figure 3.21(***a***) and 3.21(***b***), respectively. It is noticed that only homo type PP (+A) is lined outside the linear trend points for both original and cured conditions. It is the significant effect to the modulus of the blend as it is confirmed by the pareto analysis, shown in Figure 3.22(***a***) and 2.22(**b**), and also by the ANOVA testing results shown in table 3.19(***a***) and 3.19(***b***), respectively. From the conclusion of the analysis, homo PP (700J)(+**A**) is positively and significantly effect on the modulus of the PPs blend.

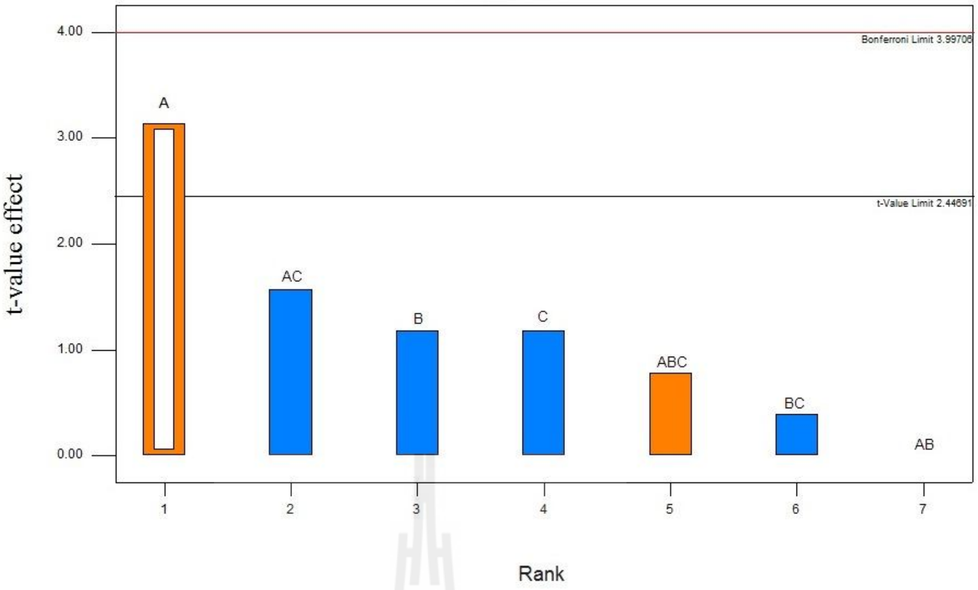


(*a*)

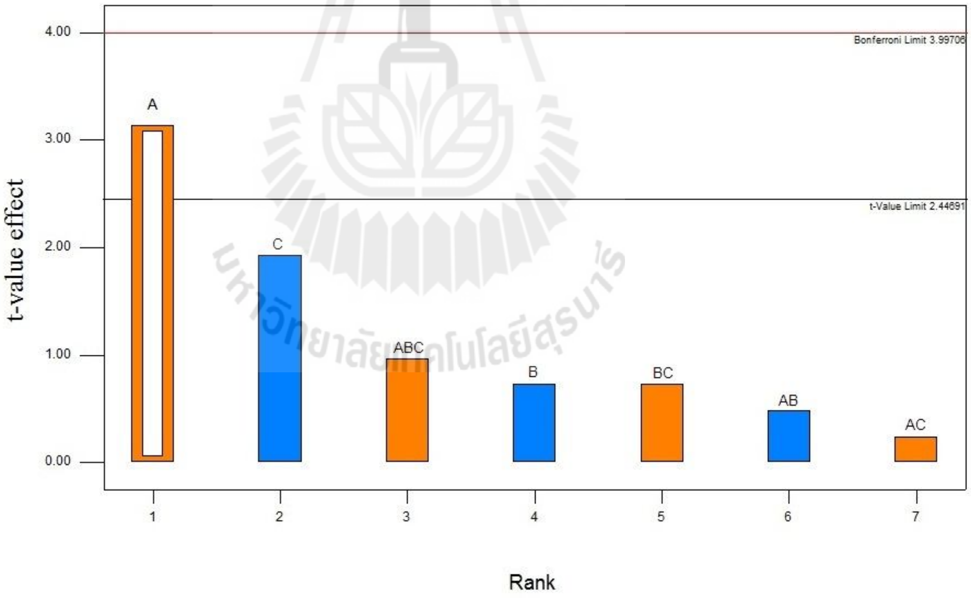


(*b*)

Figure 3.21 Normal probability plot of flexural modulus; (***a***) original and (***b***) sauna cured sample.



(*a*)



(*b*)

Figure 3.22 Pareto chart analysis of flexural modulus; (***a***) original and (***b***) sauna cured sample.

Table 3.19 ANOVA test for flexural modulus; (***a***) original and (***b***) sauna cured sample.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	3.20E-03	1	3.20E-03	9.85	0.0201
A-P700J	3.20E-03	1	3.20E-03	9.85	0.0201
Residual	1.95E-03	6	3.25E-04		
Cor Total	5.15E-03	7			

(***a***)

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	8.45E-03	1	8.45E-03	9.84	0.0201
A-P700J	8.45E-03	1	8.45E-03	9.84	0.0201
Residual	5.15E-03	6	8.58E-04		
Cor Total	0.014	7			

(***b***)

3.5.5 Regression Models

From the results of the DOE and from the analysis of variance (ANOVA) conclusions for each the respond, the regression models, which are the relationship between level of the significant parameter (s) and the respond property, can be constructed. They are summarized in Table 3.20. The obtained equations would be useful to statistically approximate the value of the respond property and the level codes, (+) and (-), of the given parameter. For example, from the HDT regressed equation for the sauna cured PPs blend is 119.57+3.52 (A). It is implied that the HDT of the sauna cured PPs blend would be equal to 123^{o}C, if high level of PP (700J)**(A** = +1) is used in the blend ingredient. The rest of the properties are also estimated in the identical manner. By using the DOE approach, the optimal formulation of PPs blend from three types of PPs can be accomplished. The mechanical and thermal properties of the blends in the present of DCP/silane can be predicted with the degree of confidence at 95%. Further investigation in term of filler addition and else to enhance the properties of PP compound in order to achieve the main ultimate target; that is PP compound having the HDT above 150^{o}C, will be continued.

Table 3.20 The predicted regression model for properties of polypropylene blend derived from ANOVA testing

Respond Properties	**Regressed models**	
	Original	**Sauna cured**
MFI	20.78-1.67(A)	na
HDT	No significant	119.57+3.52(A)
Notched impact	2.46-0.4(A)+0.32(B)	No significant
Unnotched impact	56.76-7.11(B)(C)	60.26-7.(B)(C)
Flexural strength	47.29+0.69(A)-0.71(B)	52.92+1.33(A)
Flexural modulus	0.9+0.02(A)	0.96+0.032(A)

3.5.6 Morphological observation of the PPs blends

Morphological observation by mean of SEM on the fractured surfaces of the PPs blend obtained from Run#4, #5 and #7 are illustrated in Figure 3.23 (***a***) to

3.23(*f*). The blends formula of Run#4, #5 and #7 are (+A, -B, -C), (-A, +B, -C) and (-A, -B, +C), respectively. These samples are manifested the lowest, highest and modulate notched impact strength, respectively. For the instant, it is seen that the blends are completely miscible. There is no trace of phase separation. When compare the fractured traces between the lowest and highest notched impact samples, Run#4 and Run#5, as expected, it is seen that the brittle compound show more smoother fractured traces than the tougher one. The modulate toughness, Run#7, is lined in between. However, it is difficult to distinguish between the samples with similar fracture toughness, Run#5 and Run#7. Moreover, there is no phase separation between the blending ingredients. Therefore, it is hard to draw the statement that sauna curing process either impact strength through the improvement of the interfacial adhesion between phases or the increasing in crystallinity via temperature annealing are the main causes of the change in the properties of the blends. Also, the presence of the crosslink between the polymer chains via the silane grafted intermolecular condensation reaction is still in doubt. However, from many literatures published, the crosslink reaction of the PP chains by silane/peroxide system is extremely difficult. But the chain degradation is typically occurred during the melt reaction. Therefore, the crosslink hypothesis is unlikely to occur in the present blend system.

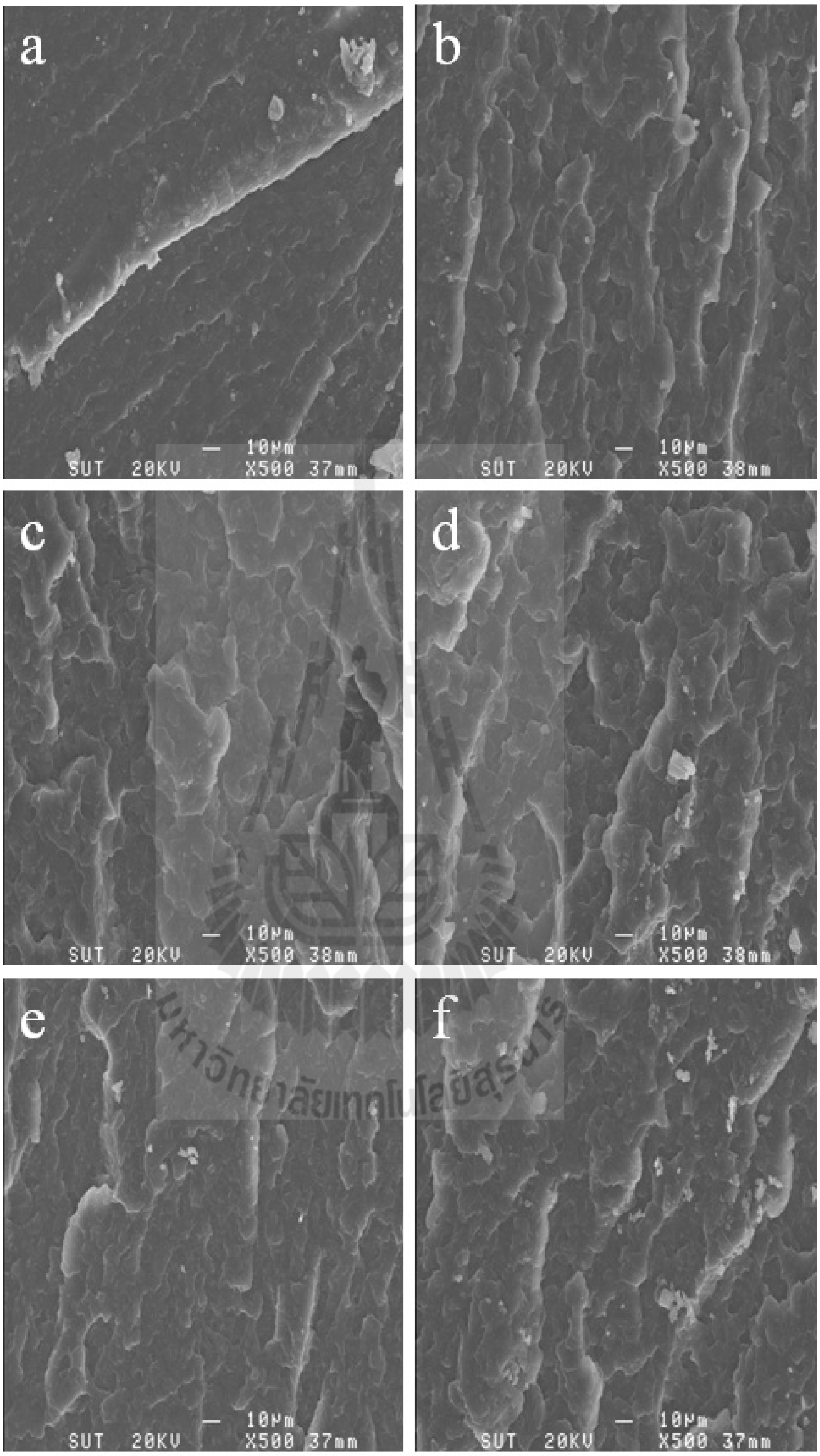


Figure 3.23 SEM micrograph of (***a***) Run#4(+,-,-)(original), (***b***) Run#4(cured), (***c***) Run#5(-,+,+)(original), (***d***) Run#5(cured), (***e***) Run#7(-,-,+)(original) and (***f***) Run#7 cured, at magnification of X500.

3.6 Conclusion

The PPs blend, with addition of peroxide/silane induce condensation, of PP700J (homo polymer)(**A**), PP740J (block copolymer)(**B**) and PP750J (random copolymer)(**C**) was performed. By using the DOE method, statistical analysis approach, the equations to predict the blends properties and the level of PPs contents were constructed. It was found that flow ability of the blends by mean of MFI, was significantly and negatively affected by homo PP (-**A**). High level of loading the homo type PP will lower the flow ability of the blends. The designed parameters did not have the significant effect on the HDT of the blends without sauna curing. The sauna cured specimen was positively affected by homo PP (+**A**). It would generate the material with higher HDT if blending with high level of loading homo PP. Blending the PPs with low level content of homo PP (-**A**), and high level of block PP (+**B**) or vice versa, would result in high impact strength for the original sample. However, sauna cured sample for the notched impact strength did not have the significant effect from the given parameters. The interaction between block and random PPs(-BC) had the negative and significant effect on the unnotched impact for both original and sauna curing treatment the blends. The flexural strength of the blend without sauna cured found that increasing the content of block PP (-**B**) caused the decreasing in flexural strength and, on the contrary, increasing the content of homo PP (+**A**) increased the flexural strength of the blend. Homo PP (+**A**) had the significant effect on flexural strength of after sauna cured. Higher in the content of homo PP showed the superior result. The flexural modulus of both original and cured samples indicated that homo PP (+**A**) had positive and significant effect on the modulus of the blends. Morphological observation by mean of SEM on the fractured surfaces of the PPs blend suggested that the compounds are miscible. There were no traces of phase separation.

3.7 References

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CHAPTER IV

EFFECT OF PEROXIDE AND PP COPOLYMER IN CROSSLINKED PP COMPOUND

4.1 Abstract

The enhancement of thermal properties by mean HDT and also mechanical properties by mean impact strength and flexural properties of the polypropylene mixed with UHMWPE was explored. The attempting methods to improve the properties of the material were varying of DCP in silane/peroxide crosslink system and also blending the homo PP with its block copolymer. Polymer melt mixing was performed in the continuous process using co-rotation twin screw extruder. The test specimens were prepared by injection molding and they were divided into two sets of samples; original and sauna cured. The morphology of the polymer compound was also examined through the SEM micrograph. The results found that the deteriorating in the toughness of the PP blend was vastly influenced by chain degradation via the free radical chain scission reaction. The PP/UHMWPE blend using the combination between homo and block copolymer PP matrix to improve the material toughness was also ineffective. The material became more brittle with increasing the copolymer fraction. The chain degradation through the free radical induced chain scission reaction was suspected for the major drawback properties.

4.2 Introduction

The radical grafting of a monomer on PP in the presence of a peroxide initiator is often accompanied by the degradation of the PP backbone. It has been well established that a free radical grafting process of PP starts with the formation of macroradicals by a so called hydrogen abstraction mechanism. These macroradicals may subsequently follow two competing pathways. They can either initiate the grafting of monomers or undergo chain scission, which is the main side reaction, perhaps major reaction, during the process. It is recognized that the grafting of PP with unsaturated monomers is easily carried out in a narrow temperature range from 80 to 150 ^{o}C (Hu, M., 2006). Previous study had been published on the dependence of peroxide/silane crosslinked and the properties of crosslinked polyolefin on reaction parameters.

Crosslinking of polyolefins can applied to all polyolefin types; however, the vast majority of the publications are concerned with polyethylenes. Few studies concerning the crosslinking of polypropylene (PP) has been reported. Crosslinking of PP gained no practical importance. This is most likely a consequence of the nature of the PP chain structure (Liu, N.C. 2000). During the crosslinking process, PP chain scission has accompanied as a main side reaction. This would negatively influence the properties of the crosslinked product (Hu, M., 2006). Polypropylene (PP) is widely used in many sectors of industry. And it is one of the most used polyolefins because it has many advantages such as ease of processing, superior in mechanical properties, light weight. But some of its properties still need to be improved, such brittleness and relative moderate service temperature compare with other engineering polymers.

Crosslinking provides an important method to improve the mechanical properties, thermal and chemical resistance of the olefin based polymers.

From previous chapters, the statistical study concluded that homo PP was positive and significant effect on the MFI, HDT and flexural properties of the PPs blends. However, the improved properties were not reached the main target, HDT equal to 150°C with decent or retaining the outstanding properties of PP. In this experimental, the PP matrix used was based on homo PP. The methods to enhance of properties, especially HDT and toughness, were the main focus. There were the varying of DCP content in the crosslink system and the blending homo with block copolymer PP.

4.3 Research methodology

4.3.1 Materials

Materials used in the study was PP homo polymer, PP 700J. It was supplied from SCG Chemical Co., Ltd. PP block copolymer with 1% ethylene content, PP740J, was also used as impact modifier. It supplied from SCG Chemical Co., Ltd. In practical, the block copolymer PP means that the homo PP matrix is modified with the rubber particle, or impact modifier rubber, of block copolymer PP chain. It does not mean that all the chain is blocked with ethylene segment. The ultra high molecular weight polyethylene (UHMWPE), UH900, was available from Asahi Chemical Industry. Co., Ltd. The properties of the polymers employed in this work as reported from the manufacturers are summarized in the Table 4.1 to 4.3, respectively.

Dicumyl peroxide (DCP) as free radical initiator was also added into the compound ingredient. The decomposed and generated radical from this initiator is relative stable at as high temperature as above 120°C. The silane coupling/grafting agent used was vinyl trimethoxy silane (VTMS), Silquest® A 171. It was use as complementary crosslink agent. The chemical was purchased from Optimal Tech Co., Ltd. The peroxide/silane crosslink process is commonly undergone condensation reaction via siloxyl/water condensation known as sauna incubation or moisture incubation. High temperature, normally slightly above T_g, was performed to accelerate the condensation reaction to completion within a short period of time. Properties of the chemical reagents were reported in chapter 3.

All chemicals and polymers were directly used without further purification or modification.

Table 4.1 Physical properties of the PP homo polymer(P700J)

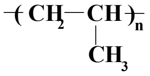
Physical Properties	**Homo PP (PP 700J)**
Melt Flow Rate(230/2.16), g/10 min	12
Density, g/cm^3	0.91
Chemical structure	 $-\!(CH_2-\underset{CH_3}{\underset{\vert}{CH}})_n-$
Melting Point, °C	163
Heat deflection temperature (@0.455MPa), °C	110
Flexural Modulus, MPa	1422
Notched Impact, kJ/m^2	3.75

Table 4.2 Physical properties of the PP block copolymer (PP 740J)

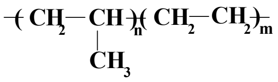
Physical Properties	**Block PP (PP 740J)**
Melt Flow Rate(230/2.16), g/10 min	27
Density, g/cm^3	0.91
Chemical structure	 $-\!(CH_2-\underset{\underset{CH_3}{\mid}}{CH})_n\!(CH_2-CH_2)_m-$
Melting Point, ^{o}C	163
Heat deflection temperature (@0.455MPa), ^{o}C	110
Flexural Modulus, MPa	1225
Notched Impact, kJ/m^2	10.0

Table 4.3 Properties of UHMWPE (UH900)

Properties	**Test Method**	**Value, Unit**
Average molecular weight	Viscosity method	33 X 10^4
Melting temp	DSC	136 ^{o}C
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^{o}C

4.3.2 Compound formula

From the previous report, the statistical outcome showed that homo PP was positive and significant effect on the MFI, HDT and flexural properties of the PPs blends. In this experimental, the PP matrix used was based on homo PP. For the sake of the bending toughness of the PP compound, 10 phr of ultra high molecular weight polyethylene (UHMWPE) was added. It could enhance the impact strength of the polymer compound. In this report, there are two research topics related to the properties improvement of the PP blends and compounding. These include;

(1) Effect of DCP contents.

and (2) Effect of PP block copolymer added as the impact improver.

4.3.3 Sample preparation

4.3.3.1 Compounding process

Polypropylene was dry blended with dicumyl peroxide (DCP) in plastic bag and vigorously shaken and placed in warmed oven at 80^{o}C for 5 min to allow DCP to liquidize. The ingredient was again vigorously shaken in order to the pellets polymer was completely coated by liquidized DCP. Then, 2.0 phr of liquid vinyl trimethoxy silane (VTMS) was added into the wet polymer. Then, it was in corporately blended with the powder of UHMWPE. The compound was achieved in closely intermeshing co-rotation twin screw extruder, with L/D ratio and screw diameter of 20/1, 25 mm, respectively. The screws were comprised of three triple kneader disc segments. The extruder barrel temperature profile from feed to die zones, five zones, was electronically controlled at 190^{o}C. The screw speed at 10 rpm was constantly monitored that give rise to the mixing residence time of approximately 4 minutes.

4.3.3.2 Sample preparation

The air cooled extruded strand was granulated in to pellet using mechanical jaw crusher. The compound pellet was dried in the vacuum oven at 80°C for 2 hr to remove the residual moisture before injection. Samples were injection molded on the Tederic TRX60c injection molding machine. The barrel temperatures were set at 160, 165, 170, 170 and 170°C from feed to nozzle tip, gradually. The mold temperature and cooling time were set at 40°C and 30 seconds, respectively.

4.3.3.3 Sauna treatment of PP sample

The injection molded specimens were divided into 2 categories of samples. One was allowed to anneal at room temperature for at least a day before testing. It was assigned as original sample in this thesis report. The other was incubated in the water vapor saturated oven at 105°C for 12 hour to accelerate and ensure the competition of the silane/moisture crosslink condensation reaction. It was finally allowed to cool down at room temperature for a day priority to conduct the test. This type of sample was named as the sauna cured or shortly as cured sample.

4.4 Properties measurement and analysis

4.4.1 Melt flow index

The rheological property of the polypropylene blends by mean of melt flow index (MFI) was perform and test in accordance with ASTM D 1238 by using the Kayeness melt flow indexer model 4004. The pellet sample obtained was dried at 80°C for at least 2 hrs in vacuum oven. Testing samples was allowed to melt at 170°C and driven through the capillary die (Ø 1 mm.) using the piston load of 2.16 kg. The melting time was set at 360 seconds. Three cuts of extrudate were performed with the cut times of 15 second. The weight of the extrudate was computed into the melt flow index (MFI) figure in the standard unit of g/10min.

4.4.2 Heat deflection temperature

Heat deflection temperature (HDT) of the polypropylene blends/compound for the original and sauna cured samples were measured in accordance with ASTM D 648. The standard testing machine from Atlas, model HDV 1, was employed. Samples were tested in the edgewise position, with the support span length of 100 mm, a simple beam with the load applied at its center of the spanned sample to give standardized stress of 0.455 MPa (66 psi). 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). It was immediately recorded when the specimen had been deflected to 0.25 mm or 0.01 inches as it was monitored by dial gauge. This temperature was recorded as the deflection temperature under given flexural load. Three samples were examined and the average value was reported.

4.4.3 Impact testing

Unnotched and notched impact strengths, in Izod mode, of both the original and sauna cured samples were tested using ASTM D 256 as standard testing procedures. The injection molded specimen with the dimension of 4x13x63 mm (WxLxH) was notched using the standard notching machine. The identical injected samples were also tested without notching. 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 mode, respectively. The Atlas impact testing machine, model BPI, was employed. The impact strength values were calculated in kJ/m^2 that was computed from lost impact energy divided by the cross section area at the fractured point.

4.4.4 Flexural properties measurement

Flexural properties both strength and modulus of the polypropylene compound for both original and sauna cured sample were examined in accordance with ASTM D 790. The testing machine, 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 computerized control. The test specimen was placed plat wise to the bending load. The test was conducted at room temperature in normal atmospheric condition. At least five piece of specimen were tested. The flexural properties both strength and modulus were taken, averaged and reported.

4.4.5 Morphological observation

Morphology of the fractured surface of the polypropylene sample was examined using scanning electron microscope (SEM). The fractured specimen obtained from notched impact test pieces was cut in to small piece. It was then attached onto the SEM sample holder. The samples were coated with layers of gold for 5 minutes 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 Effect of DCP content on the PP/UHMWPE blends

Table 4.4 summarizes the PP/UHMWPE blend formula. The DCP content was varied from 0.01 to 1.0 phr in order to find out its effect on the properties of the PP blend. The UHMWPE and silane were kept constant at 10 phr and 2.0 phr in correspondence with homo PP, respectively. The PP/UHMWPE blend without DCP and silane was used as reference material. The standard test results of the blends in corresponding with the DCP addition are being discussed.

Table 4.4 The blend formulation of PP/UHMWPE and the DCP content.

Run No.	**PP (homo) (g)**	**UHMWPE (g)(phr)**	**Silane (g)(phr)**	**DCP (g)(phr)**
1	300	**30**(10)	**0**(0.0)	**0.00**(0.0)
2	300	**30**(10)	**6**(2.0)	**0.03**(0.01)
3	300	**30**(10)	**6**(2.0)	**0.15**(0.05)
4	300	**30**(10)	**6**(2.0)	**0.30**(0.10)
5	300	**30**(10)	**6**(2.0)	**0.60**(0.20)
6	300	**30**(10)	**6**(2.0)	**0.90**(0.30)
7	300	**30**(10)	**6**(2.0)	**1.5**0(0.50)
8	300	**30**(10)	**6**(2.0)	**3.0**0(1.00)

4.5.1.1 Melt flow index

Rheological properties by mean of melt flow index (MFI) of the blends formulation as given in Table 4.4 were tested and the test results are summarized in table 4.5 and also plotted with respect to DCP the content in Figure 4.1. It is seen that the MFI is exponentially increased with increasing the DCP content for both in the original and after sauna cured specimen. At the given peroxide concentration for all formula, it is noticed that the flow index was decreased after the sauna incubation. The increasing in the melt flow index with increasing the DCP means that the viscosity of the blend was decreased. This phenomenon is very commonly observed for adding the free radical initiator into the PP, especially the homo type polymer. PP chain scission, degraded chains, was easily occurred by the free radical attacking. The molecular weight value was decreased as the peroxide concentration was increased. It means that radical induced PP chain degradation is the main reason for the vastly increasing in the MFI. However, in the present of silane coupling agent the degraded chains could be combined through the silane/moisture condensation. The increasing in the molar mass of the polymer would be resolved and hence decreasing in the melt flow index, higher in melt viscosity.

Table 4.5 MFI of PP/UHMWPE blends

DCP Content (phr)	**MFI (170/2.16)**	
	Original	**Cured**
(0)	0.15 ± 0.01	0.14 ± 0.07
(0.01)	0.83 ± 0.21	0.40 ± 0.07
(0.05)	3.83 ± 0.41	2.02 ± 0.37
(0.10)	7.84 ± 0.44	5.37 ± 0.11
(0.20)	23.92 ± 0.49	19.96 ± 0.39
(0.30)	40.54 ± 1.32	29.35 ± 0.72
(0.50)	64.61 ± 2.05	46.20 ± 6.65
(1.00)	154.48 ± 7.75	82.70 ± 2.81

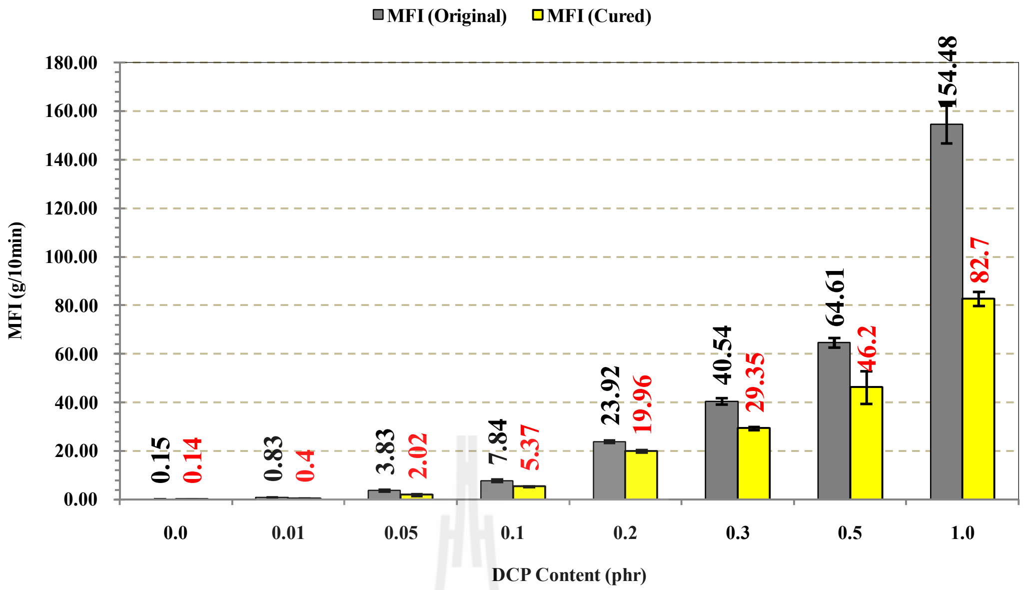


Figure 4.1 Effect of DCP on MFI of PP/UHMWPE blends

4.5.1.2 Heat deflection temperature

The HDT of PP/UHMWPE blends in the presence of silane/DCP are reported in Table 4.7. The plot of the test values in corresponding with the DCP used is obtained and shown in Figure 4.2. The results found indicate that the HDT of the blends with addition of silane/DCP is generally raised with increasing the DCP concentration, especially for the sauna cured sample. Except for that the original blends having DCP above 0.50 phr where the tested HDT are lowered. The results are contradicted with the MFI explanation earlier. Commonly, decreasing in the molecular chain, higher in MFI, would inferior in the thermal properties of polymer. According to the HDT outcome which is slightly increased with the decreasing of the chain, the chain crystallinity might be taken into consideration. Within the critical molecular weight range, the shorter chain of PP, the more likely and easily of the chain to be crystallized. Therefore, the HDT would be increased with increasing in the polymer crystallinity. On the other hand, the rising in the HDT value with increasing the DCP content of the sauna cured samples is two folds hypothesis explanation. The first one is the short chain crystallinity and the second is the chain recombination through the silane/moisture induced condensation reaction. The later would cause the chain length to expand or perhaps crosslink.

Table 4.6 HDT of PP/UHMWPE blends

DCP Content (phr)	**Heat deflection temperature(^{o}C)**	
	original	**cured**
(0)	99.0 ± 4.6	122.4 ± 0.7
(0.01)	94.7 ± 4.4	117.9 ± 1.0
(0.05)	92.2 ± 3.8	117.8 ± 1.2
(0.10)	96.1 ± 1.6	121.9 ± 0.4
(0.20)	95.1 ± 1.9	121.8 ± 0.3
(0.30)	98.0 ± 0.7	126.3 ± 0.6
(0.50)	92.3 ± 3.8	126.7 ± 0.5
(1.00)	91.1 ± 1.2	127.5 ± 0.4

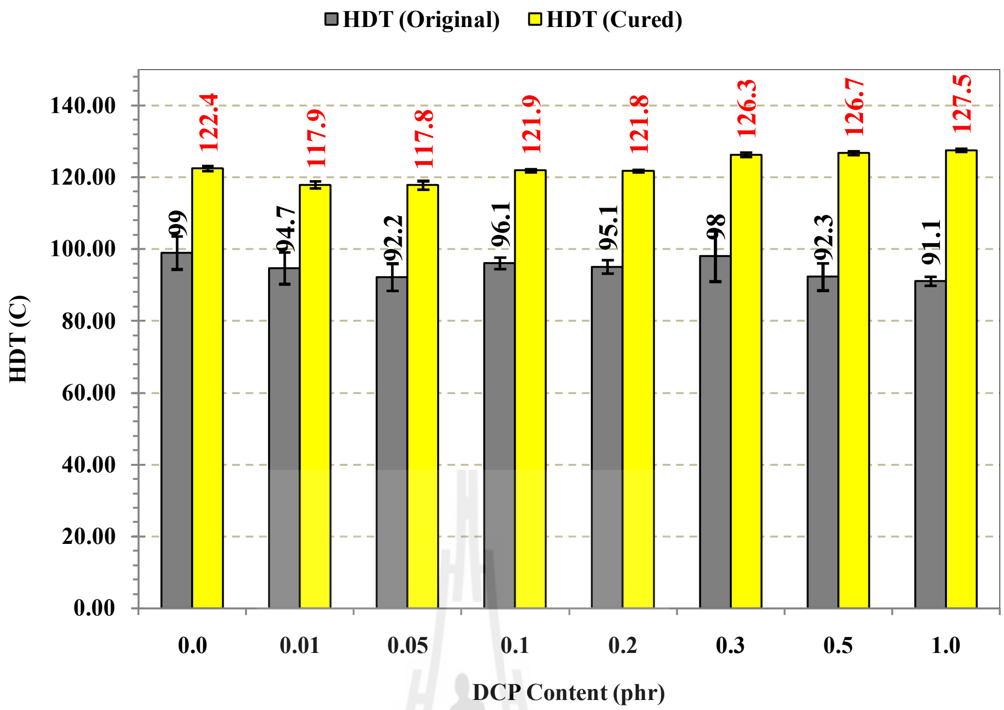


Figure 4.2 Effect of DCP on HDT of PP/UHMWPE blends

4.5.1.3 Impact strengths

Notched and unnotched impact strengths of the PP/UHMWPE blends tested by the standard method are summarized in Table 4.7 and plotted with the DCP contents in Figure 4.3, respectively. It is observed that both notched and unnotched impact strengths were lowered with increasing the DCP loading as it is expected. Because from the previous discussion, the chain scission caused by the free radical attack was suspected and evidenced. Therefore, the dramatic decreasing in the toughness of the samples by mean of the impact strengths would be obviously seen as the molar mass of PP chain is decreased. These impact results enlighten that the chain scission by the free radical degradation reaction resolved from the added peroxide initiator highly possibility to be occurred during the melt blending.

Table 4.7 Summarized of DCP content on Impact strength

DCP Content (phr)	Notched Impact Strength(kJ/m^2)		Unnotched Impact Strength(kJ/m^2)	
	Original	**Cured**	**Original**	**Cured**
(0)	2.08 ± 0.21	1.63 ± 0.19	69.97 ± 11.66	82.29 ± 6.94
(0.01)	2.28 ± 0.21	2.32 ± 0.28	74.32 ± 3.47	80.77 ± 10.42
(0.05)	2.16 ± 0.24	2.33 ± 0.14	48.97 ± 19.33	39.13 ± 15.62
(0.10)	1.74 ± 0.20	1.68 ± 0.24	42.16 ± 8.04	46.21 ± 20.58
(0.20)	1.15 ± 0.11	1.39 ± 0.20	29.62 ± 8.33	36.55 ± 3.70
(0.30)	1.26 ± 0.11	1.55 ± 0.13	25.55 ± 8.81	35.43 ± 6.60
(0.50)	1.01 ± 0.11	1.01 ± 0.11	24.76 ± 6.04	30.56 ± 4.75
(1.00)	0.97 ± 0.17	0.97 ± 0.17	17.06 ± 3.35	14.37 ± 5.48

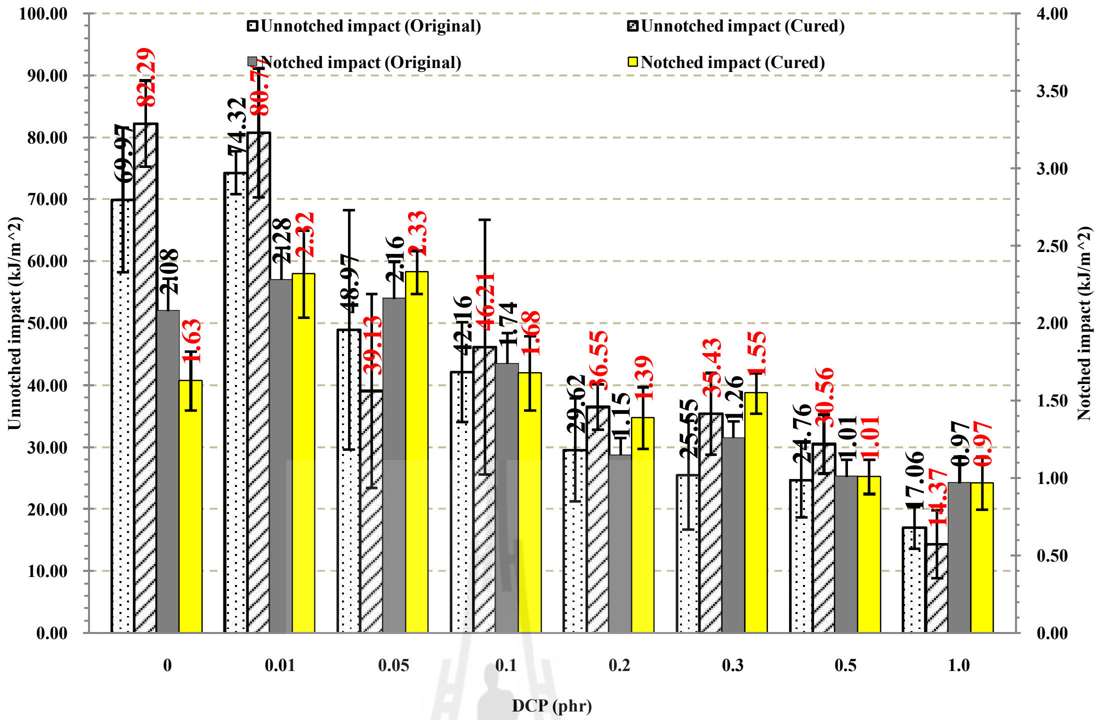


Figure 4.3 Impact strength of DCP content on the PP/UHMWPE blends

4.5.1.4 Flexural properties

Similar to those impact strengths, the flexural properties by mean of the strength and modulus of the blends as summarized in Table 4.8 and also plotted in Figure 4.4, respectively, they confirm that the bending toughness resistance of the materials is decreased with increasing the DCP addition. The test results is illustrated that the strength is decreased but the modulus is slightly increased with increasing the DCP. This observation is the common symptom of the more brittle material. So, the decreasing in the PP chain induced by the free radical chain scission does cause the blended material inferior in the toughness. Even though, the sauna cured treatment does fractionally higher the flexural strength and modulus but it cannot be overcame the incompetency of the properties due to the chain shortened. It means that the increasing in the chain by silane/moisture chain recombination through the condensation reaction and also the increasing in the chain crystallinity via the sauna prolonging do not have enough effect to compensate the loss of the toughness by the chain degradation via free radical scission reaction.

Table 4.8 Flexural properties of the PP/UHMWPE blends

Run	**Flexural Strength(MPa)**		**Flexural Modulus(GPa)**	
	Original	**Cured**	**Original**	**Cured**
1 (0)	56.79 ± 0.40	61.04 ± 0.70	1.18 ± 0.02	1.20 ± 0.03
2 (0.01)	56.73 ± 0.26	61.38 ± 0.24	0.87 ± 0.02	0.92 ± 0.02
3 (0.05)	55.25 ± 0.48	59.72 ± 0.92	0.82 ± 0.03	0.89 ± 0.04
4 (0.1)	54.62 ± 0.38	59.32 ± 0.64	1.10 ± 0.02	1.17 ± 0.03
5 (0.2)	52.73 ± 0.44	56.49 ± 2.10	1.08 ± 0.04	1.19 ± 0.02
6 (0.3)	50.26 ± 0.91	54.45 ± 1.09	1.10 ± 0.02	1.19 ± 0.02
7 (0.5)	42.65 ± 4.28	46.48 ± 1.67	1.11 ± 0.05	1.22 ± 0.02
8 (1.0)	33.68 ± 1.56	39.68 ± 4.35	1.06 ± 0.05	1.16 ± 0.03

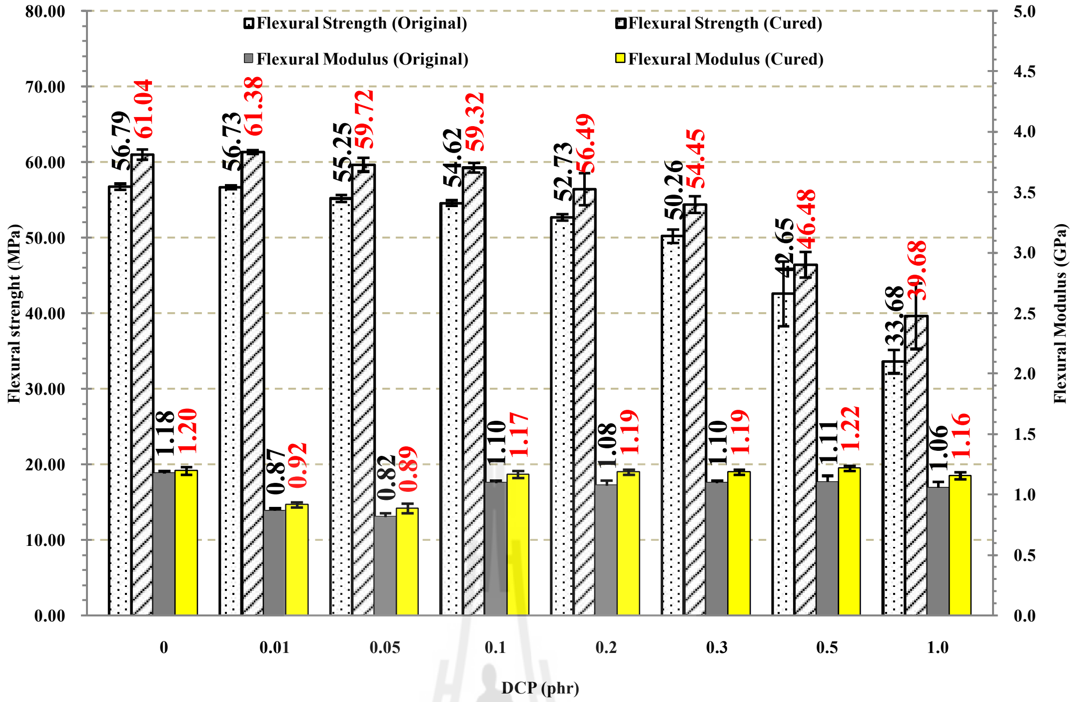


Figure 4.4 Effect of DCP content on flexural properties of the PP/UHMWPE blends

4.5.1.5 Morphological of PP/UHMWPE blends

Figure 4.5(***a***) to 4.5(***f***) present the SEM photographs, at X500, of the PP/UHMWPE blends fractured surface before and after sauna incubation, respectively. From the SEM photographs, the UHMWPE phase is obviously seen on the PP matrix phase. It is indicated that the UHMWPE particles could not be softened or molten during the melt mixing. This high molecular weight polymer has extremely high fusion temperature, normally above 300°C. Therefore, mixing the blends at 190°C, as performed in this study, the high molar mass particle would not be able to fuse into the PP phase. Closer observation on the interfacial adhesion between the UHMWPE and PP phase in the present of silane/peroxide addition as shown in figure 4.5(*c*) to 4.5(*f*), the improvement of the bonding adhesion of the UHMWPE particle with PP phase with increasing of DCP used is hardly observed. However when compare with the system without addition of DCP/silane the adhesion between PP matrix phase and UHMWPE particle is very poor as the trace of pull out hole of the UHMWPE is obviously seen. It is also difficult to differentiate in term of the good adhesion between the polymer particle and PP phase for the systems with increasing the peroxide incorporating. However, when looking at the fracture traces of the PP phases, it is noticed that the brittle fracture phenomenon is evidence when increasing the DCP loading. According to the SEM investigation, it manifests that UHMWPE phase is separated from the PP matrix. Because of it could not be fused with the matrix phase at the given mixing temperature. Moreover, adding of silane/DCP into the blend system, it does not only improve the interfacial addition between the polymers phases but also reducing the chain length of PP via free radical degradation reaction. These disadvantages phenomena cause the material become more brittle.

According to the results data derived from this experiment, it can conclude that increasing in the DCP concentration on the silane/DPC system for the PP/UHMWPE blending, it caused the vast tendency in the chain degradation via the free radical chain scission reaction. As the result, the mechanical properties especially toughness of the blends were let down. The phase separation between UHMWPE and PP was observed when the direct blending of UHMWPE with PP at low mixing temperature. Therefore, the toughening effect of UHMWPE on PP materials could not be achieved and it cannot contribute the positive effect to the chain degraded PP/UHMWPE blends.

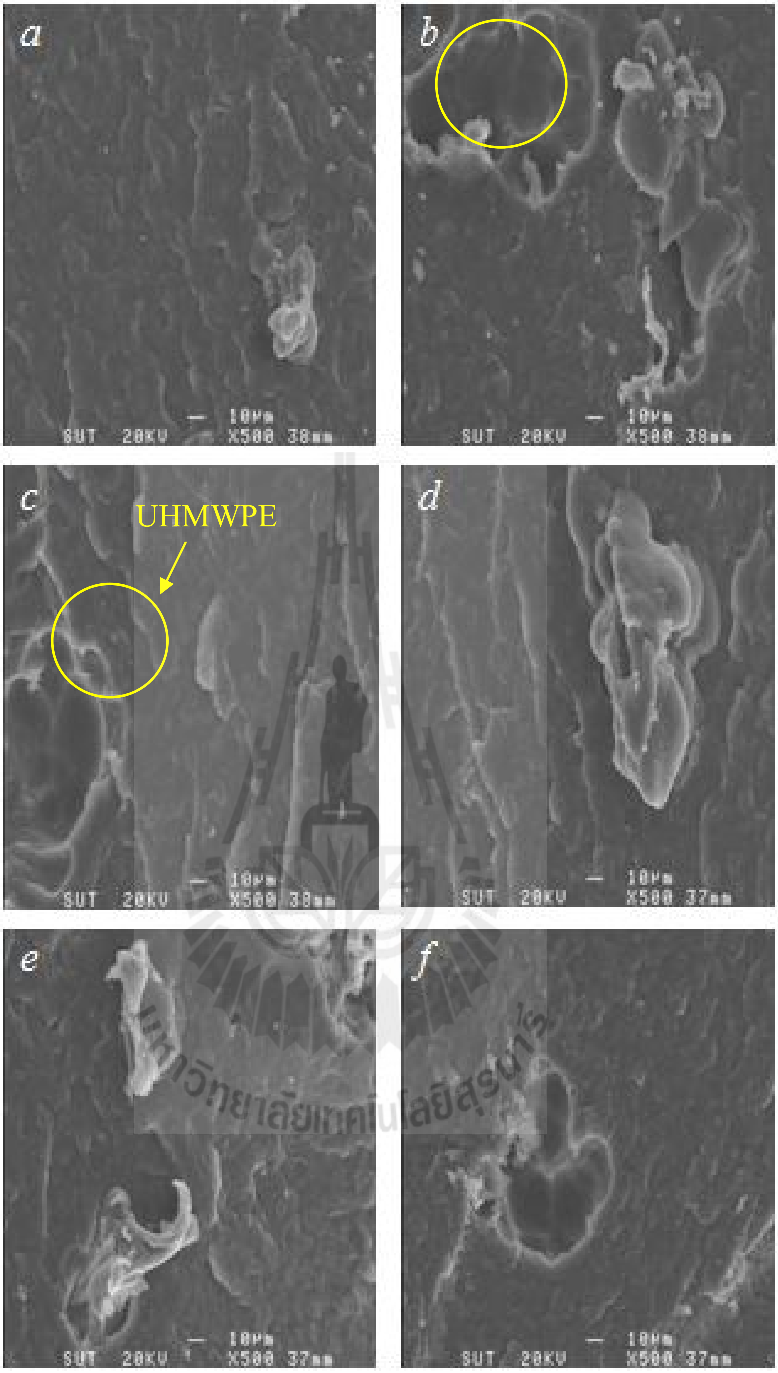


Figure 4.5 SEM of fractured surface of PP/UHMWPE blends;

(***a***) the original blend without DCP and (***b***) after sauna curing,

(***c***) original PP/UHMWPE with 0.01 phr of DCP and (***d***) sauna cured,

and (***e***) original PP/UHMWPE with 1.0 phr of DCP and (***f***) cured sample

4.5.2 Adding PP block copolymer as the blend toughener

From the previous discussion, increasing the DCP concentration had dramatically deteriorated the toughness of the blends. It was due to the PP chain shortening caused by the free radical scission reaction which is the common phenomenon characteristic of PP chain in presence of silane/DCP, especially homo type PP. Propylene ethylene copolymer is commercially used for toughening the polymer and the added copolymer is normally called "impact modifier". It has, of course, excellent compatibility with the PP chain. In the industrial practice, ethylene monomer is copolymerized with propylene chain as block copolymer molecule in the separated reactor tank. Then, it is, the block chain, transferred into another polymerisation reactor of homo PP. The block polymer is mixed and dispersed as impact modifier in the homo PP matrix to improve the impact toughness of PP polymer. In this study, it was purely science interest to incorporate the commercially available block copolymer PP (PP740J) by blending with homo type PP chain. In hope, the block copolymer could contribute its outstanding toughness into the blends. Moreover, consumption of the generated free radical during melt mixing by the ethylene segment would ease the chain degradation of homo PP. The designed experimental formulae for manufacturing the blend sample are shown in Table 4.9. The fraction of UHMWPE, silane and DCP were kept constant at 20, 2.0 and 0.1 phr, respectively. The amount of the copolymer added was varied from 10 to 40 phr with respect to the homo PP for each blend. The melt blending was conducted at 190^{o}C as same as the previous experiments. The properties of the blends tested by the standard testing method are concluded and being discussed in this section.

Table 4.9 The designed formulation of the PP/UHMWPE blends and PP copolymer contents

Batch No.	**P700J (g)(phr)**	**P740J (g)(phr)**	**UHMWPE (g)(phr)**	**Silane (g)(phr)**	**DCP (g)(phr)**
1	300	0	60(20)	0 (0)	0 (0)
2	300	30(10)	60(20)	6 (2.0)	0.3 (0.1)
3	300	60(20)	60(20)	6 (2.0)	0.3 (0.1)
4	300	90(30)	60(20)	6 (2.0)	0.3 (0.1)
5	300	120(40)	60(20)	6 (2.0)	0.3 (0.1)

4.5.2.1 Melt flow index

Melt flow index of the PP blends measured at 170/2.16 are summarized in Table 4.11 and Figure 4.6 is the plot of MFI and copolymer content, respectively. It is found that MFI is gradually increased with increasing the PP block copolymer fraction regardless to the sample treatment, with and without sauna curing. It is not much surprising result because according to the data sheet form the manufacturer, MFI of PP block copolymer is much higher than PP homo polymer. Therefore, if there is no any mean of interaction between the blend ingredients, the melt flow rate of the blend would be increased with increasing the higher melt flow rate copolymer fraction. The decreasing in the MFI of the blends after sauna curing, it might be due to the chain combining of the degraded chain through the silane/moisture condensation reaction. Attempting to establish the rule of mixture between these two polymers was conducted. Equation 4.1 is the adopted rule of mixture used for the calculation (U. Meekum, 2012). Taken MFI of homo and copolymer PPs measured at 170/2.16 which are 2.74 and 5.95 g/10 mins, respectively. The calculated MFI of the blends are also included in Table 4.10. From the calculation values, it is seen that the tendency of the MFI of blends are the same trend as found in the measurement values but the calculated is much lower than the measured one. This may because of the chain degradation effect of the blend by adding the peroxide during the mixing process. Hence, the melt flow rates of the blends are increased. More over adding the UHMWPE into the blends do not increase the flow resistance because the high molecular weight added does not infuse into the continuous phase of the blends. It acts as the filler of the blend.

$$\mathrm{MFI}_{\mathrm{blend}} = w_{\mathrm{I}} \ln(\mathrm{MFI}_{\mathrm{I}}) + w_{\mathrm{II}} \ln(\mathrm{MFI}_{\mathrm{II}}) \tag{4.1}$$

where w_{I} = weight fraction of PP homopoymer

w_{II} = weight fraction of PP block copolymer

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

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

From the MFI test result, it can state that the melt flow rate of the PP/UHMWPE blend using the homo and block PP blend as the matrix is increased with increasing the low viscosity copolymer fraction. There is no evidence of the PP chain extension, neither by grafting nor crosslinking via the ethylene block in the impact modifier block PP as were expected on the first place. If the free radical initiated silane grafted chains take place in the blend system, they would undergo chain extension or crosslinking while the sauna curing, or silane/moisture condensation reaction, treatment. As the result, the melt flow behaviour of the blend would be decreased, higher in melt viscosity.

Table 4.10 Melt flow index of the PP/UHMWPE blends and PP copolymer contents

Batch No.	**Melt flow index at 170/2.16(g/10min)**		
	original	**cured**	**Calculated**
PP(700J)	2.74± 0.02	na	na
PP(740J)	5.95 ± 0.36	na	na
1	1.78 ± 0.10	1.68 ± 0.05	1.78
2	7.55 ± 0.29	5.41 ± 0.50	2.94
3	8.40 ± 0.22	6.21 ± 0.89	3.12
4	9.07 ± 0.19	6.48 ± 0.36	3.28
5	9.61 ± 0.34	6.57 ± 0.20	3.42

4.5.2.2 Heat deflection temperature

The HDT of PP/UHMWPE based on PPs homo and copolymer blend matrix is show in Table 4.11 and plotted with respect to the copolymer content shown in Figure 4.6, respectively.

Within the standard deviation of the test, it is seen that the HDT of the original samples do not depend on the copolymer fraction. Except for the specimen with sauna treatment, it is observed that there are fractionally increased with increasing the copolymer especially at the content above 30 phr.

Table 4.11 Melt HDT of the PP/UHMWPE blends and PP copolymer contents

Batch No.	**Heat deflection temperature(°C)**	
	original	**cured**
1	92.9 ± 5.1	114.7 ± 1.2
2	89.1 ± 1.0	114.0 ± 0.0
3	90.4 ± 2.4	114.7 ± 0.3
4	88.8 ± 6.2	122.5 ± 0.5
5	89.7 ± 1.7	121.9 ± 0.5

In fact according to the manufacturer data, the HDT of these two types of PP are identical. According to previous MFI outcome, there was no obvious evidence for chain grafting or crosslinking occurred during the blending or sauna incubation. The increasing in HDT through the sauna curing process of the blends with high copolymer fraction might be due to the easily crystallization of ethylene segment in the PPs matrix after the given prolong annealing time at high temperature. Consequently, higher crystallinity and then higher in HDT would be found.

4.5.2.3 Impact strengths

Table 4.12 and plotted graph in Figure 4.7 show the notched and unnotched impact strengths of the PP/UHMWPE derived from homo and block blended matrix, respectively. Unexpectedly, the notched impact strength is decreased with increasing the PP block copolymer loading.

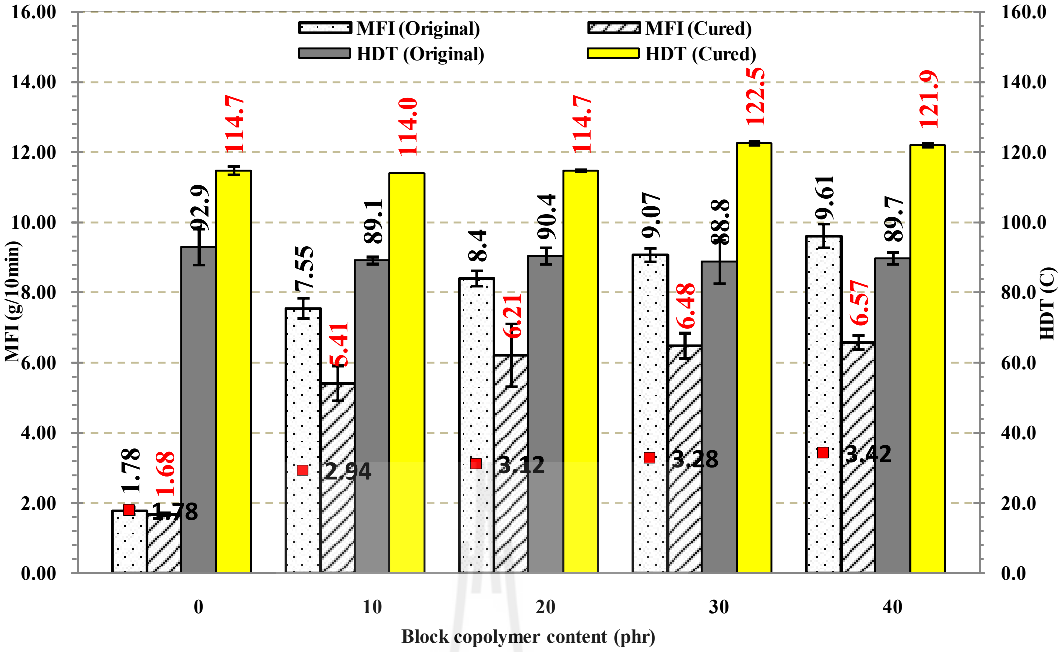


Figure 4.6 MFI and HDT of the PP/UHMWPE blends and PP copolymer contents

According to the data shown in the material section, impact modified PP copolymer has higher in the notched impact strength than the homo type. Normal miscible blending of the copolymer into homo phase would increase the impact value with increasing the copolymer fraction. The contradict results indicate that the peroxide chain degradation would take the prime control of the notched impact strength of the blends. Generally, the polymer degradation, especially during the melt processing, would lead to the decreasing in the material toughness. Similar observation is also found for the unnotched mode of test where the impact value is vastly dropped when only 10 phr of copolymer was added. Further increasing in the fraction of copolymers do not bring back of the impact toughness of the blends. Closely observation, the sauna incubation is fractionally improved the unnotched impact value. As mention earlier, the increasing in the crystallinity and also the chain recombination through the silane condensation of the PPs blend matrix would superior the unnotched impact of the blend material. But they do not overcome the negative impact caused by chain scission reaction.

Table 4.12 Impact strength of the PP/UHMWPE blends and PP copolymer contents

Batch No.	**Notched Impact Strength(kJ/m^2)**		**Unnotched Impact Strength(kJ/m^2)**	
	Original	**Cured**	**Original**	**Cured**
1	2.23 ± 0.19	2.55 ± 0.12	60.53 ± 5.76	66.71 ± 14.69
2	1.85 ± 0.13	1.85 ± 0.13	20.04 ± 4.96	21.72 ± 6.59
3	1.60 ± 0.13	1.80 ± 0.13	19.73 ± 16.59	21.67 ± 4.42
4	1.55 ± 0.13	1.75 ± 0.17	19.04 ± 2.73	25.10 ± 4.27
5	1.36 ± 0.12	1.69 ± 0.17	25.43 ± 6.49	23.56 ± 3.10

4.5.2.4 Flexural properties

Result of flexural properties, by mean of strength and modulus, of the PP/UHMWPE blends and PP copolymer contents is summarized in Table 4.13 and they are also plotted in regarding with the copolymer content in Figure 4.8, respectively. Similar to those impact strengths were noticed, the result reviews that flexural strength of both original and sauna cured samples are slightly decreased with increasing the content of PP block copolymer in the PP/UHMWPE blend.

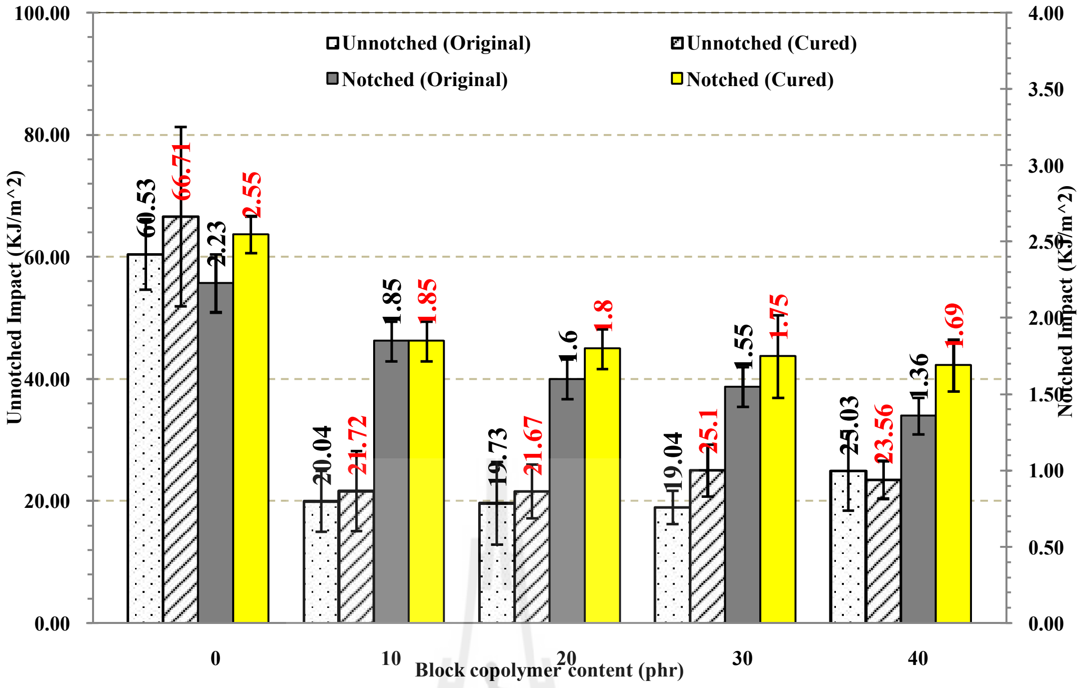


Figure 4.7 Impact strengths of the PP/UHMWPE blends and PP copolymer contents

It means that the resistance of bending force, referring to the bending toughness, is decreased when cooperate the copolymer fraction into the PPs matrix phase. This is contradicted to the fact that copolymer PP normally shows higher in ductility than homo PP. The decreasing in the toughness statement is supported by the slightly increase in the flexural modulus with increasing the block copolymer, especially for the sauna cured specimen. In the flexural testing, the more decreasing in the strength and also more increasing in the modulus, it generally means that more inferior in the material toughness. Again, the free radical induced chain scission would be largely respond for the more brittle material found in this study.

Table 4.13 Flexural properties of the PP/UHMWPE blends and PP copolymer contents.

Run	**Flexural Strength(MPa)**		**Flexural Modulus(GPa)**	
	Original	Cured	Original	Cured
1	52.77 ± 0.66	56.95 ± 0.83	1.05 ± 0.02	1.05 ± 0.01
2	46.29 ± 1.44	48.01 ± 0.97	0.97 ± 0.02	1.02 ± 0.05
3	43.95 ± 0.49	44.93 ± 1.57	1.07 ± 0.01	1.12 ± 0.01
4	42.29 ± 0.71	45.50 ± 1.21	1.03 ± 0.02	1.11 ± 0.01
5	42.31 ± 1.26	45.97 ± 0.75	1.04 ± 0.01	1.13 ± 0.01

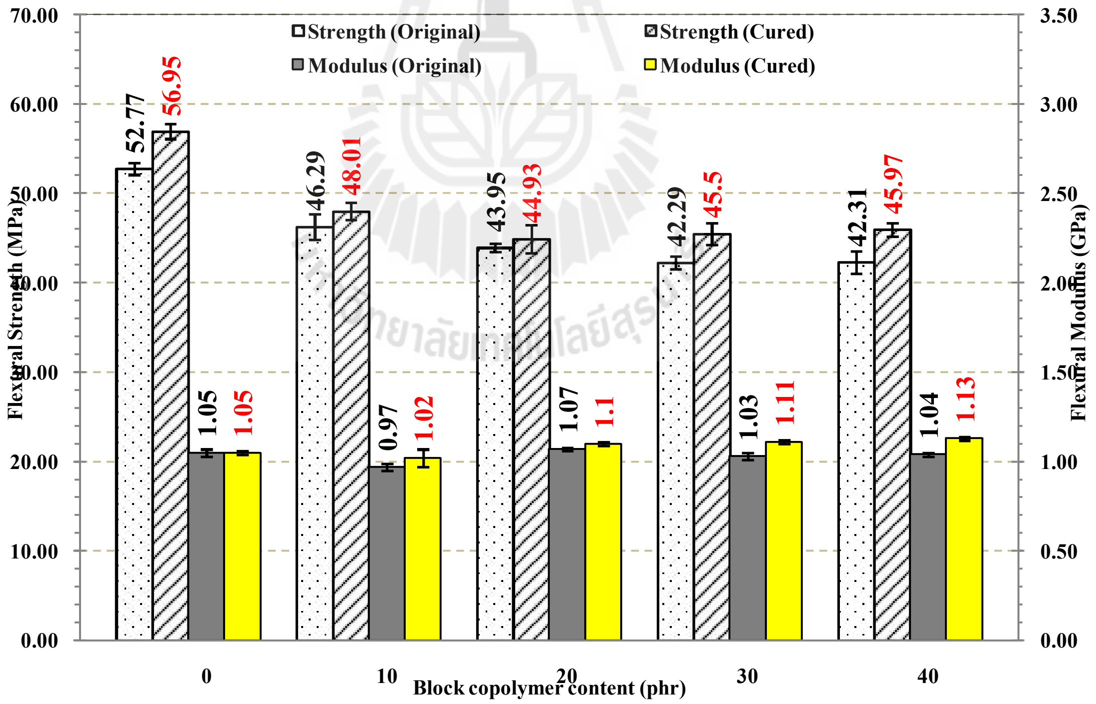


Figure 4.8 Flexural properties of the PP/UHMWPE blends on PP copolymer contents

4.5.2.5 Morphological of the PP/UHMWPE blends based on PP homo and copolymer PPs blend matrix

From the above mechanical properties of the PP/UHMWPE blends with adding the PP block copolymer into the PP matrix found, it was attempting to investigate the morphological behaviour, using SEM technique, of the blends while undergo impact fracturing. Figure 4.9(***a***) to 4.9(***d***) present the SEM photographs, at X500, of the fractured surface of the PP/UHMWPE blends with 10 and 40 phr of PP block copolymer in the PPs blend matrix before and after sauna incubation, respectively. From the SEM photographs, the UHMWPE phase is still seen as unmelted foreign phase on the PPs blend matrix. Either increasing the copolymer content in the matrix phase or undergo sauna curing process, the interfacial bonding between the continuous phase and the high molecular weight polymer particle does not obviously enhance. Adding UHMWPE into the matrix phase, in hope, would act as impact enhancer, but in fact the purpose does not succeed due to the phase separation. Taking only the SEM analysis, it is difficult to find the evidence for the toughness improvement behaviour of the copolymer fraction. Because of the blend between homo and copolymer PPs is completely miscible.

The expectation of the improving toughness of the PP/UHMWPE blends by blending PP block copolymer with homo and used as matrix was not succeed. The reverse result was found. The toughness by mean of impact and flexural properties were deceased with adding more of copolymer. The blends became more brittle. It was explained by the chain degradation through the free radical induce chain scission reaction.

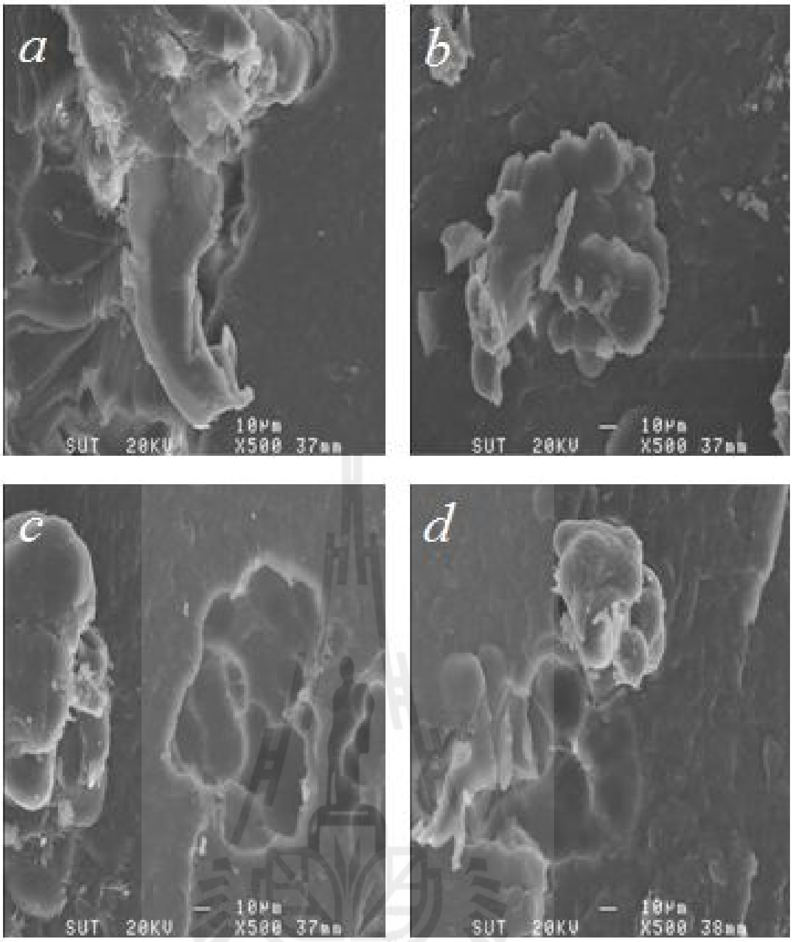


Figure 4.9 SEM of fractured surface of the PP/UHMWPE blends and PP copolymer contents;

(***a***) PP/UHMWPE with 10 phr of copolymer (original)

(***b***) PP/UHMWPE with 10 phr of copolymer (cured)

(***c***) PP/UHMWPE with 40 phr of copolymer (original)

and (***d***) PP/UHMWPE with 40 phr of copolymer (cured)

4.6 Conclusion

In attempting to further improve the properties, especially thermal property by HDT, of the PP by blending and compounding processes was experimented. It was found that increasing the DCP concentration in the silane/DPC system of PP/UHMWPE blending caused the vast chain degradation via the free radical chain scission reaction. As the result, the mechanical properties especially toughness of the blends were decreased. SEM showed phase separation between PP and UHMWPE added. Therefore, the toughening effectiveness of UHMWPE on PP blend could not be achieved.

The blended matrix between homo and block copolymer PP in the present of UHMWPE and silane/DCP in order to enhance the toughness of the blend was unsuccessful. The reverse effect was found. The toughness by mean of impact and flexural properties were also deceased with adding more of copolymer. Unexpectedly, the blends became more brittle. The chain degradation through the free radical induced chain scission reaction was the major drawback.

4.7 References

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CHAPTER V

PROPERTIES OF PP/UHMWPE COMPOUNDS

5.1 Abstract

Atempting to increase the HDT of PP/UHMWPE blends/compound to the target value at 150°C was performed by compounding with filler (s); talc, carbon black/RHA and reinforced with fiber glass in twin screw extruder. It was found that increasing in the degree of talc filling would increase the mechanical and thermal properties of the compound having PP/UHMWPE blend as matrix. The well dispersion and decent adhesion of the talc particles in the polymer blend matrix was responsible for the superiority. Using the hybrid fillers between organic and inorganic fillers; CB/RHA, showed that increasing in the CB organic filler content to some certain level could increased the melt viscosity, fracture toughness and tensile properties but lower the HDT of the PP/UHMWPE compound. The improving in the interfacial adhesion and increasing in the possibility of chain crosslinking due to the free radical degradation inhibition of the CB is hypothesized. Reinforcing the PP/UHMWPE; deriving from the homo and random PP blends and HDPE/UHMWPE master batch at 240°C, with glass fiber found that both mechanical and thermal properties of the composite were improved. Good adhesion between the matrix and fiber was resolved. However, within this design experiment, the HDT of the PP/UHMWPE compound was still below 150°C.

5.2 Introduction

The addition of fillers to polymers is a fast and cheap method to modify the properties of the polymeric materials. For this reason, filled polymers have been, and are, a subject of increasing interest in both industry and research. In this way, strength, stiffness, thermal properties, hardness and dimensional stability, among other properties, can be tailored to the required values (Gonzalez, J., 2002). The introduction of particulate filler into PP improves its mechanical properties and lowers the cost. Particulate filled thermoplastic composites have proved to be the significant commercial importance in recent years, as industrialists and technologists seek to find new and cost effective materials for specific applications (Abu Bakar, M. B. 2006). There are many types of solid fillers used to modify properties of filled PP such as talc, calcium carbonate, carbon black (CB) and rice hush ash (RHA) from the bio waste.

The fillers can be chemically categorized as inorganic and organic. In terms of inorganic fillers such as silica, calcium carbonate (CC) and talc are commonly used in PP (Hattotuwa, G.B., 2002). Talc is the softest mineral filler and the most widely used as inorganic filler in PP. Filled products exhibit excellent properties such as high stiffness, surface aesthetics, heat distortion temperature, low coefficient of thermal expansion and shrinkage, improved scratch as well as resistance to some aggressive chemical agents (Denac, M., 2003) In some cases inorganic compounds can be extracted from agricultural waste by physio chemical, thermal or biological degradation, rice husk is one of such abundant agro waste products. It can be used as it is or in the form of non cellulosic filler. Rice husk ash (RHA), which has been studied as alternative filler to commercial silica, is a classic example of extraction of inorganic fillers, predominantly silica, from rice husk, by a thermal degradation. Carbon black (CB) is a material produced by the incomplete combustion of heavy petroleum products such as FCC tar, coal tar, ethylene cracking tar, and a small amount from vegetable oil. The use of CB as an organic filler in thermoplastic polymers is not only limited to use as a pigment but it is also used to prolong the life time of plastics used for outdoor purposes. This is due to the features which can be found in modified materials and generally seen in composite materials with CB filler (Chlu, H. T. 1996). Reinforcement materials are added to plastics to improve their mechanical strength, especially in the longitudinal direction, and to reduce cost when compared to the materials of similar strength. The fiber glass superior properties including tensile strength, hardness, toughness, impact strength, and dimensional stability of polymers can be changed. Fiber polymer adhesion force can also be further improved with some addition materials. In addition, as some types of polymer and glass fiber are affected from humidity; humidity on the surfaces of these materials should be removed so that better interface adhesion force can be obtained. Due to their low cost when compared to other fiber materials and for the sake of increasing in the composite density, glass fibers are widely used in composite production (Gullu, A., 2006).

Recalling from previous chapter, it was found that adding copolymer PP into the PP/UHMWPE blend was not effective in term of the toughness enhancement. The filler addition is one of the typical compounding methods to enlighten the polymer compound toughness. In this chapter work, typical talc filler, carbon black/RHA and reinforced with fiber glass were employed. Typically, this filler shows the outstanding improved properties when it is combined with polymeric material. It includes high stiffness and high thermal resistance.

5.3 Research methodology

5.3.1 Materials

Materials used in the study were PP homo polymer and high density polyethylene (HDPE), P700J and H5814J, respectively. It was supplied from SCG Chemical Co., Ltd. The PP random copolymer, 3340H, it was available from IRPC Public Co., Ltd. The ultra high molecular weight polyethylene (UHMWPE), UH900, was obtained from Asahi Chemical Industry. Co., Ltd. The properties of the polymers employed in this work as reported from the manufacturers are summarized in the Table 5.1 to 5.4, respectively.

Dicumyl peroxide (DCP) as free radical initiator was also added into the compound ingredient. It was the commercial grade and purchased from the rubber compounder vendor. The decomposed and generated radical from this initiator is relative stable at as high temperature as above 120^{o}C. The silane coupling/grafting agent used was vinyl trimethoxy silane (VTMS), Silquest$^{®}$ A 171. It was use as complementary crosslink agent. The chemical was purchased from Optimal Tech Co., Ltd. The peroxide/silane crosslinking process is commonly undergone condensation reaction under the siloxy/water condensation known as sauna incubation. The incubation is normally succeed and accelerated in closed vapour saturated oven at temperature near glass transition temperature of the polymer.

Table 5.1 Physical properties of the PP homo polymer (P700J)

Physical Properties	**Homo PP (PP 700J)**
Melt Flow Rate(230/2.16), g/10 min	12
Density, g/cm^3	0.91
Melting Point, ^{o}C	163
Heat deflection temperature (@0.455MPa), ^{o}C	110
Flexural Modulus, MPa	1422
Notched Impact, kJ/m^2	3.75

Table 5.2 Physical properties of the PP random copolymer (3340H)

Physical Properties	**Random PP (3340H)**
Melt Flow Rate(230/2.16), g/10 min	2
Density, g/cm^3	0.91
Heat deflection temperature (@0.455MPa), ^{o}C	83
Tensile strength at yield, MPa	29.5
Charpy notched impact, kJ/m^2	11

Table 5.3 Physical properties of the HDPE (H5814J)

Physical Properties	**HDPE (H5814J)**
Melt Flow Rate(230/2.16), g/10 min	14
Density, g/cm^3	0.958
Melting Point, ^{o}C	131
Heat deflection temperature (@0.455MPa), ^{o}C	75
Flexural Modulus, MPa	1225
Notched Impact, kJ/m^2	3.75

Table 5.4 Properties of UHMWPE (UH900)

Properties	**Test Method**	**Value, Unit**
Average molecular weight	Viscosity method	33 X 10^4
Melting temp	DSC	136 ^{o}C
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^{o}C

Fillers employed in this work were talc, carbon black (CB), rice hush ash (RHA) and short carbon fiber. The talc, Jetfine® 3CA, is manufactured from Luzenac. The carbon black, N110, as organic filler is manufactured from Thai carbon black public co., Ltd. The rich rice hush ash (cRHA) is the solid waste from the local biomass power plant. It was powdered in ball mill before undergoing incinerate at 900°C for 4 hours. Most of the carbon was removed after the incineration process. It was called low carbon content rice hush ash (RHA). The average particle size less 106 µm was collected by sorting through the standard sieve shaker. Short glass fiber as the reinforcement filler, it was also the waste fiber from composite manufacturer. It was originally in the form of woven fabric. It was cut into small pieces, size less than 10 mm. It was used without any further treatment at all. The physical properties the particle fillers used provided by the manufacturer are summarized in table 5.5 and 5.6. The chemical compositions of the rice husk ask available from the literature is given in Table 5.7 (Oyetola, E. B., 2006). The talc and RHA were represented as inorganic filler but short fiber glass was the reinforcing filler.

All chemicals and polymers were directly used without further purification or modification.

Table 5.5 Physical properties of Talc, Jetfine® 3CA

Physical Properties	**Value**
Particle size, µm	1.2-1.4
Density, g/cm^3	2.78
Specific surface area, m^2/g	14.5
Chemical Composition	SiO_2(61%), MgO(32%), Al_2O_3(0.3%), Fe_2O_3(0.2%) and CaO(0.9%)
Decomposition temperature, °C	900-1000

Table 5.6 Physical properties of Carbon black, N110

Physical Properties	Value
Particle size, µm	11-19
Density, g/cm^3	0.31-0.38
Specific surface area, m^2/g	140-160

Table 5.7 Typical chemical composition of rice husk ash (Oyetola, E. B., 2006)

Constituent	% Composition
Fe_2O_3	0.95
SiO_2	67.30
CaO	1.36
Al_2O_3	4.90
MgO	1.81
L.O.I	17.78

5.3.2 Compound formula

From the previous chapter, DCP underwent chain degradation via the free radical chain scission reaction. The optimal content of peroxide was 0.1 phr. The silane and UHMWPE portion were kept constant at 2.0 phr and 20 phr, respectively. In this chapter, the further improvement properties of PP compound, especially thermal property, are also the main objective. There were several attempts regarding to the improvement properties of the PP compound. They can be classified as following;

(1) addition of talc

(2) adding the combined filler, CB and RHA

and (3) reinforcing with short glass fibre

5.3.3 Sample preparation

5.3.3.1 Compounding process

Polypropylene was dry blended with dicumyl peroxide (DCP) in plastic bag and vigorously shaken and placed in warmed oven at 80^{o}C for 5 min to allow DCP to liquidize. The ingredient was again vigorously shaken in order to the pellets polymer was completely coated by liquidized DCP. Then, 2.0 phr of liquid vinyl trimethoxy silane (VTMS) was added into the polymer ingredient. Then, it was in corporately blended with powder filler (s) and UHMWPE. The compound was achieved in closely intermeshing co-rotation twin screw extruder, with L/D ratio and screw diameter of 20/1, 25 mm, respectively. The screws were comprised of three triple kneader disc segments. The extruder barrel temperature profile from feed to die zone was electronically controlled at 190^{o}C. The screw speed at 10 rpm was constantly monitored that give rise to the mixing residence time of approximately 4 minutes.

5.3.3.2 Mater batching of PP and short glass fiber

It was difficult to directly feed the short fiber with others ingredient into the twin screw barrel. Glass fiber was pulped during the feeding and it was float on the top of the solid particle. Therefore, only solid form of the ingredients would be fed at the beginning of mixing. The inconsistency of the PP compound would be resulted. To overcome this problem, the cut fibre glass was initially master batched with random PP (3340H) in internal mixer at the concentration of 50 phr. The master batch was performed at pre-calculated degree of fill at the mixing batch size of 150 g mixed. The temperature of mixing chamber was electronically controlled at 180°C. The rotor speed was 80 rpm, and 6 minutes of mixing time was allowed. Master batch of PP/glass fiber obtained was cooled down and then crushed into small pieces by using mechanical crusher.

5.3.3.3 Materbatching of HDPE/UHMWPE

The master batch of HDPE and UHMWPE was prepared by high density polyethylene (HDPE), H5814J, and ultra high molecular weight polyethylene (UHMWPE), UH900 at the concentration of 60 phr of UHMWPE in HDPE. Normally, the processing temperature of UHMWPE, especially injection molding, is above 350°C. The molten temperature of UHMWPE only is also normally more than 300°C. It would be dangerous by mean of chain degradation of polymer in the presence of silane/DCP at high temperature of mixing. The masterbatching of UHMWPE with HDPE would lower the flow ability of UHMWPE. Shear force from high viscosity molten HDPE would induce the UHMWPE particle to soft or event melt. Consequently, it would easily incorporate with other ingredient in the form of liquidized phase. The master batch was achieved in closely intermeshing co-rotation twin screw extruder. The extruder barrel temperature profile from feed to die zone was electronically and equally set at 240°C, the screw speed at 10 rpm was performed. The master batch strand was air cooled and afterward gridded in small piece by using mechanical crusher.

5.3.3.4 Specimen preparation

The extruded strand of the PP compound exited from the twin screw die was then air cooled and granulated in to pellet using mechanical jaw crusher. The compound pellet was dried in the vacuum oven at 80°C for 2 hours to remove the possible residual moisture before injection. Test specimens were injection molded on the Tederic TRX60c injection molding machine. The barrel temperatures were set at 160, 165, 170, 170 and 170°C from feed to nozzle tip, gradually. The mold temperature and cooling time were set at 40°C and 30 seconds, respectively. The artificial balanced runner family mold comprised of impact, tensile and flexural specimen was employed.

5.3.3.5 Sauna treatment of PP compounds

The injection molded specimens were divided into 2 sets of sample. One was allowed to anneal at room temperature for at least a day before testing. It was assigned as original sample in this report. The latter was incubated in the water vapour saturated oven at 105°C for 12 hour to ensure the competition of the silane/moisture crosslink condensation reaction. It was finally allowed to cool down at room temperature for at least a day priority to conduct the test. This type of sample was named as the sauna cured or shortly as cured sample.

5.4 Measurement and Testing of Samples

5.4.1 Melt flow index measurement

The rheological property of the polypropylene blends/compounds was performed by mean of melt flow index (MFI). The test was conducted in accordance with ASTM D 1238 using the Kayeness melt flow indexer, model 4004. The pellet sample obtained was dried at in the vacuum oven at 80°C for at least 2 hours. Dehumidified pellet was allowed to melt at 170°C and driven through the standard capillary die (Ø 1 mm.) using the calibrated piston load of 2.16 kg. The melting time was set at 360 seconds. Three cuts of extrudate were performed at the designed cut times. The weight of each cut was computed into the melt flow index at the standard unit of g/10min. The average value was reported.

5.4.2 Heat deflection temperature

Heat deflection temperature (HDT) of the polypropylene blends/compounds for the original and sauna cured samples were measured in accordance with ASTM D 648. The standard testing machine from Atlas, model HDV 1, comprised of three test stations was employed. Thee specimens were simultaneously tested in the edgewise position, with the support span length of 100 mm, a simple beam with the load applied at its centre of the spanned sample to give standardized stress of 0.455 MPa (66 psi). The raising temperature at a uniform rate of 2±0.2°C/min was assigned. Liquid silicone oil was used as heating transfer media. The HDT value was reported in degree Celsius (°C). It was immediately recorded when the specimen had been deflected to 0.25 mm or 0.01 inches as it was monitored by calibrated dial gauge. This temperature was recorded as the deflection temperature under the given flexural load. The average value was calculated and reported.

5.4.3 Impact testing

Unnotched and notched impact strengths, in Izod mode, of both the original and sauna cured samples were tested using ASTM D 256 as the standard testing procedures. The injection molded specimen with the dimension of 4x13x63 mm (WxLxH) was V-notched using the standard notching machine. The identical injected samples were also tested without notching. Notched and unnotched impact strength tests 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 mode, respectively. The Atlas impact testing machine, model BPI, was employed. The impact strength values were transformed in the SI unit as kJ/m^2. It was done by dividing the lost impact energy with the cross section area at the fractured point.

5.4.4 Flexural properties measurement

Flexural properties both strength and modulus of the polypropylene samples for both original and sauna cured samples were examined in accordance with ASTM D 790. The testing machine, Instron Universal Testing machine (UTM, model 5565) with load cell of 5 kN and three point bending test fixture with the predetermined span length of 72 mm, was employed. The crosshead speed of 10 mm/min was computerized control. The test specimen was placed plat wise to the bending load. The test was conducted at room temperature in the normal atmospheric condition. At least five piece of specimen were tested. The flexural properties both strength and modulus were taken, averaged and reported. The tested values beyond the upper and lower specification limit, $\pm 3\sigma$, were excluded.

5.4.5 Tensile properties

For determining the tensile properties of the PP specimen, the standard test, ASTM D638, using the type I sample was followed. The Instron Universal Testing machine, model 5565 with the standard load cell of 5 kN, was used. The constant strain rate of the cross head speed was electronically controlled at 50 mm/min. Commonly, five samples were conducted and the obtained test values were averaged for each set of sample. The tensile properties comprised of tensile strength, % strain at break, and Young's modulus (E), were reported.

5.4.6 Morphological observation

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

5.5 Results and discussions

5.5.1 PP/UHMWPE blend filled with talc filler

Table 5.8 summarizes the compound formula of PP/UHMWPE blend filled with talc. Six formulae with talc content varied from 0 to 50 phr were designed. DCP, silane and UHMWPE were constantly added at 0.1, 2.0 phr and 20 phr, respectively to the compound ingredient. The formulation without talc addition was used as reference material. The compounding process was performed in the twin screw extruder and the specimen was obtained by injection molding. The results of the standard tests are being discussed as follow.

Table 5.8 The blend formulation of PP/UHMWPE and the Talc content

Batch No.	P700J (g) (phr)	UHMWPE (g) (phr)	Silane (g) (phr)	DCP (g) (phr)	Talc (g) (phr)
1	300	60(20)	6 (2.0)	0.3 (0.1)	0
2	300	60(20)	6 (2.0)	0.3 (0.1)	30(10)
3	300	60(20)	6 (2.0)	0.3 (0.1)	60(20)
4	300	60(20)	6 (2.0)	0.3 (0.1)	90(30)
5	300	60(20)	6 (2.0)	0.3 (0.1)	120(40)
6	300	60(20)	6 (2.0)	0.3 (0.1)	150(50)

5.5.1.1 Melt flow index of PP/UHMWPE compound

Melt flow index (MFI) at 170/2.16 of the designed formulation given in Table 5.8 is summarized in Table 5.9 and it is also plotted with respect to the talc content shown in Figure 5.1, respectively.

Table 5.9 MFI of the talc filled PP/UHMWPE compounds

Run No.	MFI (170/2.16)	
	Original	**Cured**
1	9.97 ± 0.20	8.95 ± 0.17
2	5.52 ± 0.13	5.18 ± 0.18
3	4.08 ± 0.10	4.61 ± 0.26
4	2.45 ± 0.06	2.58 ± 0.03
5	1.60 ± 0.03	1.99 ± 0.04
6	1.38 ± 0.23	2.46 ± 0.09

From the test outcome, it can be seen, MFI value is exponentially decreased with increasing the talc content. It also indicates that the viscosity is increased as increasing the talc content. As expectedly, adding the particulate solid filler into the polymer compound is normally higher the material melt viscosity. But, in some case, a few amounts of round shaped particulate filler would act as compound lubricant, then the lower the flow ability. From the table, it also reports the MFI of the compound after undergoing sauna treatment. If the chain extension either by grafting or crosslinking through condensation between the silane grafted chain and water molecule occur during the sauna treatment, the viscosity of the polymer would be increased, lowered the MFI. But, from the result seen, the MFI of cured PP compound is generally and fractionally increased via the sauna curing. So, it is strongly suggested that there is no chain extension phenomenon during the incubation. The expectation that crosslinked PP chain would be formed by adding silane/DCP into the PP compound ingredient is not succeed. Not only no crosslinking reaction occurred in the PP compound but also the small trace of moisture residual contaminated in the material during moisture incubation would cause the chain degradation while melting in the MFI tester barrel.

5.5.1.2 Heat deflection temperature

The HDT of the talc filled PP/UHMWPE compounds tested at the standard load of 0.445 MPa is reported in table 5.10. When the test data is plotted against the talc content shown in Figure 5.2, it is seen that the HDT is gradually increased with increasing the talc loading. It is also observed that, at the given talc loading, the HDT of the sample is further higher after the sauna treatment. For the original sample, the HDT values of the talc filled PP/UHMWPE compounds are increased by approximately 11.6 to 25.8% to the value above 110°C when compare with the unfilled PP/UHMWPE blend. However, this gap is narrowed when the samples are sauna cured. As mention earlier, adding talc filler into the polymer compound typically enhance the thermal property of the material because the particulate filler would act as heat deformation resistance.

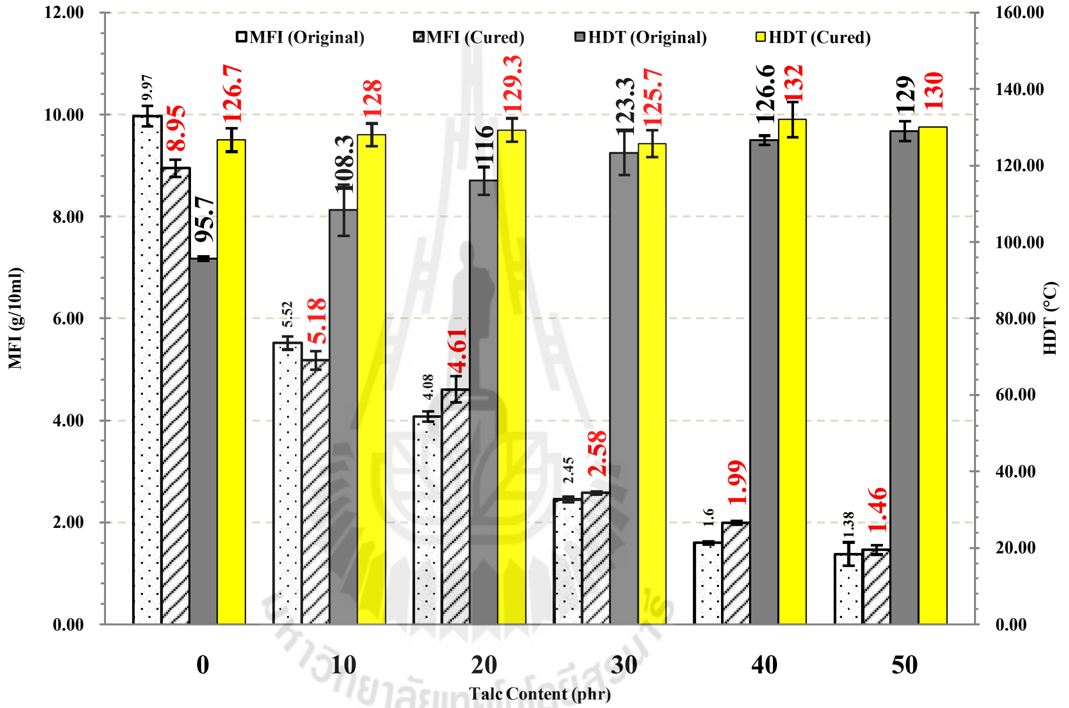

Figure 5.1 Plot of MFI and HDT of the talc filled PP/UHMWPE compounds

Further treatment process via the sauna incubation that probably lead to either by chain crosslinking/grafting through silane/moisture condensation, or increasing in the crystallinity of polymer matrix via the prolong thermal annealing, would typically responsible for the higher in HDT of the compound sample. But when closer observation of the tested HDT value, it is noticed that the degree of increasing in the HDT resulted from the sauna incubation of the PP/UHMWPE blend is much higher than in the talc filled PP/UHMWPE compound. This observation indicates that the crystallinity via the thermal annealing has much of effect on the HDT than the chain crosslinking/grafting. The later hypothesis is objected by the MFI result mention earlier. It is less possible for chain extension to be occurred in this compounding system.

Table 5.10 HDT of PP of the talc filled PP/UHMWPE compounds

Batch No.	Heat deflection temperature(^{o}C)	
	original	cured
1	95.7 ± 0.6	126.7 ± 3.1
2	108.3 ± 6.7	128.0 ± 3.0
3	116.0 ± 3.6	129.3 ± 3.1
4	123.3 ± 5.8	125.7 ± 3.5
5	126.6 ± 1.2	132.0 ± 4.6
6	129.0 ± 2.6	130.0 ± 0.0

5.5.1.3 Impact strengths of the talc filled PP/UHMWPE compounds

Table 5.11 and Figure 5.2 are shown test results and graphical presentation of notched and unnotched impact strengths of the talc filled PP/UHMWPE compound, both original and sauna cured samples, respectively. As commonly found in the polymer compound based on talc filler, the notched impact strength is linearly increased, especially for the original sample, with increasing the talc loading. Vice versa, the unnotched impact is marginally decreased with increasing the filler content. It is obviously seen that the unnotched impact of the sauna cured samples are superior to the original ones.

Table 5.11 Impact strengths of the talc filled PP/UHMWPE compounds

Batch No.	Notched Impact Strength (kJ/m^2)		Unnotched Impact Strength (kJ/m^2)	
	Original	**Cured**	**Original**	**Cured**
1	1.06 ± 0.14	2.19 ± 0.60	38.30 ± 6.49	43.17 ± 18.13
2	1.54 ± 0.11	2.05 ± 0.11	18.84 ± 0.13	16.92 ± 2.32
3	1.73 ± 0.01	2.09 ± 0.14	16.35 ± 2.02	15.43 ± 1.87
4	1.63 ± 0.13	2.43 ± 0.11	16.97 ± 1.21	15.81 ± 0.75
5	2.03 ± 0.12	2.45 ± 0.12	14.03 ± 1.05	15.12 ± 0.88
6	2.14 ± 0.14	2.29 ± 0.21	14.06 ± 0.91	13.22 ± 1.09

However, for the notched impact, the agreement on the statement does not concur because some are lower for the sauna cured. It is difficult to make the solid conclusion that the strengths are improved by the sauna treatment. However, general consideration, the sauna incubation shows the positive effect on the strength of the PP/UHMWPE compound. With a fine particle size of the filler and with relative good adhesion between polymer matrix and the solid particle, it typically provides a positive contribution to the cracked propagation resistance. Because the absorb impact energy is normally high therefore, the propagation rate is inhibited. The phenomenon leads to the increasing in the material toughness. However, the unnotched impact exhibits the contrarily responds. It is found that the increasing in the talc content gradual decrease the strength. In the sudden impact striking on the unnotched specimen, when poor adhesion occur between the polymer matrix and filler, the small cracks would immediately generate after the impact pendulum striking the test sample. Consequently, the cracks tips would rapidly propagate and penetrate inside the sample. This phenomenon would easily fail the sample. The brittle material would be indentified.

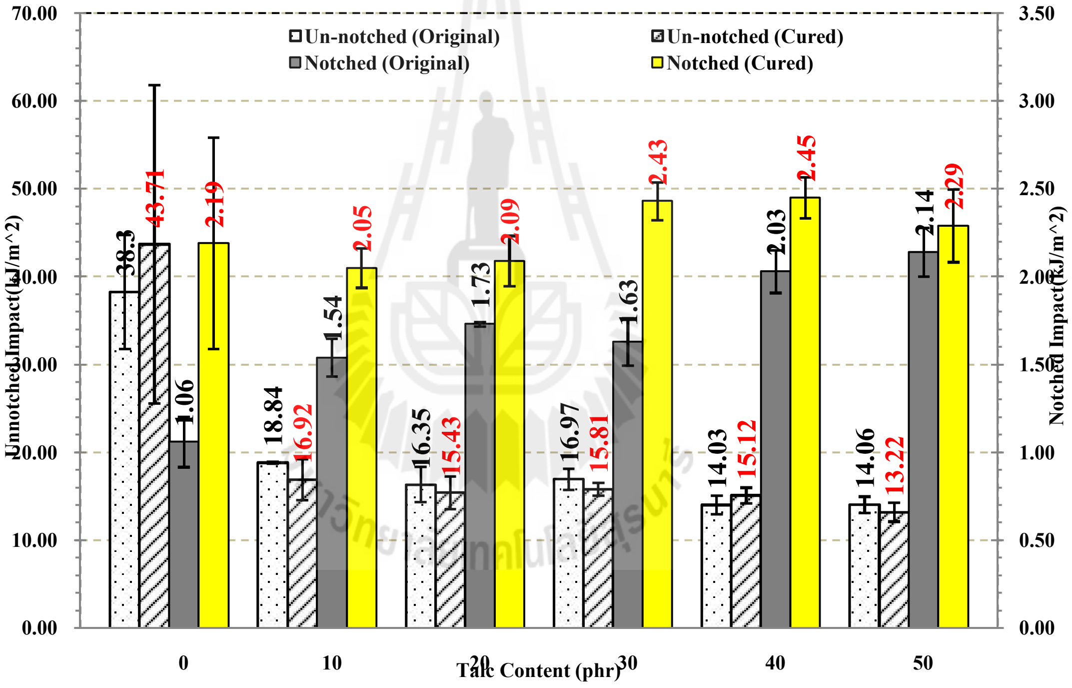

Figure 5.2 Plot of Impact strength of the of the talc filled PP/UHMWPE compounds

5.5.1.4 Flexural properties

Table 5.12 and Figure 5.3 illustrate the flexural test values, by mean of strength and modulus, and plotted graph against the talc filled PP/UHMWPE compounds.

Table 5.12 Flexural properties of the talc filled PP/UHMWPE compounds

Run	Flexural Strength(MPa)		Flexural Modulus(GPa)	
	Original	Cured	Original	Cured
1	53.04 ± 0.35	55.62 ± 0.46	1.05 ± 0.02	1.02 ± 0.04
2	50.70 ± 0.42	51.28 ± 0.73	1.41 ± 0.03	1.43 ± 0.04
3	51.43 ± 0.73	52.75 ± 0.31	1.65 ± 0.03	1.71 ± 0.05
4	52.49 ± 0.55	52.69 ± 0.71	1.91 ± 0.10	1.93 ± 0.03
5	51.57 ± 1.01	52.35 ± 0.83	2.21 ± 0.06	2.23 ± 0.05
6	51.13 ± 1.57	52.21 ± 0.62	2.54 ± 0.07	2.60 ± 0.04

It is found that the flexural strength of both with and without sauna curing samples is almost unchanged with increasing the content of talc. On the other hand, the flexural modulus is linearly increased with increasing the content. Generally, increasing in both flexural strength and the modulus, it means that the material is strong but the more brittle in characteristic as normally found for the thermosets polymer. Somehow, constant in the strength but rising in the modulus, it is interpreted that the material shows the superior resistance to the bending load. In the case of PP/UHMWPE compound filled with talc it is seen that the flexural strength does not change much with the talc content but the modulus is vastly increased.

Therefore, it could be interpreted that the compound can withhold more of the bending load when talc filler is compounded with the PP/UHWPE blend. So, the compound is stronger but more brittle. There is no significant difference in the properties of original and sauna cure compound.

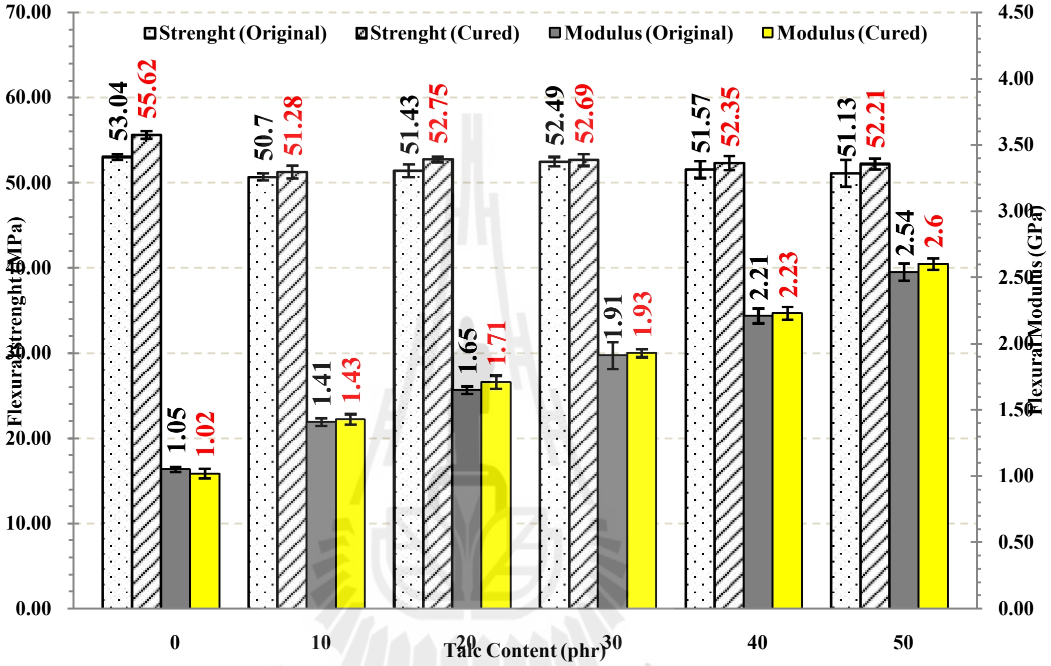

Figure 5.3 Plot of flexural properties of the talc filled PP/UHMWPE compounds

5.5.1.5 Morphological of the talc filled PP/UHMWPE compounds

From the above discussion, the adhesion between polymer matrix and talc filler was mentioned and touched. It is suspected that the phenomenon in the improvement or depression of the test properties is contributed from the filler/polymer interfacial adhesion. Therefore, the morphological investigate of the PP/UHMWPE compound using SEM is necessary to verify the statement. Figure 5.4 (***a***) to 5.4 (***f***) present the SEM photographs, at X500, of the fractured surface of the

PP/UHMWPE compound filled with 10, 30 and 50 phr of talc before and after sauna incubation, respectively.From the SEM pictures, it is difficult to see the trace of talc particles on the fractured surface at the given magnification. The talc used has the average particle size of 15 µm. However, carefully observe on the fracture surfaces, it can be seen that fine particle of talc is well distributed on matrix. The particle is also shown the good adhesion with the matrix phase especially after the sauna treatment. According the notched impact strength result, the strength was slightly increased with increasing the talc content. So, the fine talc particles dispersed within the matrix and well dispersed into the matrix, the higher in the stress is needed to initiate the micro crack on a particle/matrix interface. Hence, the higher in impact energy would be required to break the compound sample.

Within the experimental boundary and according to the test results found in this study, it could draw the statement that increasing in the degree of talc filling would increase the mechanical and thermal properties of the compound having PP/UHMWPE blend as matrix. The well dispersion and decent adhesion of the talc particles in the polymer blend matrix is responsible for the superiority.

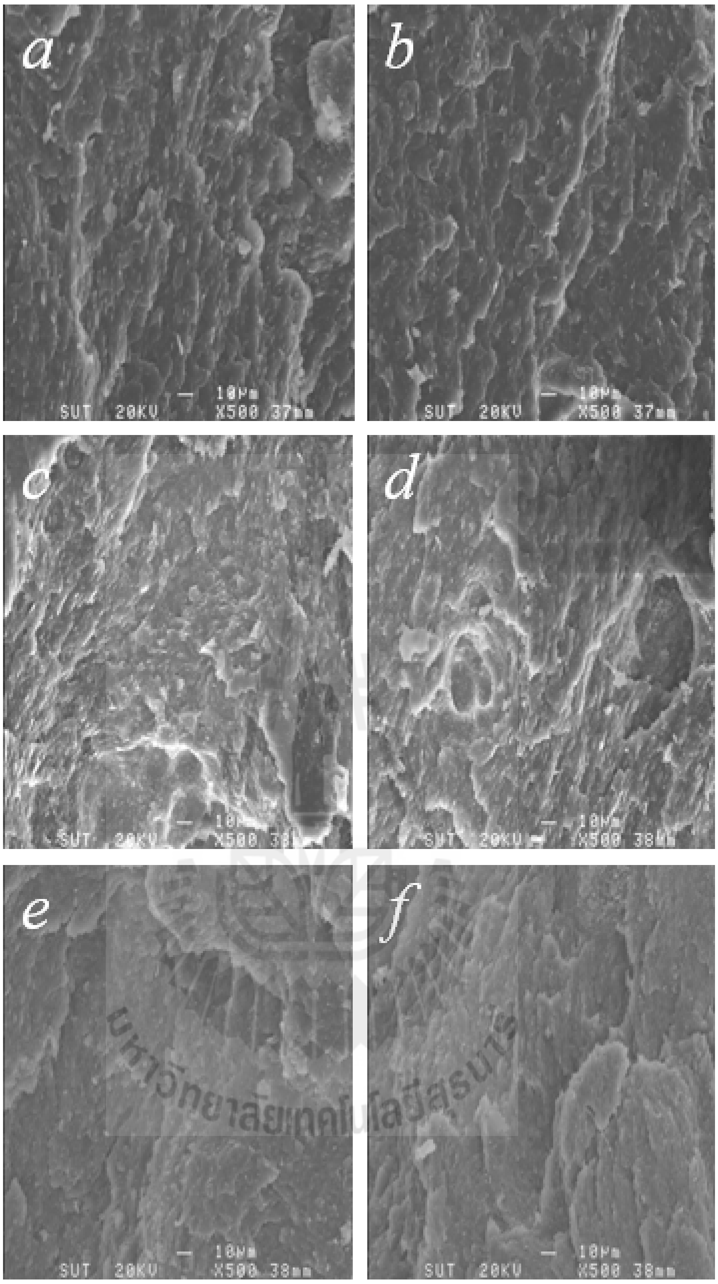

Figure 5.4 SEM of fractured surface of the PP/UHMWPE blends with talc contents; (***a***) PP/UHMWPE filled with 10 phr of talc (original), (***b***) the sauna cured, (***c***) PP/UHMWPE filled with 30 phr of talc(original), (***d***) the sauna cured, and (***e***) PP/UHMWPE filled with 50 phr of talc(original), (***f***) the sauna cured.

5.5.2 Carbon black and RHA filled compound based on the PP/UHMWPE blend

As report earlier that the carbonized rice hush is comprised of mainly the high silica content of filler. On the other hand, talc is the silica/magnesium oxide filler. Both are classified as inorganic filler. It would be interested to use the combination between inorganic and organic fillers in the PP/UHMWPE compounding. In this section the hybrid filler derived from carbonized rice husk ash (RHA) and carbon black (CB) was used as the filler for compounding of the polymer blends in order to improve of thermal and mechanical properties of the compound. Compositions of compound ingredients are shown in Table 5.13.

Table 5.13 Formulation of talc/CB/RHA filled PP/UHMWPE compounds

Batch No.	**P700J (g)(phr)**	**UHMWPE (g) (phr)**	**Silane (g)(phr)**	**DCP (g)(phr)**	**Talc (g)(phr)**	**CB (g)(phr)**	**RHA (g)(phr)**
PP	300	0	0	0	0	0	0
0XPP	300	60(20)	6(2.0)	0.3(0.1)	0	0	0
20/0/30XPP	300	60(20)	6(2.0)	0.3(0.1)	60(20)	0(0)	90(30)
20/10/20XPP	300	60(20)	6(2.0)	0.3(0.1)	60(20)	30(10)	60(20)
20/15/15XPP	300	60(20)	6(2.0)	0.3(0.1)	60(20)	45(15)	45(15)
20/20/10XPP	300	60(20)	6(2.0)	0.3(0.1)	60(20)	60(20)	30(10)
20/30/0XPP	300	60(20)	6(2.0)	0.3(0.1)	60(20)	90(30)	0(0)
0/0/50XPP	300	60(20)	6(2.0)	0.3(0.1)	0	0	150(50)
0/50/0XPP	300	60(20)	6(2.0)	0.3(0.1)	0	150(50)	0

RHA and CB weight ratios were varied from 0:30, 10:20, 15:15, 20:10 and 30:0, respectively. DCP, silane, UHMWPE and talc were kept constant at 0.1, 2.0, 20 phr and 20 phr, respectively. The total of 50 phr of the solid filler (s) for each of the compound was assigned. The formulation without filler addition was used as reference material. The compounding procedures were achieved in twin screw extruder and the test specimens were prepared by injection molding. The effects of the RHA/CB ratio on the properties of the PP/UHMWPE compound are being discussed.

5.5.2.1 Melt flow index of talc/CB/RHA filled PP/UHMWPE compounds

The melt flow index (MFI) of the compound formulations given in Table 5.13 tested at 170/2.16 are summarized in Table 5.14. It is also presented as the plotted graph with respect to the fillers ratio in figure 5.5. From the outcome, it is seen that, at the given talc loading at 20 phr, the MFI value of PP/UHMWPE compound is decreased with increasing the CB to RHA weight ratio for both original and cured samples. Further increasing in the CB content to 50 phr without addition of talc, the flow index of the compound is lowered. It is indicated that high ratio of CB the viscosity of compound is increased. On the other hand, the RHA acts as lubricator because the MFI of the RHA filled compound is increased at higher RHA ratio. Because, the difference of particle size and shaped particulate of CB and RHA. It suggests that the organic filler of CB inhibit the chain degradation caused by silane/DCP added during the mixing step. According the molecular aspect, the CB is comprised of the C=C in the molecule. Because burn kerosene under limited oxygen, the unsaturated C=C is normally found. The existing vinyl bonds would easily react with the generated free radical. Consequently, the free radical chain scission would be reduced; the higher viscosity of the compound would be evidenced. The higher melt index of PP/UHMWPE in the presence of only silane/DCP can be used to confirm this statement.

Table 5.14 MFI of the talc/CB/RHA filled PP/UHMWPE compounds

Run No.	**MFI (170/2.16)**	
	Original	**Cured**
PP	3.34 ± 0.05	3.18± 0.04
0XPP	7.42 ± 0.18	5.44 ± 0.10
20/0/30XPP	2.94 ± 0.09	2.30 ± 0.03
20/10/20XPP	1.00 ± 0.07	1.05 ± 0.06
20/15/15XPP	0.71 ± 0.05	0.82 ± 0.04
20/20/10XPP	0.49 ± 0.03	0.48 ± 0.02
20/30/0XPP	0.13 ±0.01	0.19 ± 0.01
0/0/50XPP	3.08 ± 0.13	2.45 ± 0.20
0/50/0XPP	0.11 ± 0.02	0.15 ± 0.03

5.5.2.2 HDT of talc/CB/RHA filled PP/UHMWPE compounds

The HDT of talc/CB/RHA filled PP/UHMWPE compounds obtained at 455 kPa is shown in Table 5.15. It is plotted with the fillers ratio given in Figure 5.5. It is observed that the HDT of compounds is gradually, with tiny margin, decreased when the weight ratio of CB is increased, especially for the original specimen. As expected, sauna treatment does superior the HDT by at least 12^{o}C, regardless to the fillers. However, when compare the HDT of virgin PP and XPP, PP/UHMWPE blend with addition of silane/DCP, with the PP/UHMWPE compounds it is evidenced that the HDT of the compounds are at least 10^{o}C higher for both original and cured samples. It exhibits that the organic and RHA inorganic fillers can enhance heat deformation resistance similarly to those common inorganic talc filler. However, from this study it can also point out that the silica rich filler, RHA, has the similar effect on HDT to the talc filler. The HDT of the PP/UHMWPE compound obtained from the single and combined fillers seen in this experiment does not reach to the target value need at 150°C. More attempts are required.

Table 5.15 HDT of the talc/CB/RHA filled PP/UHMWPE compounds

Run No. (Talc:CB:RHA)	**HDT (°C)**	
	Original	**Cured**
PP	97.1± 1.9	117.8± 1.4
0XPP	89.3 ± 4.7	116.3 ± 0.3
20/0/30XPP	120.3 ± 3.4	126.3 ± 2.1
20/10/20XPP	116.5 ± 1.9	126.9 ± 1.9
20/15/15XPP	116.0 ± 2.2	128.0 ± 0.9
20/20/10XPP	117.9 ± 1.3	128.0 ± 1.4
20/30/0XPP	115.8 ±0.9	125.7 ± 1.0
0/0/50XPP	114.3 ± 4.6	128.0 ± 0.0
0/50/0XPP	105.3 ± 2.5	121.9 ± 0.3

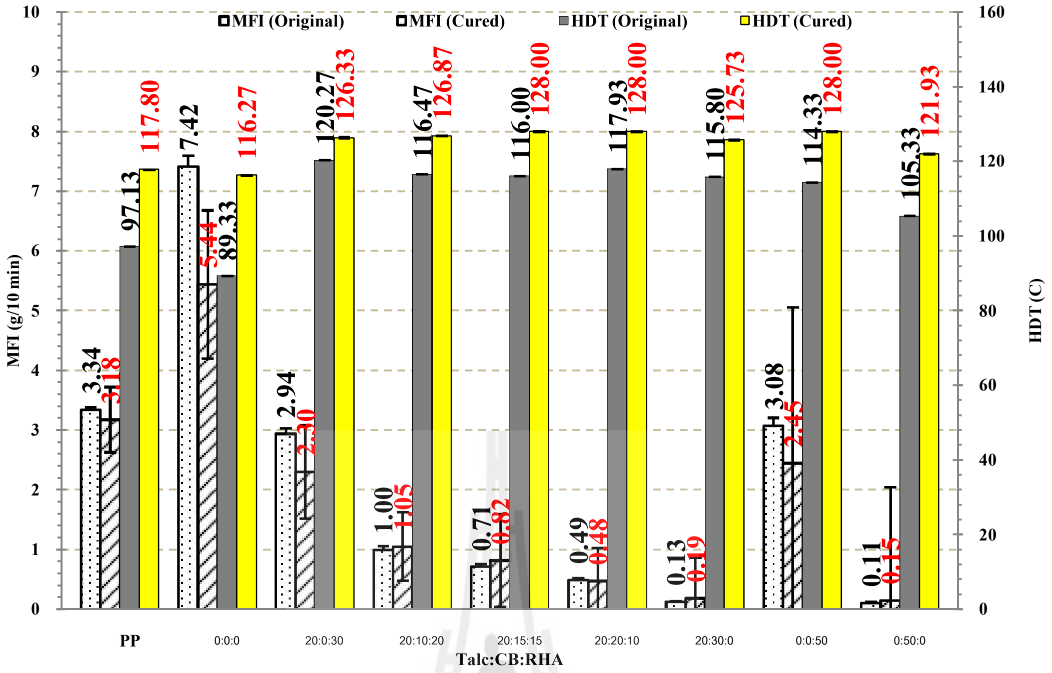

Figure 5.5 MFI of the talc/CB/RHA filled PP/UHMWPE compounds

5.5.2.2 Impact strength of the talc filled PP/UHMWPE compounds

Table 5.16 and Figure 5.6 are shown the impact test results of the PP/UHMWPE compounds with difference fillers, both original and sauna cured samples, respectively. From test results it is noticed that the unnotched impact strength of both original and sauna cured has the tendency to be decreased with increasing the ratio of CB in the hybrid fillers. The lowest unnotched impact value is found when only 50 phr of CB is employed. For the notched impact strength, the opposite trend is found when the CB/RHA ratios are increased from 0:30 to 15:15. But after that, even at only 50 phr of RHA filled, the test values are decreased. It seems that at the high ratio of CB but low ratio of RHA the inhibition of chain scission take the dominant effect but at the reversed ratios the poor adhesion between solid fillers take over the impact properties. The solid inorganic filler with low surface adhesion would normally deplete the impact toughness of the polymer compound.

Table 5.16 Impact strengths of the talc/CB/RHA filled PP/UHMWPE compounds

Batch No.	**Unnotched Impact Strength(kJ/m^2)**		**Notched Impact Strength(kJ/m^2)**	
	Original	**Cured**	**Original**	**Cured**
PP	74.32 ± 4.04	92.87 ± 6.38	1.65 ± 0.16	2.51 ± 0.79
0XPP	36.72 ± 3.08	47.75 ± 3.76	1.96 ± 0.16	2.14 ± 0.31
20/0/30XPP	17.94 ± 1.72	18.67 ± 0.83	1.90 ± 0.25	2.21 ± 0.13
20/10/20XPP	13.79 ± 1.98	15.09 ± 1.33	2.33 ± 0.17	2.56 ± 0.27
20/15/15XPP	14.71 ± 2.06	13.86 ± 1.19	2.59 ± 0.17	2.69 ± 0.26
20/20/10XPP	14.75 ± 0.35	14.29 ± 2.04	2.08± 0.13	2.44 ± 0.22
20/30/0XPP	14.97 ± 0.66	15.46 ± 0.68	2.38 ± 0.13	2.31 ± 0.27
0/0/50XPP	23.39 ± 0.85	21.55 ± 1.50	1.93 ± 0.17	1.88 ± 0.25
0/50/0XPP	9.21 ± 2.50	12.14 ± 2.42	2.06 ± 0.14	2.17 ± 0.39

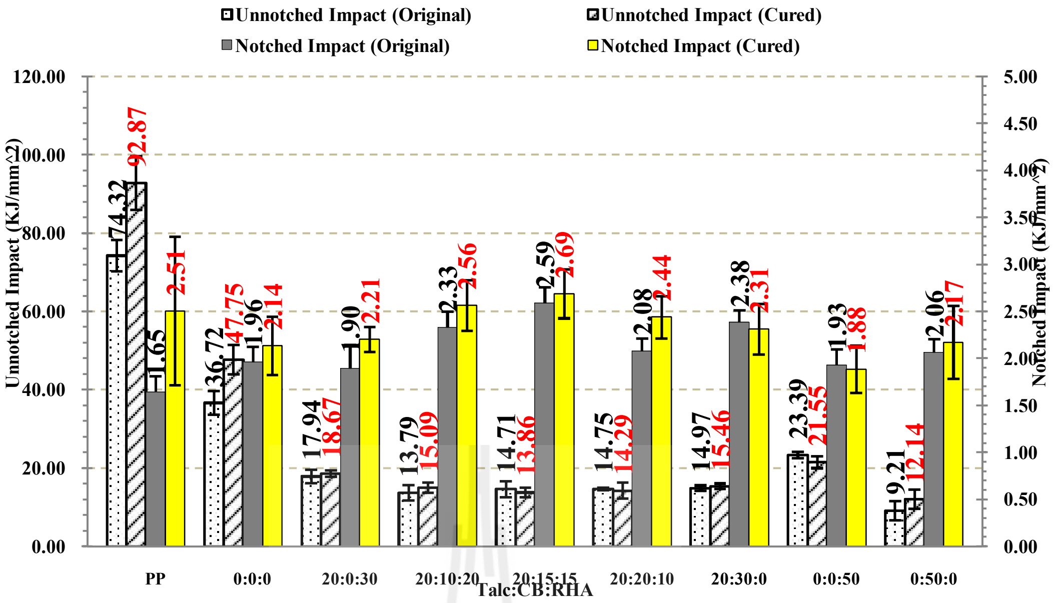

Figure 5.6 Impact strength of the talc/CB/RHA filled PP/UHMWPE compounds

5.5.2.4 Flexural properties of the talc/CB/RHA filled PP/UHMWPE compounds

The flexural properties by mean flexural strength and flexural modulus of the talc/CB/RHA filled PP/UHMWPE compounds are presented in Table 5.17 and Figure 5.7, respectively. Similar to those unnotched impact strength, it can be seen that the flexural strength is slowly decreased when increasing the ratio of CB filler, higher the ratio of RHA higher in flexural strength value. On the other hand, the flexural modulus is increase when increasing ratio of CB, both of original and sauna cured. As mention previously that lower the strength but higher in modulus it mean that the thermoset characteristic, brittle solid, of the material is obeyed. From this experiment, it manifests that the more CB loading the more brittle material. It could be due to the increasing in the crosslink density due to the silane/moisture condensation. Inhibition of chain scission but promoting the networking formation by the CB is hypothesized. However, in generally, the flexural properties of filled PP/UHMWPE are better than the virgin PP and PP/UHMWPE blend.

Table 5.17 Flexural properties of the talc/CB/RHA filled PP/UHMWPE compounds

Run	**Flexural Strength(MPa)**		**Flexural Modulus(GPa)**	
	Original	**Cured**	**Original**	**Cured**
PP	57.97 ± 0.85	61.86 ± 0.55	1.33 ± 0.01	1.35 ± 0.03
0XPP	50.65 ± 1.00	54.22 ± 1.24	1.12 ± 0.01	1.15 ± 0.01
20/0/30XPP	52.97 ± 0.73	54.26 ± 0.78	2.07 ± 0.07	2.10 ± 0.16
20/10/20XPP	53.08 ± 0.89	53.76 ± 0.57	2.25 ± 0.06	2.30 ± 0.03
20/15/15XPP	52.09 ± 1.19	52.81 ± 0.78	2.20 ± 0.07	2.34 ± 0.04
20/20/10XPP	51.71 ± 1.09	53.42 ± 0.55	2.39 ± 0.05	2.47 ± 0.06
20/30/0XPP	53.51 ± 0.85	53.06 ± 0.69	2.51 ± 0.02	2.54 ± 0.02
0/0/50XPP	58.92 ± 0.76	61.94 ± 2.61	2.14 ± 0.06	2.39 ± 0.12
0/50/0XPP	55.50 ± 3.85	59.70 ± 1.89	2.31 ± 0.06	2.51 ± 0.08

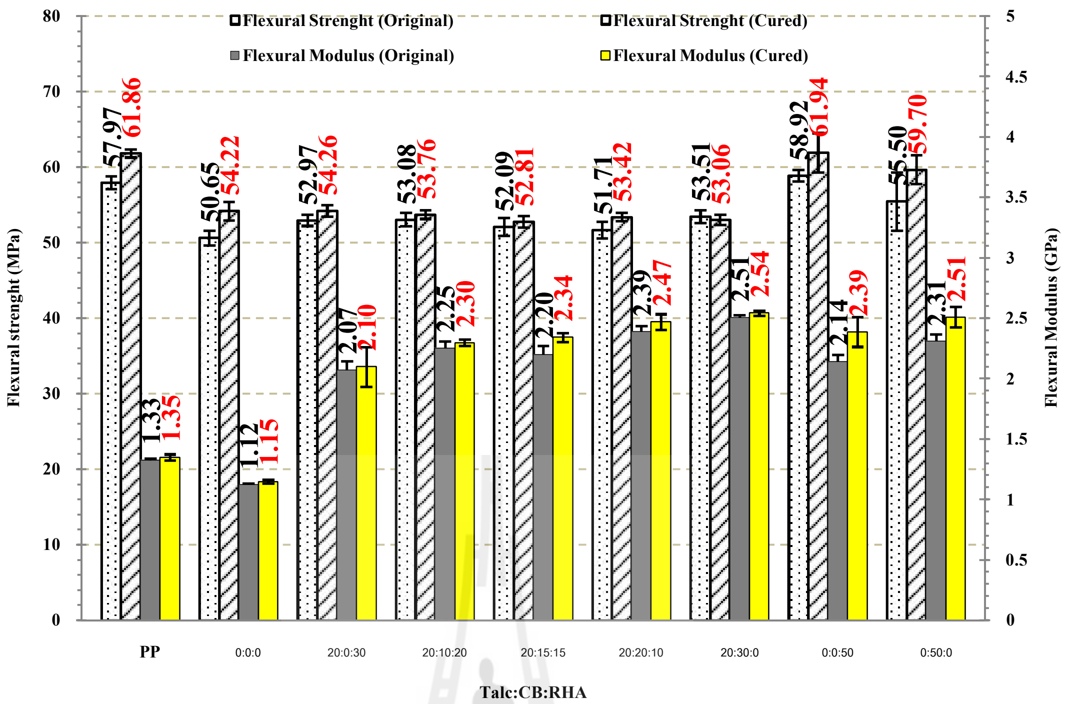

Figure 5.7 Flexural properties of the talc/CB/RHA filled PP/UHMWPE compounds

5.5.2.5 Tensile properties of the talc/CB/RHA filled PP/UHMWPE compounds

Table 5.18 and Figure 5.8 are shown the tensile properties of original and cured PP/UHMWPE compound specimens. Almost exact trend to those flexural properties is observed. The tensile strength is marginally decreased with increasing the CB fraction. Vice versa, the modulus is noticeably increased. Further increasing in the CB ratio more than 15 phr shows the modulus in reverse order. The explanation by the magnitude of crosslink density given in the above section would, again, is taken into consideration.

Table 5.18 Tensile strength and modulus of the talc/CB/RHA filled PP/UHMWPE compounds

Run	**Tensile Strength(MPa)**		**Tensile Modulus(GPa)**	
	Original	**Cured**	**Original**	**Cured**
PP	18.92 ± 13.33	27.94 ± 5.89	1.32 ± 0.06	1.35 ± 0.05
0XPP	29.47 ± 0.25	31.19 ± 0.26	1.10 ± 0.06	1.21 ± 0.05
20/0/30XPP	30.08 ± 0.46	31.47 ± 0.44	1.95 ± 0.05	1.84 ± 0.13
20/10/20XPP	28.92 ± 0.69	30.96 ± 0.27	2.04 ± 0.13	2.05 ± 0.13
20/15/15XPP	29.15 ± 0.38	30.05 ± 0.33	2.01 ± 0.09	1.93 ± 0.20
20/20/10XPP	29.25 ± 0.10	30.04 ± 0.75	2.09 ± 0.09	1.97 ± 0.05
20/30/0XPP	30.27 ± 0.25	30.91 ± 0.63	2.17 ± 0.09	2.14 ± 0.15
0/0/50XPP	27.58 ± 1.63	29.43 ± 0.91	1.62 ± 0.08	1.51 ± 0.09
0/50/0XPP	28.08 ± 0.14	29.24 ± 0.53	1.63 ± 0.10	1.68 ± 0.11

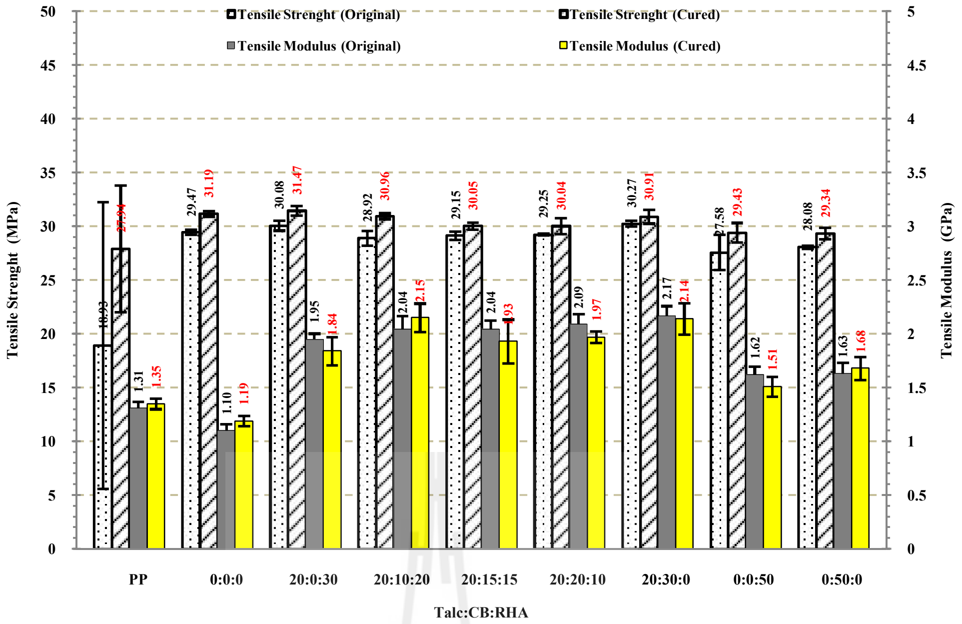

Figure 5.8 Tensile properties of the talc/CB/RHA filled PP/UHMWPE compounds

For elongation at break presented in Table 5.19 and Figure 5.9 respectively, it is enlighten that the chain crosslink and poor adhesion between polymer matrix and solid fillers are the most likely existence phenomena for the compound system studied. Because it is seen that the vast lower in % elongation at break when compare with the original PP is observed. Also, the higher CB ratios and the lower in % elongation at break.

Table 5.19 Elongation at break of the CB and RHA filled PP/UHMWPE compounds

Run No.	**Elongation at break (%)**	
	Original	**Cured**
PP	34.49 ± 26.97	15.43 ± 3.93
0XPP	9.54 ± 1.01	8.74 ± 0.58
20/0/30XPP	3.90 ± 0.43	3.98 ± 0.36
20/10/20XPP	3.44 ± 0.23	3.36 ± 0.13
20/15/15XPP	3.45 ± 0.16	3.35 ± 0.12
20/20/10XPP	3.41 ± 0.19	3.19 ± 0.17
20/30/0XPP	2.97 ± 0.13	2.89 ± 0.07
0/0/50XPP	4.44 ± 1.14	4.52 ± 1.03
0/50/0XPP	3.55 ± 0.08	3.58 ± 0.52

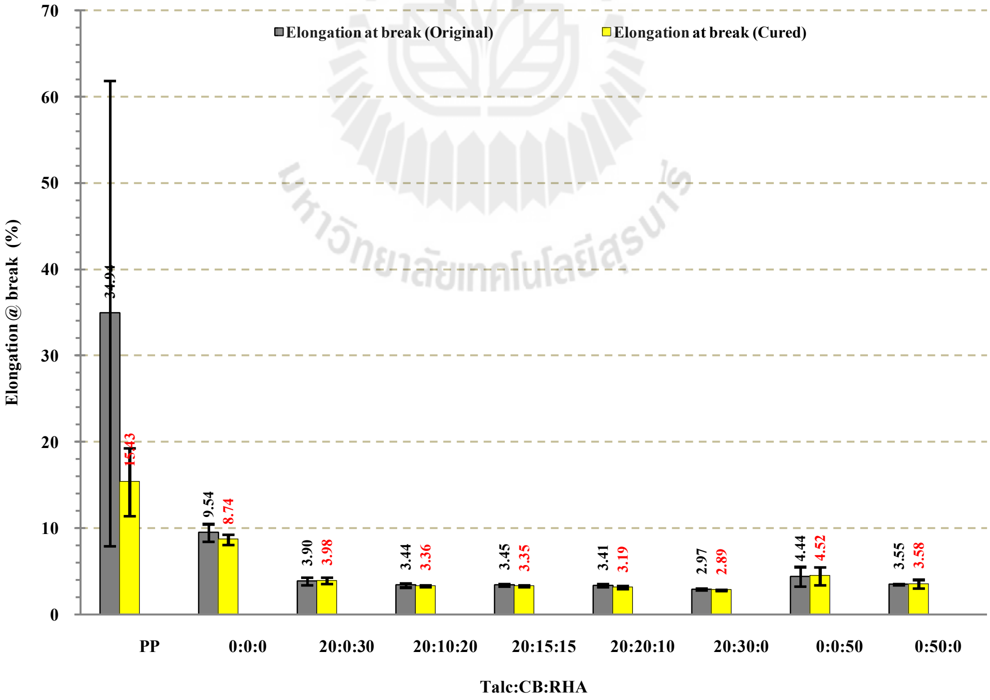

Figure 5.9 Elongation at break of the talc/CB/RHA filled PP/UHMWPE compounds

5.5.2.6 Morphological investigation of the talc/CB/RHA filled PP/UHMWPE compounds

The SEM investigation of the PP/UHMWPE compound using SEM is crucial piece of evidence to see the interfacial adhesion between matrix and filler. Figure 5.10 (***a***) to 5.10 (***l***) present the SEM photographs, at X500, of the fractured surface of the PP/UHMWPE compound without and with various filler (s). Figure 5.10 (***a***) and 5.10 (***b***) are the fractured surfaces of PP/UHMWPE blend. The small white separated particles are observed. These particles are the unmelted UHMWPE particle. From the previous discussion, blending PP with UHMWPE at 190^{o}C by using PP/UHMWPE master batch found that the UHMWPE particle could not be soft or melted. The phase separated particle was remained. Comparing between the compound filled with only RHA and CB at 50 phr as seen in Figure 5.10 (***i – l***), respectively, it is seen that the rougher fractured surface is presented for the RHA filled PP/UHMWPE compound. On the other hand, the CB filled compound shows the smoother surface. As indicated by the notched impact strength, higher in CB ration was better in the strength than the high loading RHA compound. The similar evidence is found for the talc/CB/RHA filled PP/UHMWPE compound having the fillers ratio of 20:30:0 and 20:0:30 that are given in Figure 5.10(***c***) to 5.10(***f***), respectively. Moreover, the extra separated tiny particles are seen. These particles are derived from talc filler. Also, the tiny holes are observed. There are the footprints of talc particle that fallen apart during the specimen fracturing. It indicates that the interfacial adhesion between polymer matrix and talc is not good enough to withstand the particle during the cracking process. Fill ratio of the talc/CB/RHA at 20:15:15 in PP/UHMWPE is also presented in Figure 5.10 (***g***) and 5.10 (***h***) for the original and after sauna curing, respectively. More or less, the characteristic of fracture surfaces are lined between the compound obtained from the fill ratio of 20:30:0 and 20:0:30, respectively. According to the SEM investigation, when compare those six compositions of the compound ingredient, 5.10(***c***) to 5.10(***h***), it can be concluded that the higher CB content the less footprint of the fallen away of inorganic solid fillers. It strengthen that higher in the inorganic loading lower the notched impact strength. From the SEM analysis, it could say that loading of inorganic fillers, talc and RHA, introduce the poor interfacial adhesion between the filler and PP/UHMWPE matrix phase. Consequently, the lowered in the impact or toughness of the compound was observed. There is no obvious indication from the SEM to show the huge differentiate between the sample before and after sauna treatment.

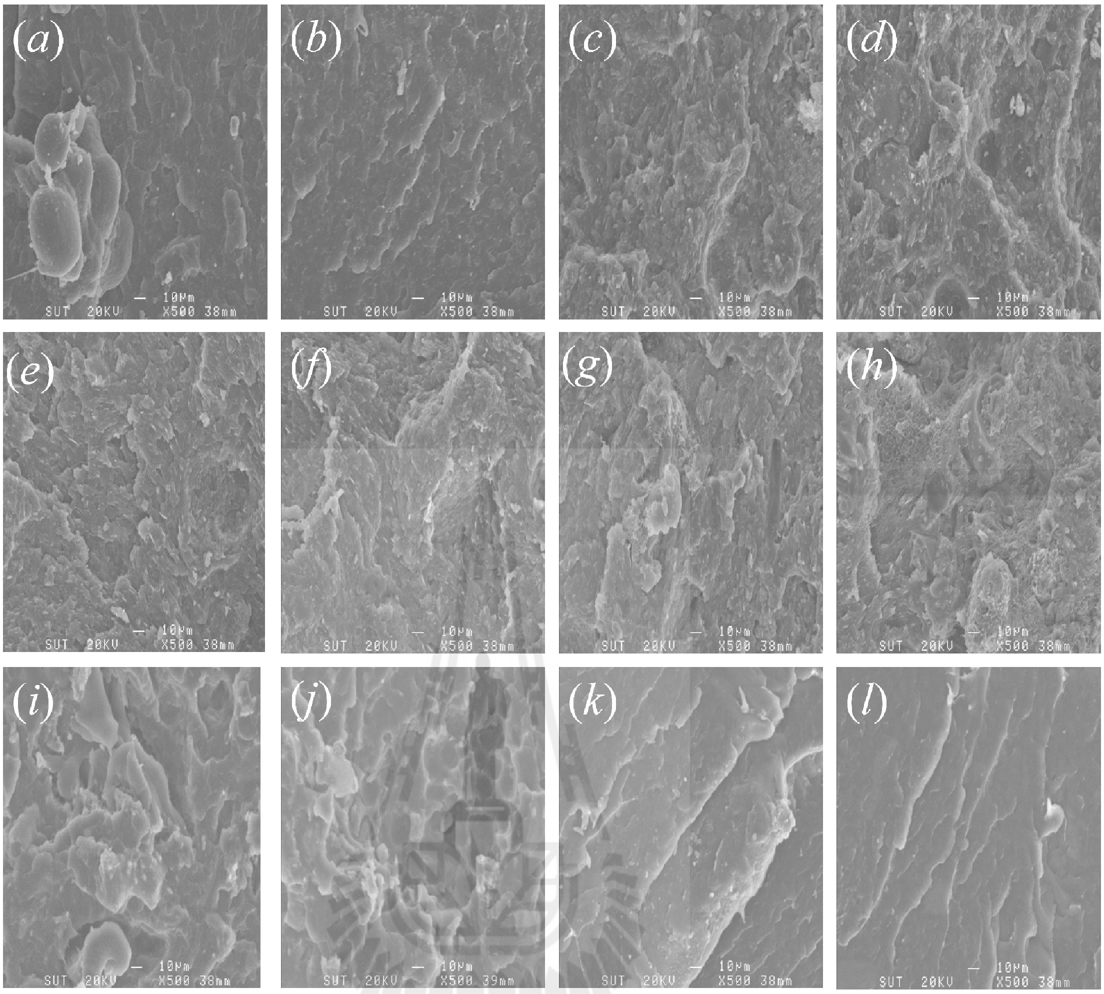

Figure 5.10 SEM of fractured surface of the talc/CB/RHA filled PP/UHMWPE compounds;

(***a***) original sample of PP/UHMWPE without filler, (***b***) sauna cured,
(***c***) original sample of PP/UHMWPE filled with 0:30 CB/RHA, (***d***) sauna cured,
(***e***) PP/UHMWPE 30:0 phr of CB and RHA(original), (***f***) sauna cured,
(***g***) original sample of PP/UHMWPE filled 15:15 of CB/RHA, (***h***) sauna cured,
(***i***) original sample PP/UHMWPE filled 50 phr of RHA, (***j***) sauna cured,
and (***k***) original sample PP/UHMWPE filled 50 phr of CB and (***l***) sauna cured.

According to this experimental, the test results found indicate that increasing in the CB organic filler content to some certain level could increase the melt viscosity, fracture toughness and tensile properties but lower the HDT of the PP/UHMWPE compound. The improving in the interfacial adhesion and increasing in the possibility of chain crosslinking due to the free radical degradation inhibition of the CB is hypothesized. However, within this design experiment, the HDT of the PP/UHMWPE compound is still below 150^{o}C.

5.5.3 PP/UHMWPE compound reinforced with short glass fiber

In this section, the final attempt to increase the HDT and enhancement of properties of PP compound was performed. The PP used in experiment section is the 50:50 blending between homo PP (PP700J) and random PP (3340H). The purpose of using random PP is to promote the crosslink site on the PP chain. As known from the previous works that the crosslink reaction via the silane/DCP system is easily occurred through the ethylene segment. Therefore, introducing the ethylene monomer onto the PP chain would not only induce the crosslinked chain but also inhibit the PP chain scission due to the free radical reaction.

As the early conclusion by SEM investigation found that the blended UHMWPE was not molten by mixing with PP at temperature 190^{o}C. From the related work, using the PP/UHMWPE masterbatch mixed at 280^{o}C for blending between PP and UHMWPE at 190^{o}C was also found that the UHMWPE particle was remained solid dispersed in the PP matrix (Meekum, U., 2012). The UHMWPE underwent liquidized by masterbatching with HDPE at 240^{o}C. In this experiment, the UHMWPE was added into the compound ingredient in the form of HDPE/UHMWPE masterbatch having the concentration of UHMWPE with respect to HDPE of 60 phr. The PP compound was performed at 190°C as usual. Therefore, in the PP compound, additional amount of HDPE was included.

The glass fiber reinforcement was varied from 5 to 25 phr with respect to the PP blend matrix. It was preliminary masterbatched with random PP (3340H) at 50 phr before mixing. The calculated amount of random PP and glass fiber was carefully computed to give the right amount of both materials in the compound in gradients.

Table 5.20 summarizes the final compound formula based on PP-blend/UHMWPE with fillers; talc and RHA, and fiber glass reinforcement. DCP, silane, UHMWPE master batch, talc and RHA were kept constant at 0.1, 2.0, 20, 20 and 30 phr, with respect to PP(700J)/PP(3340H) blend, respectively. The compound was performed in twin screw extruder at 190°C and the sample was molded through the injection machine. The material characterization was performed and the test results are being presented and discussed.

Table 5.20 Formulation of glass fiber content on PP/UHMWPE compounds

Fibre glass (phr)	**PP Blend** (g)(phr)	**Fiber Glass** (g)(phr)	**HDPE/UHMWPE Master Batch** (g)(phr)	**DCP** (g)(phr)	**Silane** (g)(phr)	**Talc** (g)(phr)	**RHA** (g)(phr)
PP Blend	400	0	0	0	0	0	0
XPP0FG	400	0	213(53)	0.4(0.1)	8(2.0)	80(20)	120(30)
XPP5FG	400	20(5)	213(53)	0.4(0.1)	8(2.0)	80(20)	120(30)
XPP10FG	400	40(10)	213(53)	0.4(0.1)	8(2.0)	80(20)	120(30)
XPP20FG	400	80(20)	213(53)	0.4(0.1)	8(2.0)	80(20)	120(30)
XPP25FG	400	100(25)	213(53)	0.4(0.1)	8(2.0)	80(20)	120(30)

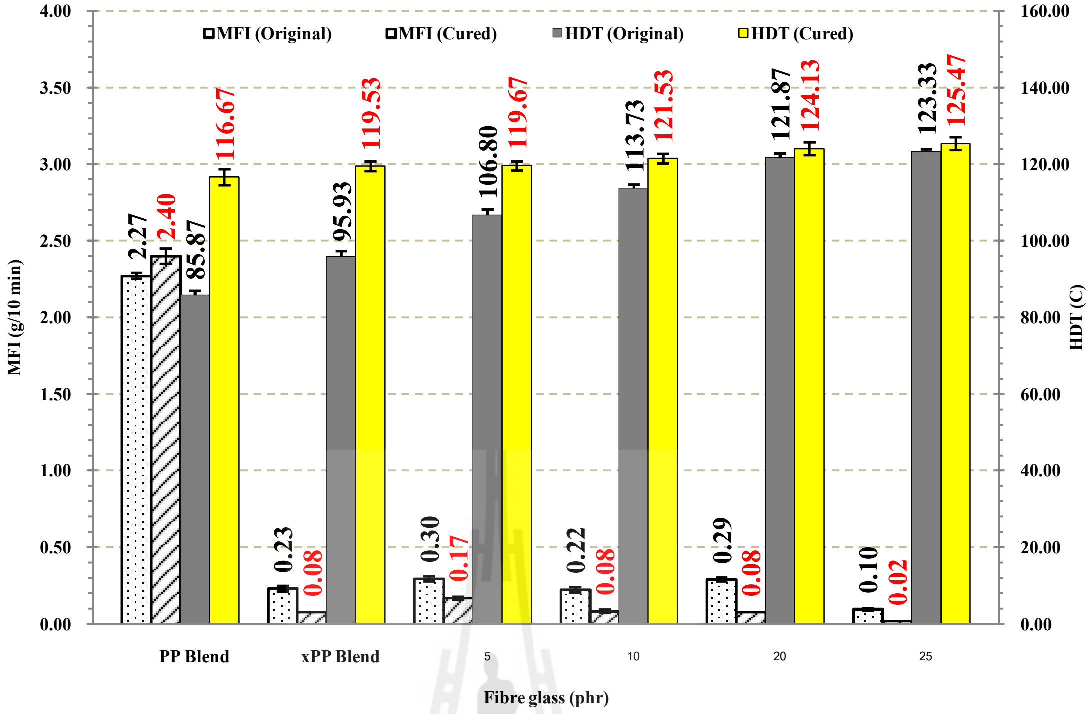

Figure 5.11 MFI and HDT of glass fiber reinforced PP compounds

5.5.3.1 Melt flow index of PP compound reinforced with glass fiber.

Melt flow index (MFI) of the fibre reinforced PP compound derived from the assigned composition shown in Table 5.20 is summarized in Table 5.21. It is also plotted with glass fiber content given in Figure 5.11. As expected, from the test results, it is found that MFI value is decreased with increasing the glass fiber content. The further decreased was observed when the compound pellet was undergone sauna incubation at 80°C for more than 12 hours. The decreasing in the MFI with increasing the fiber contents exhibit that the glass fiber inhibit the flow ability of material therefore the melt viscosity of the compound is increased. Further increasing in the viscosity via the sauna treatment is might due to the increasing in the crosslink density of the polymer matrix by crosslinking process of silane/moisture condensation reaction. It is indicated that introducing random PP (3340H) into the polymer matrix would promote the crosslink reaction via the ethylene segment.

Table 5.21 MFI of glass fiber reinforced PP compounds

Fibre glass (phr)	**MFI (190/2.16)**	
	Original	**Cured**
PP Blend	2.27 ± 0.02	2.40 ± 0.05
XPP Blend	0.23 ± 0.02	0.08 ± 0.00
XPP5FG	0.30 ± 0.02	0.17 ± 0.01
XPP10FG	0.22 ± 0.02	0.08 ± 0.01
XPP20FG	0.29 ± 0.01	0.08 ± 0.00
XPP25FG	0.10 ± 0.01	0.02 ± 0.00

5.5.3.2 Heat distortion temperature of PP compound reinforced with glass fiber.

The HDT of the glass fiber reinforced PP compounds, both of with and without sauna treated was summarized in Table 5.22. The test result is graphically presented with glass fiber content in Figure 5.11, Form Figure 5.11, it is obviously evidenced that the HDT is gradually increased with increasing the glass fiber loading. It is also observed that, at the given loading the glass fiber, the HDT of the sample is further hurdled after the sauna curing. The maximum HDT of 125°C is found when 25 phr of glass fiber is used. It is very common for increasing in HDT with fiber loading of thermoplastic fiber reinforced composite. Normally, the fiber used had higher resistance to the thermal deformation than polymer matrix. Therefore, increase the loading of fiber would typically increase the HDT of the composite. However, disappointedly, within this experiment composition, the HDT of prepared materials are lower than the target value at 150°C. Further increase the fiber content would probably attain the HDT goal. However, it could be done by careful consideration because further loading of fiber would have higher chance for mechanical properties, especially toughness, to be depleted.

Table 5.22 HDT of glass fiber reinforced PP compounds

Fibre glass (phr)	**HDT (°C)**	
	Original	**Cured**
PP Blend	85.9 ± 1.2	116.7 ± 2.1
XPP Blend	95.9 ± 1.5	119.5 ± 1.3
XPP5FG	106.8 ± 1.1	119.7 ± 1.2
XPP10FG	113.7 ± 1.4	121.5 ± 1.3
XPP20FG	121.9 ± 1.0	124.1 ± 1.6
XPP25FG	123.3 ± 0.6	125.5 ± 1.7

5.5.3.3 Impact strength of glass fiber filled PP/UHMWPE compound.

Fracture toughness of composite, both original and sauna cured samples, by mean of notched and unnotched impact strength is measured and reported in Table 5.23 and Figure 5.12, respectively. Similar to those HDT results, it is seen that impact strengths, especially notched, are increased with increasing the fiber loading. However, for the unnotched mode of testing, the strengths of PP blend and PP blend with presence of silane/DCP are higher than the fiber reinforced composite. The PP blend specimen was not broken within the given test condition. Poor interfacial adhesion between fiber and polymer matrix could be taken into account. This evidence will be proved by SEM later on. The glass fiber is included in the impact energy absorption. The main fracture mechanisms are regarded as the debonding between glass fiber and PP matrix and fiber pull out. Gupta et al (1997) suggested that, in glass fiber /PP system, the fracture energy absorption was dominated by fiber/polymer adhesion. With good bonding, fiber debonding mechanism, the impact strength would be elevated with increasing the fiber fraction in the composite.

Table 5.23 Impact strengths of glass fiber reinforced PP compounds

Glass fibre (phr)	**Unnotched Impact Strength(kJ/m^2)**		**Notched Impact Strength(kJ/m^2)**	
	Original	**Cured**	**Original**	**Cured**
PP Blend	No Break	No Break	1.83 ± 0.26	2.25 ± 0.18
XPP Blend	23.71 ± 1.50	22.49 ± 1.33	1.64 ± 0.16	1.88 ± 0.17
XPP5FG	20.35 ± 1.31	20.31 ± 1.14	1.91 ± 0.15	2.11 ± 0.15
XPP10FG	21.85 ± 1.65	21.90 ± 0.96	2.20 ± 0.16	2.45 ± 0.15
XPP20FG	21.55 ± 1.47	22.39 ± 0.67	2.90 ± 0.20	3.02 ± 0.17
XPP25FG	22.98 ± 0.82	22.86 ± 0.94	3.18 ± 0.19	3.36 ± 0.16

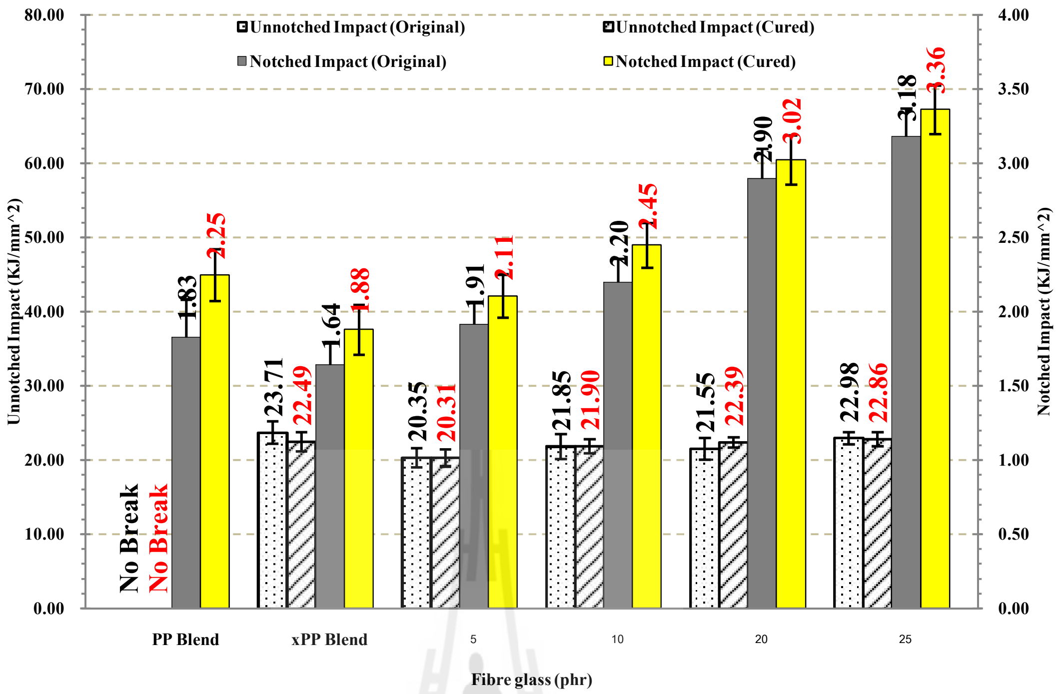

Figure 5.12 Impact strength of glass fiber reinforced PP compounds

5.5.3.4 Flexural properties of glass fiber filled PP/UHMWPE compound.

There is in good agreement with the impact testing. The test outcome of the flexural properties by mean strength and modulus of the glass fiber reinforced PP compound is summarized in Table 5.24 and plotted in Figure 5.13, respectively. It is clearly seen that the both strength and modulus obtained are linearly hurdled with the fibre loading. And the sauna curing was further excellent the properties. Closer observation, it is notice that degree of increasing is lower when the fibre loading is attended at 20 phr. The flexural strength of fiber reinforce PP is much higher than PP blends.

Table 5.24 Flexural properties of glass fiber reinforced PP compounds

Glass fibre (phr)	Flexural Strength(MPa)		Flexural Modulus(GPa)	
	Original	Cured	Original	Cured
PP Blend	42.11 ± 2.88	44.91 ± 3.48	1.02 ± 0.02	1.06 ± 0.01
XPP Blend	45.02 ± 0.88	48.07 ± 0.52	1.24 ± 0.02	1.42 ± 0.03
XPP5FG	47.09 ± 0.73	49.91 ± 1.13	1.46 ± 0.05	1.68 ± 0.03
XPP10FG	50.55 ± 0.52	52.97 ± 0.99	1.68 ± 0.03	1.81 ± 0.02
XPP20FG	55.12 ± 0.92	59.42 ± 1.18	2.01 ± 0.05	2.19 ± 0.03
XPP25FG	59.31 ± 0.59	62.05 ± 0.98	2.22 ± 0.04	2.34 ± 0.01

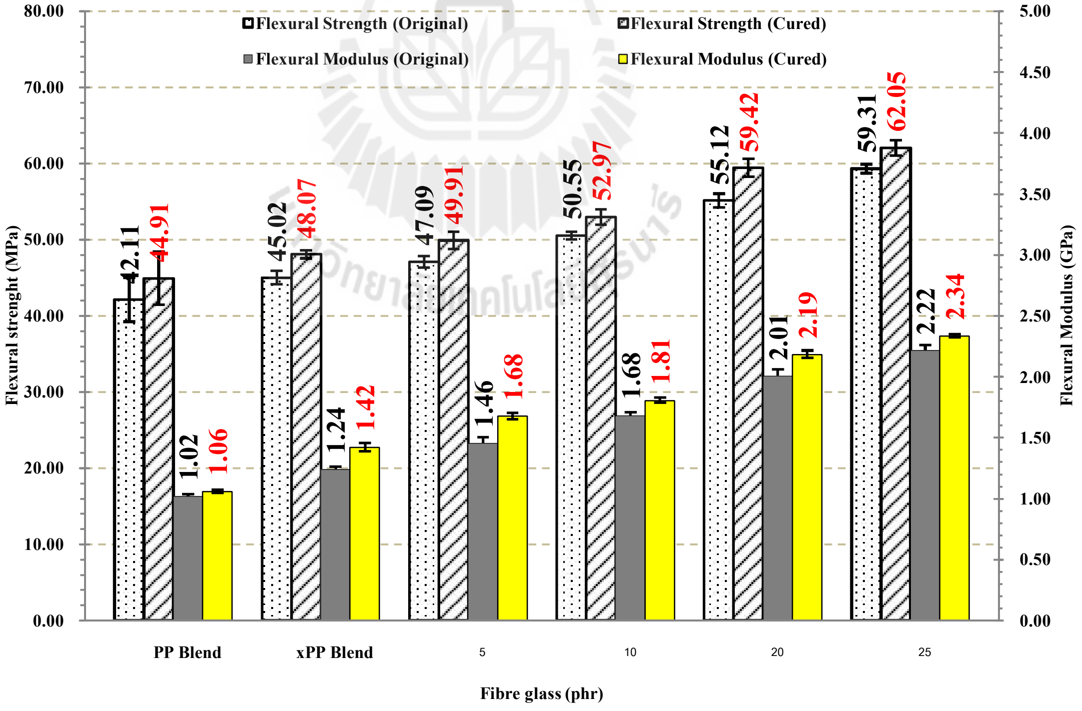

Figure 5.13 Flexural properties of glass fiber reinforced PP compounds

5.5.3.5 Tensile properties of glass fiber filled PP/UHMWPE compound.

Exact trend with the flexural properties is found for the tensile properties by mean of strength and modulus obtained. At constant strain rate of the cross head speed at 50 mm/min, the tensile strength and modulus of the samples are summarized in Table 5.25 and plotted result in Figure 5.14, respectively.

Table 5.25 Tensile properties of glass fiber reinforced PP compounds

Glass fibre (phr)	**Tensile Strength(MPa)**		**Tensile Modulus(GPa)**	
	Original	**Cured**	**Original**	**Cured**
PP Blend	15.54 ± 3.06	17.71 ± 4.40	1.04 ± 0.02	1.10 ± 0.02
XPP Blend	26.00 ± 0.21	27.56 ± 0.29	1.45 ± 0.08	1.57 ± 0.03
XPP5FG	27.60 ± 0.30	28.71 ± 0.47	1.64 ± 0.05	1.74 ± 0.04
XPP10FG	29.57 ± 0.47	31.46 ± 0.35	1.74 ± 0.10	1.84 ± 0.03
XPP20FG	33.36 ± 0.45	36.52 ± 0.42	2.18 ± 0.06	2.11 ± 0.15
XPP25FG	35.00 ± 0.47	38.34 ± 0.16	2.37 ± 0.07	2.33± 0.09

It is undoubtedly seen that both strength and modulus are increased with increasing the fibre loading. Moreover, the sauna cure sample obviously inhibit superior the tensile strength than the original one. But it is not always for the tensile modulus. The results found are indicated that highly possible of chain crosslink via the silane/DCP system is manifested. Increasing in network density, thermosetting characteristic, normally increase the tensile strength by decreasing the modulus.

Again carefully observation, the degree of increasing in the strength is reduced when the critical fiber loading is obtained, around 20 phr. Far beyond this critical loading, the strength or mechanical properties of the compound might be decreased because the lack of fiber/matrix adhesion.

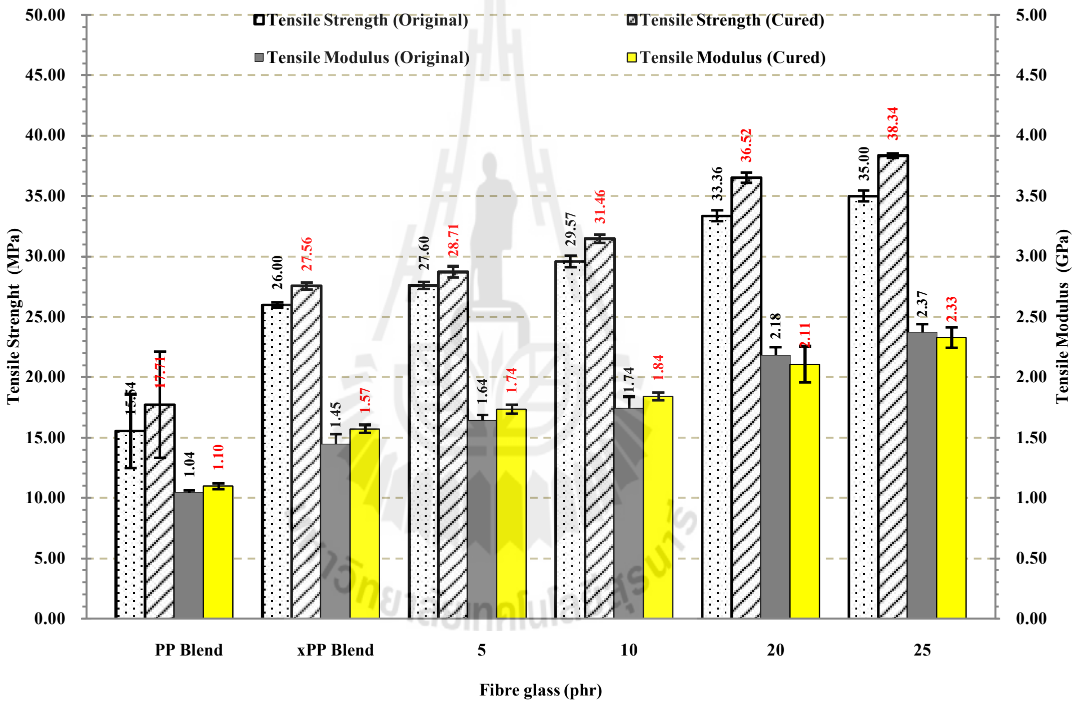

Figure 5.14 Tensile properties of glass fiber reinforced PP compounds

For % tensile elongation at break of the glass fiber reinforced PP compound, the test values are summarized in Table 5.26 and Figure 5.15, respectively. The test figures show that the % elongation at break is almost unchanged. It does not depend on the fiber content. However, when compare with the sample with no fiber reinforcement, PP blend, it is seen that the % elongation of the composites are much lower the blend. It is the common characteristic for the composite materials that they are lack of the elasticity. Therefore, the lower % elongation at break is typically found for the composite material.

Table 5.26 Elongation at break of glass fiber reinforced PP compounds

Fibre glass (phr)	**Elongation at break (%)**	
	Original	**Cured**
PP Blend	96.62 ± 21.15	29.31 ± 8.02
XPP Blend	6.79 ± 0.27	5.33 ± 0.30
XPP5FG	5.37 ± 0.26	4.55 ± 0.42
XPP10FG	5.11 ± 0.08	4.78 ± 0.16
XPP20FG	4.40 ± 0.12	4.19 ± 0.15
XPP25FG	4.23 ± 0.25	4.27 ± 0.10

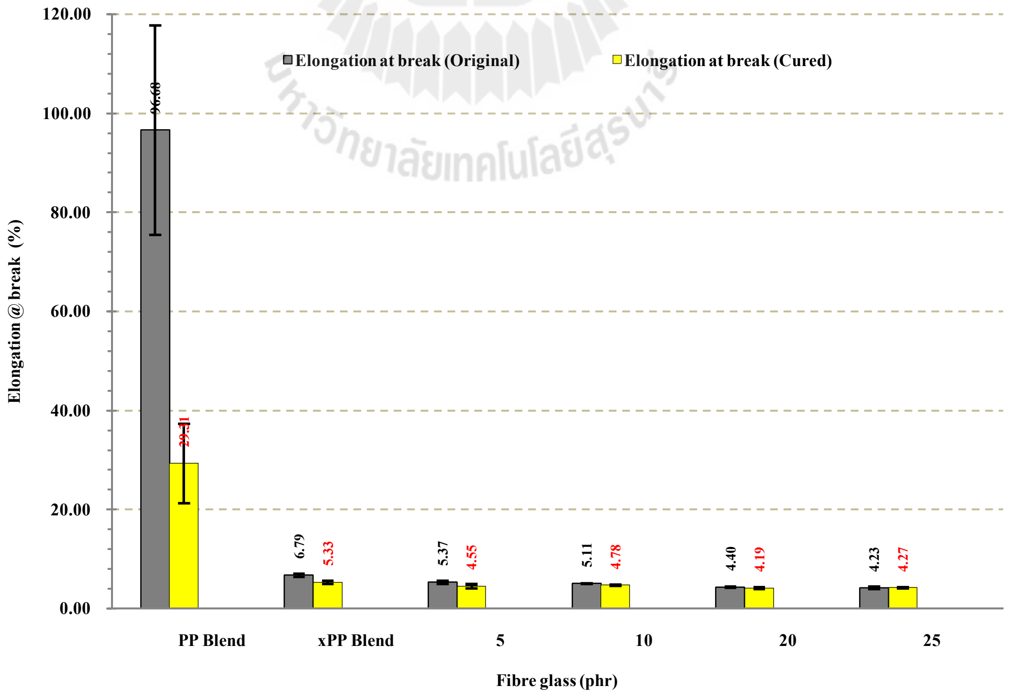

Figure 5.15 Elongation at break of glass fiber reinforced PP compounds

5.5.3.6 Morphological of glass fiber reinforced PP/UHMWPE compound.

Figure 5.16 (***a***) - 5.16 (***c***) are the SEM photograph at X1000 of the fractured strand of the HDPE/UHMWPE master batch manufactured at 200°C, 240°C and 280°C, respectively. It is seen that the UHMWPE can soft or melt at the mixing of 200°C using HDPE as the matrix. However, at mixing temperature as low as 200°C, the complete melt of the ultimate high molecular polymer is not clear. Further increase the melt temperature to 240°C or even 280°C, more complete melt of the polymer is observed. Therefore, from the SEM evidence, materbatching of UHMWPE with HDPE at the mixing temperature of 240°C is sufficient for the ultra high molecular weight polymer to be fused and dissolved into the HDPE matrix. In this experiment section the UHMWPE was used in the form of HDPE/UHMWPE master batch that manufactured in the twin screw extruder at 240°C.

The Figure 5.17 (***a***) to 5.17 (***f***) are the SEM photographs at X500 of the fractured surface of the glass fiber reinforced PP/UHMWPE composite at 0, 10 and 25 phr of fiber content, respectively. It is obviously seen that the fibers are randomly oriented in the matrix. Phase separation on the matrix phase is still evidenced. It could be the phase or talc, RHA or unmelted UHMWPE particles. The later is unlikely because during the masterbatching with HDPE at 240°C, UHMWPE is completely molten. Nevertheless, the UHMWPE phase could be returned during the PP/UHMWPE compounding if the compatibility between PPs blend and UHMWPE is low compare with HDPE matrix.

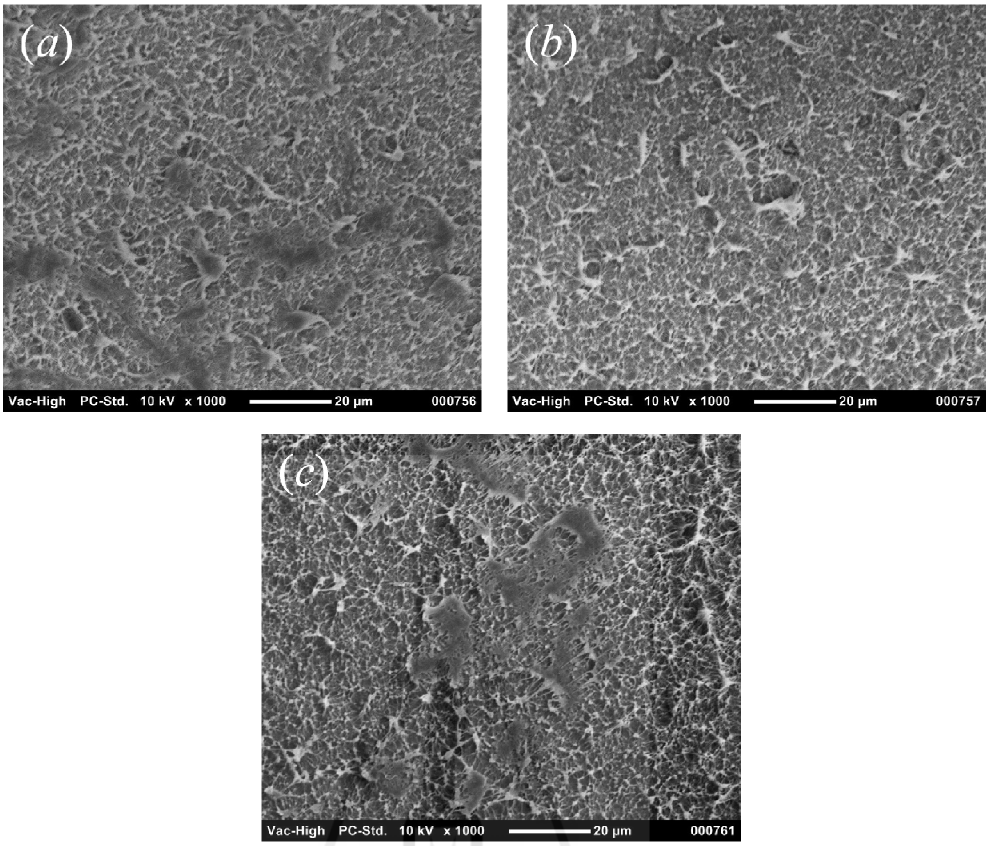

Figure 5.16 SEM of the strand HDPE/UHMWPE master batch at;

(***a***) HDPE/UHMWPE at 200^{o}C

(***b***) HDPE/UHMWPE at 240^{o}C

and (***c***) HDPE/UHMWPE at 280^{o}C

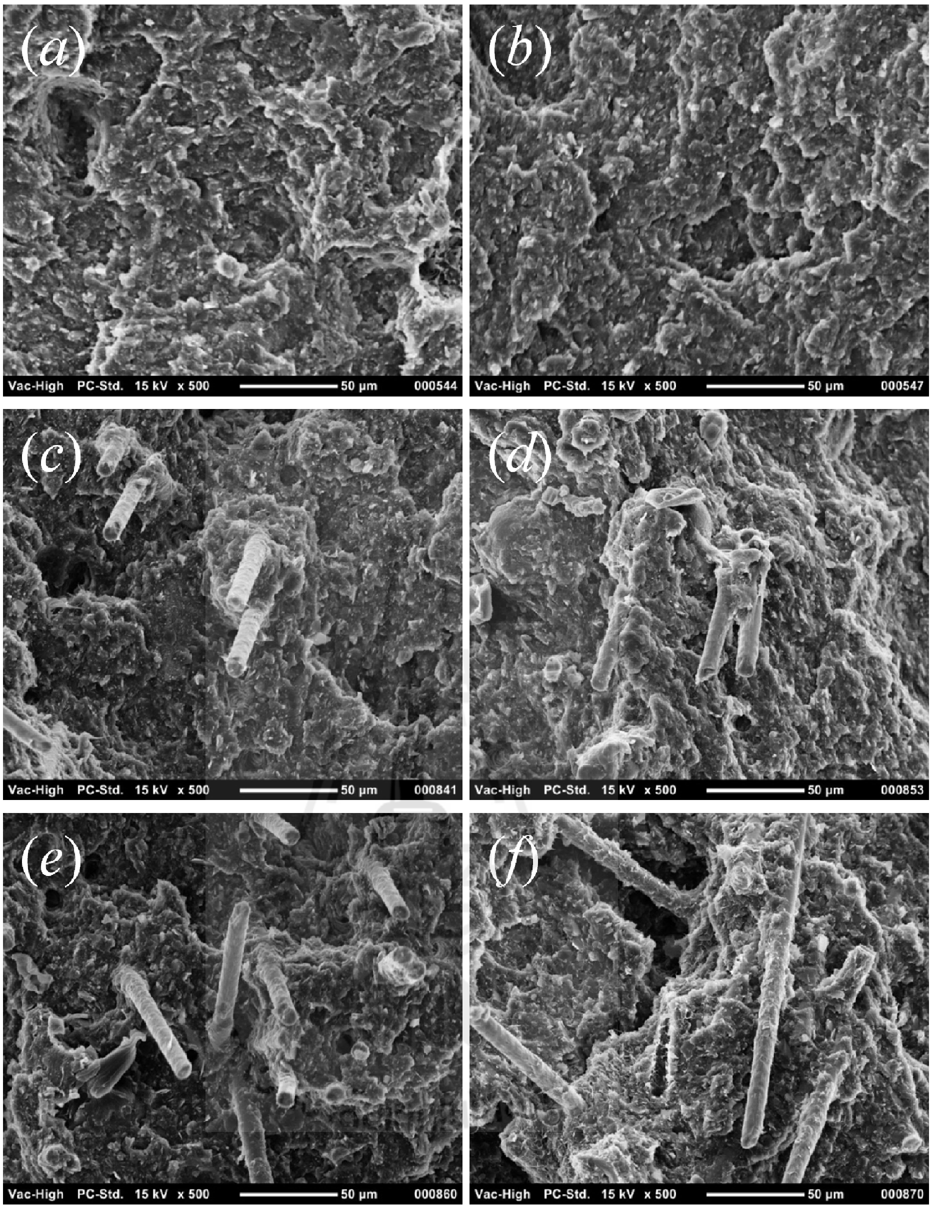

Figure 5.17 SEM of glass fiber reinforced PP compounds;

(***a***) original sample PP/UHMWPE without glass fiber (***b***) sauna cured,

(***c***) original sample PP/UHMWPE with 10 phr of glass fiber (***d***) sauna cured,

and (***e***) original sample PP/UHMWPE with 25 phr of glass fiber (***f***) sauna cured.

Observation the interfacial adhesion between the polymer matrix and glass fiber by taking the mode of fracturing into consideration, it is seen that there is no dominate traces of the fiber pull-out. The fibers are in well intake with the polymer matrix. Therefore, fiber debonding mode is suspected. It means that the interfacial adhesion between glass fiber and PP/UHMWPE in the present of silane/DCP is relatively good. Stronger interfacial adhesion between fiber and matrix than the strength of the fiber would resulting the higher in the composite strength with increasing the fiber fraction as found for the present composite system.

From the SEM investigation, it could conclude that materbatching of UHMWPE with HDPE in twin screw extruder at 240^{o}C is sufficient for the UHMWPE particle to be fused into the HDPE matrix. The good adhesion interfacial between short glass fiber and PP/UHMWPE matrix in the presence of silane/DCP was verified.

5.6 Conclusion

In attempting to increase the HDT of PP/UHMWPE blends/compound to the target value at 150^{o}C was performed by addition of filler(s); talc, carbon black/RHA and reinforced with fiber glass. It was found that increasing in the degree of talc filling would increase the mechanical and thermal properties of the compound having PP/UHMWPE blend as matrix. The well dispersion and decent adhesion of the talc particles in the polymer blend matrix was responsible for the superiority. Using the hybrid fillers between organic and inorganic fillers; CB/RHA, showed that increasing in the CB organic filler content to some certain level could increased the melt viscosity, fracture toughness and tensile properties but lower the HDT of the

PP/UHMWPE compound. The improving in the interfacial adhesion and increasing in the possibility of chain crosslinking due to the free radical degradation inhibition of the CB is hypothesized. Reinforcing the PP/UHMWPE; deriving from the homo and random PP blends and HDPE/UHMWPE master batch at 240^{o}C, with glass fiber found that both mechanical and thermal properties of the composite were improved. Good adhesion between the matrix and fiber was resolved. However, within this design experiment, the HDT of the PP/UHMWPE compound was still below 150^{o}C.

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CHAPTER VI

CONCLUSIONS

The main study of this research was to enhance thermal property by mean HDT of PP compound. The HDT higher than 150^{o}C was the prime target. It would be used for the oil cooking grade microwave ware and others appropriate high temperature applications. The main methods to enhance the properties of PP were crosslinking, blending and adding fillers/reinforcement.

Polypropylenes(PPs) blends with addition of peroxide/silane induce condensation, of homo polymer, block copolymer and random copolymer. They were studied by the design of experiment approach using the 2^k design method. The statistical results showed that homo type PP was positive effect on HDT and flexural properties. In contrast, homo type PP had negative effect on MFI. The lower of homo and high of block PP had the positive effect on the notched impact strength. The statistic conclusion suggested that the higher in MFI, HDT and flexural properties were attained when the high level of content of homo PP was employed.

Effect of DCP concentration in silane/peroxide crosslink system and also blending the homo PP with its block copolymer was also studied. For the sake of the bending toughness of the PP compound, the UHMWPE was used as toughener. The results found that the UHMWPE as toughener was ineffective. The property of the PP blends were decreased with increase content of DCP caused the vast chain degradation via the free radical chain scission reaction. As the result, the mechanical properties especially toughness of the blends was decreased, the optimal of peroxide content was 0.1 phr. The blended matrix between homo and block copolymer PP in the present of UHMWPE and silane/DCP in order to enhance the toughness of the blend was unsuccessful. The reverse effect was found. The toughness by mean of impact and flexural properties were also deceased with adding more of copolymer. The material became more brittle with increasing the copolymer fraction.

In attempting to enhance thermal and mechanical properties of the PP/UHMWPE blends/compound, they were performed by addition of filler(s); talc, carbon black(CB) and rice hush ash(RHA), and reinforced with fiber glass. It was found that talc enhanced the thermal and mechanical properties of the compound having PP/UHMWPE blend as matrix. The well dispersion and decent adhesion of the talc particles in the polymer blend matrix was responsible for the superiority. The 20 phr of talc was used. Addition of the hybrid fillers derived from carbonized rice husk ash and carbon black was studied. It indicated that the HDT decreased when the weight ratio of CB was increased. The carbon black fraction increased the fracture toughness but lower the HDT. Reinforcing the PP/UHMWPE; deriving from the homo and random PP blends and HDPE/UHMWPE master batch at 240^{o}C, with glass fiber found that both mechanical and thermal properties of the composite were improved. Good adhesion between the matrix and fiber was resolved. The fiber glass was used as reinforcement. The result exhibited that the fiber glass enhanced the thermal and mechanical properties. However, the target value of HDT at 150^{o}C has not been obtained by the above compound techniques.

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APPENDIX A

PUBLICATION

Publication

Khongrit, A., and Meekum, U. (2012). Enhance properties of crosslinked PP/UHMWPE blend. In **Proceedings of the Polymer Processing Society 28th** (pp. 226). December 11-15, 2012, Pattaya, Thailand.

ENHANCE PROPERTIES OF CROSSLINKED PP/UHMWPE BLEND

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Abstract:The enhancement of HDT without scarifying the mechanical properties of the DCP/silane induced crosslinked PP in the presence of UHMWPE was explored. The effect of DCP in the crosslink system, blending with block PP and adding the talc filler were attempted. The mixing was performed in co-rotation twin screw extruder. The injection molded specimen was prepared. The sauna treatment was applied and compared. Both mechanical testing and morphological investigation using the standard procedures were conducted. It was found that increasing the DCP concentration on the silane/DPC crosslink system of PP/UHMWPE blending had vastly chain degraded via the free radical chain scission. Hence, the mechanical properties especially toughness of the blends were inferior. Using homo and block PP blended matrix mixed with UHMWPE to enhance the toughness of the tertiary blends was ineffective. The reverse effect was found. The toughness was deceased with copolymer loading. The chain degradation through the free radical induced chain scission was the major drawback. Adding talc filler into the PP/UHMWPE revealed that mechanical and thermal properties of the compound were increased with increasing the degree of fill. The well dispersion and decent adhesion of the talc particles in the polymer blend matrix is responsible for the superiority.

Keywords: PP/UHMWPE Blends, Homo and block PP blend, Talc filled PP compound, Mechanical properties.

Introduction

Crosslinking of polyolefins can be done to all polyolefin types. However, the vast majority of the publications are concerned with polyethylenes. Few studies concerning the crosslinking of PP have been reported. Crosslinking of PP by free radical reaction is difficult. This is most likely a consequence of the nature of the PP chain degradation[1]. During the mixing process, PP chain scission has accompanied as a main reaction. This would be negatively influence the properties of the final product. The macroradicals formed may subsequently follow two competing pathways. They can either initiate the grafting of monomers or undergo chain scission, which is the main side reaction, perhaps major reaction, during the process[2]. A polymeric alloy is one of the important routes for preparation alternative materials with synergistic and tailored properties. Developments of polymer blends have been mainly focused on two component systems; matrix and dispersed morphology[3]. Blending of different polymers has long been practiced in the manufacturing industry for various reasons including: (*i*) tailor made blends to meet specific processing and performance requirements that cannot be satisfied by a single component; (*ii*) blending of polymers can be used in the field of recycling post consumer wastes to upgrade their properties, (*iii*) scientific interests; and (*iv*) financial incentives[4]. The addition of fillers to polymers is a fast and cheap method to modify the properties of the polymeric materials. For this reason, filled polymers have subjected of increasing interest in both industry and research. Normally, strength, stiffness, thermal properties, among other properties, can be superior to the required values[5]. Talc is the most commonly used because it is the softest mineral, abundant and inexpensive filler. Filled products typically exhibit excellent properties such as high stiffness, surface aesthetics, excellent HDT, low coefficient of thermal expansion and shrinkage, improved scratch as well as resistance to some aggressive chemical agents[6]. In this research, attempting to enhance the HDT of PP without scarifying the mechanical properties of DCP/silane induced crosslinked polypropylene is the main objective.

Experimental

Materials

Main materials used in the study were PP, PP 700J, and PP, PP740J, which are homo and block copolymer, respectively. It was supplied from SCG Chemical Co., Ltd. The UHMWPE, UH900, was available from Asahi Chemical Industry. Dicumyl peroxide(DCP) and silane(VTMS), Silquest® A 171, were used as coupling/grafting system. They were also used as complementary crosslink agent. The chemicals were commercially available. Talc as filler with the average particle size of 1.4 μm was employed.

Specimen preparation

PPs was dry blended with DCP in warmed oven at 80°C for 5 min to allow DCP to liquidize and then was vigorously stirred in tight container. Then, 2.0 phr of VTMS was added into the polymer ingredients. After that, it was in corporately blended with UHMWPE and talc powder. The melt compounding was achieved in closely intermeshing co-rotation twin screw extruder, with L/D ratio and screw diameter of 25/1, 25 mm, respectively. The extruder barrel temperature profile from feed to die zone was at 190°C and screw speed at 10 rpm. Samples were injection molded on Tederic TRX60c injection molding machine. The barrel temperatures were profiled at 160, 165, 170, 170 and 170°C from feed to nozzle tip, gradually. The injection molded specimens were divided into 2 sets of samples. One was allowed to anneal at room temperature for a day before testing, assigned as "original". Latter was incubated in the water vapour saturated oven at 105°C for 12 hour to accelerate the competition of silane/moisture crosslink condensation reaction. Then, it was cooled down at room temperature for day priority to conduct the test. It was named as "cured" sample.

Materials testing
MFI test was performed at 170/2.16. HDT were measured at the 455 kPa. Unnotched and notched impact strengths were obtained. Flexural properties both strength and modulus sample were examined. The tests were conducted in accordance with ASTM standards. Phase morphology of the fractured surface of compound samples were examined by SEM.

Results and Discussion

Effect of DCP on the PP/UHMWPE blends
MFI and HDT of PP/UHMWPE blends with various DCP content is given in Fig. 1. It is seen that the MFI is exponentially increased with increasing the DCP content for both in the original and after sauna cured specimen. Sauna incubation does lower the index. Chain scission of PP by the free radical biting is the main suspect for this phenomenon. The higher in peroxide, hence free radical, concentration, the faster in chain degradation. HDT of the blends are more or less in depended on the DCP concentration, especially for the original samples. Within the critical chain length, the HDT of polymer does not depend much on the molar mass. Rising of HDT after sauna curing of the blends is two folds hypothesis explanation. The first one is the easily short chain crystallinity while annealing and the second is the chain recombination through the silane/moisture induced condensation. The later would cause the chain length to expand or perhaps forming network chain.

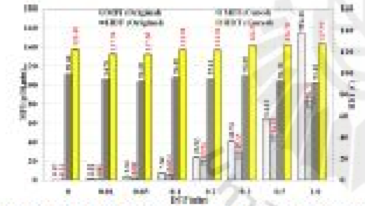

Figure 1 MFI and HDT of PP/UHMWPE blends with DCP contents

Fig. 2 reveals the impact strengths of the PP/UHMWPE. It is observed that both notched and unnotched impact strengths were lowered with increasing the DCP loading as expected. Because from the flow index, the short chain formation caused by the free radical scission would lower the material toughness. Chain recombination by sauna curing would slightly hurdle the impact values.

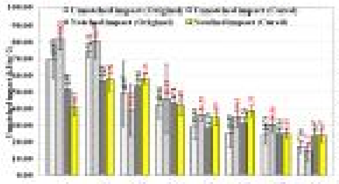

Figure 2 Impact strengths of PP/UHMWPE blends at given DCP contents

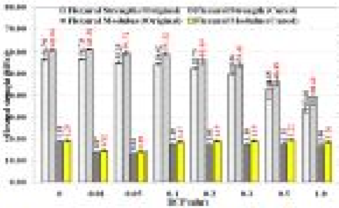

Figure 3 Flexural properties of the PP/UHMWPE blends and DCP contents

Similar to the impact outcome, the flexural strength and modulus of the PP/UHMWPE blends are presented in Fig. 3. The test results are illustrated that the strength is decreased but slightly increased in modulus with increasing the DCP. Results refine that the bending toughness of the materials is lost with adding the DCP. This observation is the common symptom of the brittle material caused by chain degradation.

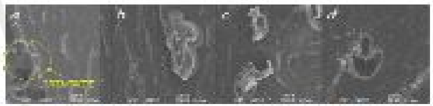

Figure 4 SEM photographs of PP/UHMWPE blends with: (*a*) 0.01 phr(original) (*b*) 0.01 phr(cured), (*c*) 1.0 phr(original) and (*d*) 1.0 phr(cured) of DCP, respectively.

Fig. 4 shows SEM pictures of PP/UHMWPE with 0.01 and 1.0 phr of DCP, before and after sauna incubation, respectively. It is seen that UHMWPE phase is obviously unmelted and dispersed in the PP matrix. It indicates that the UHMWPE powder could not be fused during the melt mixing. It becomes the foreign and non-adhere particles in the blend, creating more voids. Consequently, they accelerate the crake propagation. The brittle material fractured surface characteristic is observed on the PP phases. It is noticed that more rougher traces at higher DCP loading.

Effect of PP block on PP/UHMWPE Blends

The amount of the PP copolymer, 10 to 40 phr, was blended with homo PP in the PPs/UHMWPE blends. MFI and HDT of the blends obtained are presented in Fig. 5. It is found that MFI is gradually increased with increasing the PP block. Again, sauna incubation does lower the flow index values. According to the manufacturer data sheet, MFI of the block is much higher than homo PP. Attempting by using the rule of mixture between these two polymers, the calculated MFI of the blends suggest that the calculated MFI of blends are in same trend as the measured values. The higher in measured than the calculated ones is due to the greater chain scission via free radical effect.

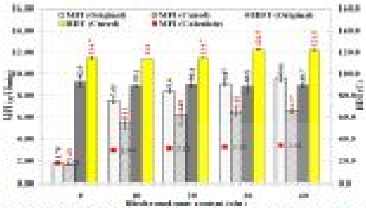

Figure 5 MFI and HDT of the PPs/UHMWPE blends and copolymer fraction

HDT of the original samples do not depend on the copolymer fraction but sauna treated specimen are fractionally increased with increasing the copolymer especially at the content above 30 phr. The increasing in HDT through the sauna curing process of the blends with high copolymer fraction might be due to the easily crystallization of ethylene segment in the PPs matrix after the given prolong annealing time at high temperature.

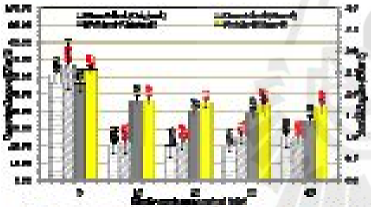

Figure 6 Impact strengths of the PPs/UHMWPE blends

Fig. 6 represents the notched and unnotched impact strengths of the PPs/UHMWPE blends. Unexpectedly, the notched strength is decreased with increasing the PP block loading but not much changed for the unnotched mode. The results indicate that the peroxide chain degradation would take the prime control of the notched impact strength of the blends over the characteristic of copolymer. Generally, the polymer degradation, especially during the melt processing, would lead to the decreasing in the material toughness.

Flexural strength and modulus of the PPs/UHMWPE blends is illustrated in Fig. 7. Similar to those impact strengths, the result reviews that flexural strength of both original and sauna cured samples are slightly decreased with increasing the block fraction. This is also contradicted to the fact that copolymer PP normally has the higher ductility than the homo. The modulus is slightly increased with increasing the block. In the flexural interpretation, if the strength decreases but increases in the modulus, it means inferior in the material toughness. Again, the free radical induced chain scission would be largely respond for the more brittle material found in this blends system.

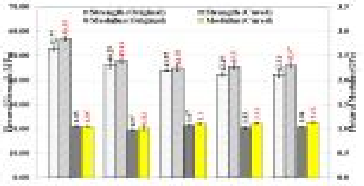

Figure 7 Flexural properties of the PPs/UHMWPE blends and block copolymer loading

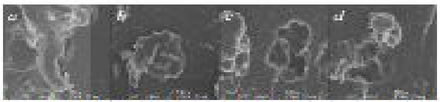

Figure 8 SEM of the PPs/UHMWPE blends with; (a) 10 phr and (b) 10 phr(cured), (c) 40 phr(original) and (d) 40 phr(cured) of PP copolymer, respectively.

According to the mechanical properties found for the PPs/UHMWPE blends. Phase morphology of the blends were examined and presented in Fig. 8. It is seen that the UHMWPE phase is still unmelted. Either by adding the copolymer or underwent sauna curing, the interfacial bonding between the matrix phase and UHMWPE particle does not obviously enhance. Thus, the toughening of the blends by UHMWPE cannot be achieved.

Talc filled PP/UHMWPE compound

Talc at 10 to 50 phr was added into the PP/UHMWPE blends to form the polymer compounds. MFI and HDT of the compound obtained are shown in Fig. 9. It is seen that the flow index is exponentially decreased with increasing the talc load. It indicates that the viscosity of the compound is increased by adding talc. HDT is slightly increased with the talc loading. Both viscosity and HDT of the compound at the given talc loading are increased by sauna treatment. Commonly, adding particulate filler into the polymer compound can enhance the rheological and thermal properties of the material.

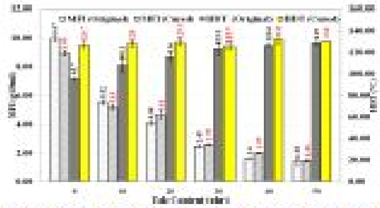

Figure 9 MFI and HDT of talc filled PP/UHMWPE compounds

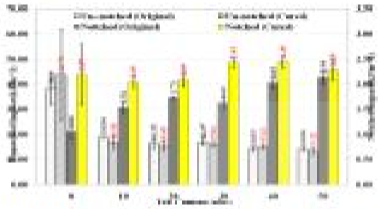

Figure 10 Impact strengths of the talc filled PP/UHMWPE compounds

Fig. 10 shows the impact strengths of the talc filled compound. As commonly found in the talc filled polymer compound, the notched impact strength is linearly increased, with increasing the talc loading. The contribution to the cracked propagation resisting by filler particles is respond for this positive effect. However, unnotched impact exhibits the contrarily responds. When poor adhesion occur between the polymer matrix and filler, the cracks tips would rapidly propagate and penetrate inside the sample. This phenomenon would easily fail the sample. The brittle material would be indentified.

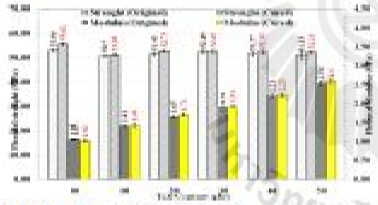

Figure 11 Flexural properties of the talc filled PP/UHMWPE compounds

Flexural properties of talc filled PP/UHMWPE compound are given in Fig 11. It is evidenced that the strengths of both original and cured samples is unchanged with the talc contents. On the other hand, the modulus is linearly increased with increasing the filler loading. Somehow, flat in the strength but rising in the modulus, it is interpreted that the materials indicate the superiority to the bending load.

Figure 12 SEM of the talc filled PP/UHMWPE at; (a) 10 phr(original), (b) 10 phr(cured), (c) 50 phr(original), and (d) 50 phr(cured) loading, respectively

SEM investigation of 10 and 50 phr talc filled PP/UHMWPE compound before and after sauna incubation are presented in Fig. 12, respectively. From the morphological observation, with carefully observe at the traces, well distributed of fine particle of talc is seen on matrix phase. The particle has good adhesion with the matrix phase especially after the curing. Consequently, the fracture toughness of the samples would slightly increase with increasing the talc content.

Conclusions

In attempting to improve the HDT of the PP without scarifying the mechanical properties by blending and compounding techniques, it was found that increasing the DCP concentration on the silane/DPC crosslink system of PP/UHMWPE blending had vastly chain degraded via the free radical chain scission. Hence, the mechanical properties especially toughness of the blends were inferior. Using homo and block PPs blended matrix mixed with UHMWPE to enhance the toughness of the tertiary blends was ineffective. The reverse effect was found. The toughness was deceased with copolymer loading. The chain degradation through the free radical induced chain scission was the major drawback. Adding talc filler into the PP/UHMWPE revealed that mechanical and thermal properties of the compound were increased with increasing the degree of fill. The well dispersion and decent adhesion of the talc particles in the polymer blend matrix is responsible for the superiority.

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BIOGRAPHY

Mr. Anucha 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: Peroxide/silane crosslinked polypropylene* blend" at the 3rd International Conference on Advances in Petrochemicals and Polymers, Bangkok, Thailand.