Fabrication and Characterization of Thin Films from Natural Rubber Blending with Thermoplastics

Kritsada Phatcharasit

A Thesis Submitted in Fulfillment of the Requirements for the Degree of
Doctor of Philosophy in Polymer Science and Technology
Prince of Songkla University
2014

Thesis Title	Fabrication and Characterization of Thin Films from Natural Rubber Blending with Thermoplastics
Author	Mr. Kritsada Phatcharasit
Major Program	Polymer Science and Technology

Major Advisor :	**Examining Committee :**
………………………………………	…………………….……...…….Chairperson
(Asst. Prof. Dr. Wirach Taweepreda)	(Asst. Prof. Dr. Kanoktip Boonkerd)
Co-Adivisor :	…..………………………….……….
	(Asst. Prof. Dr. Wirach Taweepreda)
…..…………………….….....	…..…………………….….....
(Prof. Dr. Kim, Jin Kuk)	(Prof. Dr. Kim, Jin Kuk)
	..……….……………………….………..
	(Asst. Prof. Dr. Chiraphon Chaibundit)

The Graduate School, Prince of Songkla University, has approved this thesis as fulfillment of the requirements for the Doctor of Philosophy Degree in Polymer Science and Technology

…….…………………………...............
(Assoc. Prof. Dr. Teerapol Srichana)
Dean of Graduate School

This is to certify that the work here submitted is the result of the candidate’s own investigations. Due acknowledgement has been made of any assistance received.

....Signature
(Asst. Prof. Dr. Wirach Taweepreda)
Major Advisor

....Signature
(Mr. Kritsada Phatcharasit)
Candidate

I hereby certify that this work has not already been accepted in substance for any degree, and is not being concurrently submitted in candidature for any degree.

....Signature
(Mr. Kritsada Phatcharasit)
Candidate

ชื่อวิทยานิพนธ์ กระบวนการขึ้นรูปและการวิเคราะห์ฟิล์มบางจากยางธรรมชาติเข้ากับเทอร์โมพลาสติก
ผู้เขียน นายกฤษฎา พัชรสิทธิ์
สาขาวิชา วิทยาศาสตร์และเทคโนโลยีพอลิเมอร์
ปีการศึกษา 2556

บทคัดย่อ

การเตรียมฟิล์มบางจากพอลิเมอร์ผสมระหว่างยางธรรมชาติกับเทอร์โมพลาสติก เช่น พอลิเอทิลีน และพอลิไวนิลคลอไรด์ ด้วยเทคนิคการบีบอัดเข้าเบ้าด้วยความร้อน และเทคนิคอิเล็กโตรสปินนิ่ง ทำให้ได้ชิ้นงานที่มีความแตกต่างกันทั้งลักษณะทางสัณฐานวิทยาสมบัติเชิงความร้อน และสมบัติการนำไฟฟ้า เทคนิคการบีบอัดพอลิเมอร์ผสมเข้าเบ้าด้วยความร้อนที่อุณหภูมิ 150°C จะทำให้ได้แผ่นฟิล์มบางเนื้อแน่นที่มีความหนาประมาณ 0.1-0.2 มิลลิเมตร พอลิเอทิลีนที่ผสมเข้ากันกับยางธรรมชาติจะแยกตัวและซึมผ่านออกมาที่ผิวของแผ่นฟิล์มบาง ซึ่งจะช่วยเพิ่มความต้านทานต่อการเสื่อมสภาพ เนื่องจากปฏิกิริยาออกซิเดชั่นที่ทำการทดสอบโดยเครื่องทดสอบความต้านทานต่อโอโซน การผสมพอลิไวนิลคลอไรด์ในปริมาณที่ต่ำกว่าร้อยละ 5 โดยน้ำหนัก เข้ากับยางพบว่าแผ่นฟิล์มบางเนื้อแน่นที่ได้จากเทคนิคการบีบอัดเข้าเบ้าด้วยความร้อนที่ 170°C มีความแข็งแรงเพิ่มขึ้น แต่เมื่อผสมพอลิไวนิลคลอไรด์ในปริมาณที่มากขึ้นพอลิไวนิลคลอไรด์จะแยกตัวและซึมออกมาที่ผิวของแผ่นฟิล์ม ทำให้แผ่นฟิล์มบางที่ได้มีความแข็งแรงลดต่ำลง แต่สมบัติการนำไฟฟ้าเพิ่มสูงขึ้น เมื่อเตรียมแผ่นฟิล์มจากสารละลายพอลิไวนิลคลอไรด์ด้วยเทคนิคอิเล็กโตรสปินนิ่ง พบว่าความเข้มข้นของสารละลายพอลิไวนิลคลอไรด์ แรงดันไฟฟ้า และระยะห่างระหว่างปลายเข็มกับแผ่นรองรับที่ทำให้ได้เส้นใยพอลิไวนิลคลอไรด์ระดับนาโนเมตรที่ดีที่สุดคือร้อยละ 10 โดยน้ำหนัก 12 กิโลโวลต์ และ 15 เซนติเมตร ตามลำดับ โดยสารละลายพอลิไวนิลคลอไรด์สามารถผสมเข้ากันกับสารละลายยางธรรมชาติอิพอกไซด์ได้ และสามารถเตรียมเป็นแผ่นฟิล์มบางเทคนิคอิเล็กโตรสปินนิ่ง ที่มีความหนาประมาณ 0.01-0.05 มิลลิเมตร ซึ่งยางธรรมชาติอิพอกไซด์จะช่วยเพิ่มความยืดหยุ่น และความเสถียรทางความร้อนให้กับเส้นใยพอลิไวนิลคลอไรด์ระดับนาโนเมตร โดยสมบัติการนำไฟฟ้าจะเพิ่มขึ้นตามปริมาณการเพิ่มขึ้นของพอลิไวนิลคลอไรด์

Thesis Title Fabrication and Characterization of Thin Films from
Natural Rubber Blending with Thermoplastics
Author Mr. Kritsada Phatcharasit
Major Program Polymer Science and Technology
Academic Year 2013

ABSTRACT

Thin films of polymer blends between natural rubber (NR) and thermoplastics including polyethylene (PE) and poly(vinyl chloride) (PVC) were prepared using hot compression molding and electrospinning. Their surface morphology, thermal property, and electrical property were investigated. The films of NR/PE blend preparing by hot compression molding were dense with the thickness of 0.1-0.2 mm. From prepared using hot compression molding at temperature 150^{o}C, it was observed that PE partially migrated to the surface, forming the PE layer on the surface of the NR/PE films. Due to this, the NR/PE dense film showed higher thermal oxidation resistance than the pure NR dense film. For the dense films of the NR/PVC blend preparing by hot compression molding, it was found that when PVC content was less than 5% by weight, the strength of the films was higher than that of the pure NR films. The further increase in PVC content resulted in decreasing of the strength of the films. The SEM images showed that at high PVC content, PVC partially migrated to the surface and then formed lamelle crystalline. This might contribute to the reduction of the strength of the NR/PVC thin films when adding high PVC content. However, the electrical properties of the dense NR/PVC film increased with increasing in PVC contents. When blending epoxidized natural rubber (ENR) with PVC, the non-woven thin films with a thickness of 0.01-0.05 mm were successfully prepared using electrospinning. The obtained NR/PVC non-woven thin films showed high flexibility. The thermal properties of the NR/PVC non-woven thin films increased with the increase of PVC content.

ACKNOWLEDGMENT

The work presented in this thesis was carried out at the Polymer Science and Technology, Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Thailand and Department of Polymer Science and Engineering, Gyeongsang National University, Republic of South Korea. It was financially supported by the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission and The Graduate School Prince of Songkla University Scholarships.

It is a pleasure to complete this thesis work. I have received generous support of a lot of people from the beginning till the end of the present thesis work. On this occasion, I would like to express my gratitude to all of them.

Asst. Prof. Dr. Wirach Taweepreda, my supervisor who was abundantly helpful and offered invaluable assistance, support and guidance. I could not have imagined having a better advisor and mentor for my PhD study and research.

Asst. Prof. Dr. Kanoktip Boonkerd, Thank you so much for your encouragements, suggestions and always great recommendations.

Prof. Dr. Kim, Jin Kuk, Thank you for accepting me as a student in the laboratory, continuous guidance, patience, kindness, inspiration and for putting a lot of pressure to get the papers out during my stay.

Asst. Prof. Dr. Chiraphon Chaibundit, Thank you for always kindness, practical useful tips, suggestions and discussions.

I have furthermore to thanks all committees.

My senior and junior colleagues from our labmates member supporting me in my research work, sharing the literature and invaluable assistance. I also want to thanks my beloved families for their understanding and endless love, through the duration of my studies.

Thank you all so much!

Kritsada Phatcharasit

CONTENTS

Introduction

Results and Discussion

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

Figure **Page**

ABBREVIATIONS

ºC	degree celsius
ENR-10	10 mole percent epoxidized natural rubber
ENR-25	25 mole percent epoxidized natural rubber
ENR-50	50 mole percent epoxidized natural rubber
ΔH_f	Heat of fusion
HDPE	High Density Polyethylene
kV.	Kilovolt
kGy	kilogray
LCR meter	Inductance (L), Capacitance (C), and Resistance (R) meter
LDPE	Low Density Polyethylene
LLDPE	Liner Low Density Polyethylene
LNR	liquid natural rubber
MeV	megaelectronvolt
MPa	Mega pascal
mm/s	millimeter/second

NaCl	Sodium chloride
nm.	Nanometer
phr	Part per hundred rubber
rpm	revolutions per minute
Tg	Glass transition temperature
T_m	melting temperature
µm.	Micrometer
UV-vis	Ultraviolet-visible spectroscopy
wt%	weight percent

LIST OF PAPERS

This thesis is based on the following papers, which will be referred to the text by their Roman numerals:

I. **Phatcharasit, K.** and Taweepreda, W. 2011. Polyethylene Thin Film Coating Preventing the Degradation of Natural Rubber. Engineering Journal, 16(3):53-58.

II. **Phatcharasit, K.**, Taweepreda, W. and Saesia, W. 2012. TPNR Membrane Reinforcing with Cotton Fibre Spun. Journal of Chemistry and Chemical Engineering, 6:799-802.

III. **Phatcharasit, K.** and Taweepreda, W. 2012. In Situ Coating of Natural Rubber Film with Poly(vinyl chloride) Resin. Procedia Chemistry, 4: 232-237.

IV. **Phatcharasit, K.,** Taweepreda, W., Boonkerd, K. and J. K., Kim. 2013. Preparation and Properties of Electrospun PVC Nanofiber. Advanced Materials Research, 770:193-196.

V. **Phatcharasit, K.,** Taweepreda, W., Boonkerd, K. and J. K., Kim. 2014. Electrospun Epoxidized Natural Rubber with Poly(vinyl chloride)(ENR-PVC) nanofibrous for PEMFC Applications. Advanced Materials Research, 844:507-510.

Paper I

Reprint was made with permission from the publisher

[Fwd: Re: Aksing for reprint submission]

---------------------------- Original Message ----------------------------
Subject: Re: Aksing for reprint submission
From: yan.z@chula.ac.th
Date: Thu, April 17, 2014 10:59 pm
To: "Dr.Wirach TAWEEPREDA" <wirach.t@psu.ac.th>

Dear Dr. Wirach,

We agree to grant the permission for your student to reprint the contents or figures in his/her thesis. Please also cite the paper published in Engineering Journal where appropriate.
Again, we thank you for your contribution to Engineering Journal.

Regards,

Yan Zhao, PhD
Managing Editor
Engineering Journal (EJ)
http://engj.org/
ISSN: 0125-8281

Dear Sit,

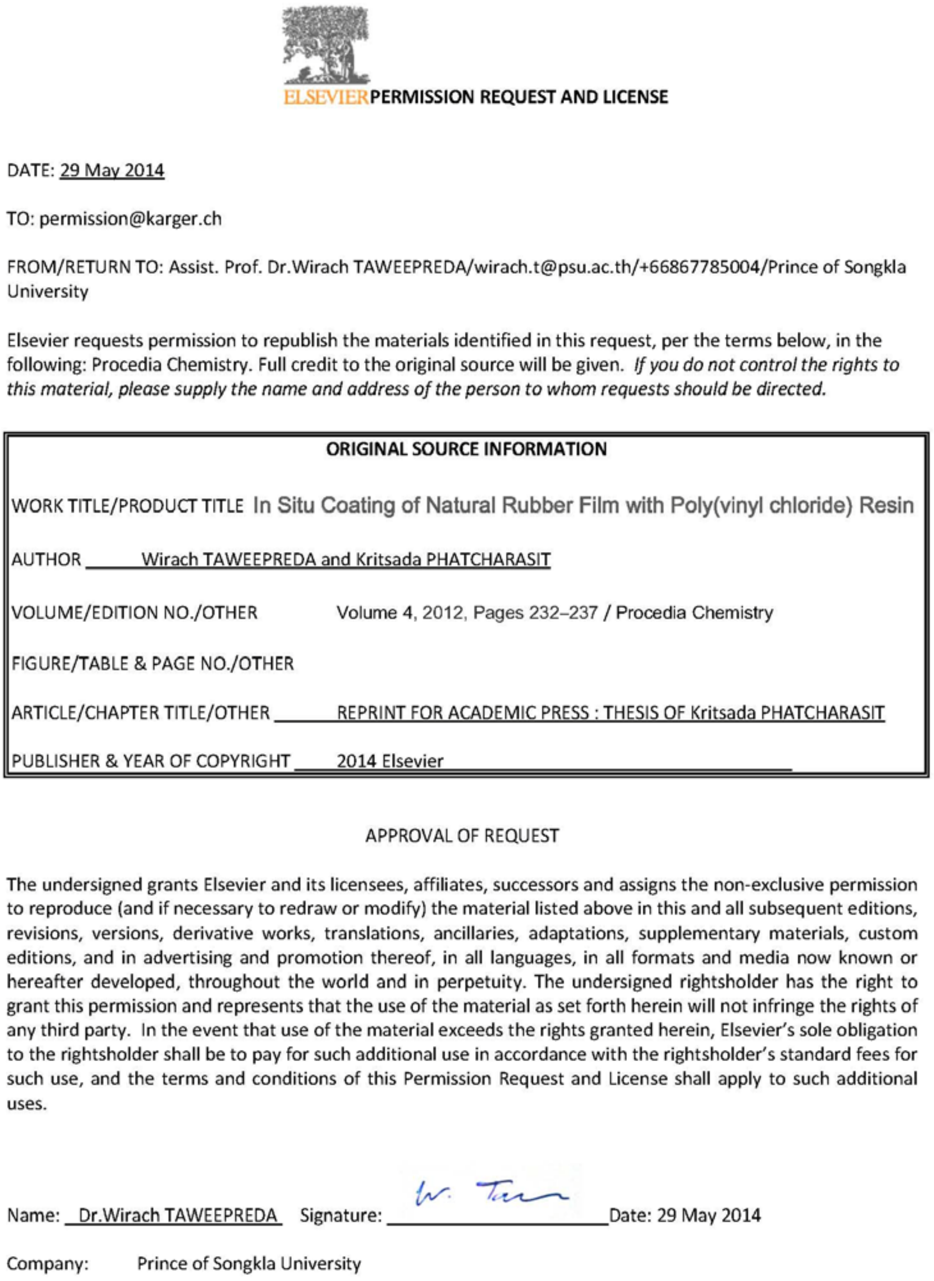
According to my paper in the title of Polyethylene Thin Film Coating Preventing the Degradation of Natural Rubber which was published in Engineering Journal, Vol 16, No 3 (2012), I would like to ask for the permission to my student (Mr.Kritsada Phatcharasit) for reprint to his Ph.D. thesis. Could you please let me know your journal policy for student
reprint? I will look forward to hearing from you.

Best Regards,

Assist.Prof.Dr.Wirach TAWEEPREDA
Department of Materials Science and Technolgy
Faculty of Science
Prince of Songkla University, Hat-Yai, Songkhla 90110

Paper III

Reprint was made with permission from the publisher



ELSEVIER **PERMISSION REQUEST AND LICENSE**

DATE: 29 May 2014

TO: permission@karger.ch

FROM/RETURN TO: Assist. Prof. Dr.Wirach TAWEEPREDA/wirach.t@psu.ac.th/+66867785004/Prince of Songkla University

Elsevier requests permission to republish the materials identified in this request, per the terms below, in the following: Procedia Chemistry. Full credit to the original source will be given. *If you do not control the rights to this material, please supply the name and address of the person to whom requests should be directed.*

ORIGINAL SOURCE INFORMATION

WORK TITLE/PRODUCT TITLE	In Situ Coating of Natural Rubber Film with Poly(vinyl chloride) Resin
AUTHOR	Wirach TAWEEPREDA and Kritsada PHATCHARASIT
VOLUME/EDITION NO./OTHER	Volume 4, 2012, Pages 232–237 / Procedia Chemistry
FIGURE/TABLE & PAGE NO./OTHER	
ARTICLE/CHAPTER TITLE/OTHER	REPRINT FOR ACADEMIC PRESS : THESIS OF Kritsada PHATCHARASIT
PUBLISHER & YEAR OF COPYRIGHT	2014 Elsevier

APPROVAL OF REQUEST

The undersigned grants Elsevier and its licensees, affiliates, successors and assigns the non-exclusive permission to reproduce (and if necessary to redraw or modify) the material listed above in this and all subsequent editions, revisions, versions, derivative works, translations, ancillaries, adaptations, supplementary materials, custom editions, and in advertising and promotion thereof, in all languages, in all formats and media now known or hereafter developed, throughout the world and in perpetuity. The undersigned rightsholder has the right to grant this permission and represents that the use of the material as set forth herein will not infringe the rights of any third party. In the event that use of the material exceeds the rights granted herein, Elsevier's sole obligation to the rightsholder shall be to pay for such additional use in accordance with the rightsholder's standard fees for such use, and the terms and conditions of this Permission Request and License shall apply to such additional uses.

Name: Dr.Wirach TAWEEPREDA Signature: ______________ Date: 29 May 2014

Company: Prince of Songkla University

Introduction

Polymer

A polymer is a high molecular weight by polymer is composed of repeating units of monomers in reaction units. When polymer is composed of subunits or monomers of the same type, it is organized into homopolymer group. But if polymer derived from two (or more), it is organized into copolymer group.

Polymers, both natural and synthetic, are created via polymerization of many monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, (Michael et al., 1995) including toughness, viscoelasticity, and a tendency to form glasses and semi-crystalline structures rather than crystals. (MaCrum et al., 1997) Natural polymer includes starch, cellulose, proteins, nucleic acids, and natural rubber while synthetic polymer includes plastics, fibers, foams and adhesives. Because of their broad range of properties, both synthetic and natural polymers play an essential and ubiquitous role in everyday life. And each polymer has different properties wide variety of applications. (Jensen, 2008)

Polymer blends

Polymer blends were macroscopically homogeneous mixture of two or more different species of polymer. (Work et al., 2004) The most important characteristic of a polymer blend of two (or more) polymers is the phase behavior. Polymer blends (like low molecular weight solvents) can exhibit miscibility or phase separation and various levels of mixing in between the extremes (e.g., partial miscibility). (Robeson, 2007) And polymer blends as a mixture of at least two macromolecular substances, polymer or copolymer, in which the ingredient content is above 2 wt%. (Utracki 2002) Later, (Utracki and Lyngaae-Jørgensen, 2003) defined Most properties of immiscible polymer blends depend on the morphology or the two-phase structure.

There is a great diversity of immiscible polymer blends morphology, but, from the point of view of the performance, they may be divided into two categories:

(1) Blends with discrete phase structure (DPS, or drop-in matrix), and
(2) Blends with bicontinuous phase structures (BPS, or co-continuous).

From over definition, we can conclude that polymer blend is a combination of two or more homopolymer or copolymer, obtained through different processes and technique.

Method of blending

Blending process of plastic, blending and compounding have different importance. Mixed indicates that the physical act of homogenization, blending often refer to the preparation of the polymer blends, while blending is the combination of additives into the polymer matrix, includes lubricants, pigments, antioxidants and reinforcement. (Utracki, 2002)

Mechanical blending of polymers is the easiest and most direct method of preparing a polymer blend. This may be accomplished on two-roll mill or internal mixers like Banbury. The nature of the resulting dispersion depends on the time of mixing, the shear field in equipment, temperature, rheological properties of the component polymers etc. Also, there is a possibility of chemical effects being produced by the milling operation.

Polymer blends were prepared commercially by melt mixing, solution mixing and latex blending

a) Melt mixing

Melt mixing technique is a simple way and economical way of blending different polymers to avoid contamination removal of solvent or water and others. Mixing can be accomplished on heated roll mills. Nonetheless, this is not actually much because the plastic has a high melting point. The open mixing mill is in the air at high temperatures causes oxidative degradation. Internal mixers, mixing extruder, and twin-screw extruder are more efficient and their use gives less oxidative degradation. (Mohamad, 2005) A melt mixing has been reported, such as (Davis et al., 2010) study, preparation polypropylene/single-walled carbon nanotube (PP/SWNT) nanocomposites prepared by initial mixing methods process was followed by melt extrusion. After that the nanotubes were vacuum dried overnight at 120 ºC before mixing 0.5 vol% SWNT or C12SWNT by placing PP and the nanotubes in a vial and shaking for 1 min before feeding into the extruder. The results showed that the observed for C12SWNTs. The nanotubes that were tended to remain as large agglomerates and possess poor adhesion to the polymer surface. And (Pötschke et al., 2005) study, preparation single-walled carbon nanotubes (SWNT) with polycarbonate (PC) by melt compounding was carried out using a Brabender PL-19 single screw extruder at screw speed of 50 rpm and temperatures between 240 ºC and 260 ºC, was found at the nanotube dispersion as observed by TEM investigations is quite homogeneous. The direct incorporation method is discussed in composites of polycarbonate with MWNT and SWNT. For commercial MWNT percolation was found between 1.0 and 3.0 wt% depending on the aspect ratio and purity of the materials. (Wang et al., 2012) Study, rubber/Ca-montmorillonite (Ca-MMT) nanocomposites were prepared by combination of latex compounding and melt mixing. The masterbatch was added in the system of styrene butadiene rubber (SBR) and epoxidized natural rubber (ENR) by melt mixing subsequently. Results showed that intercalated and exfoliated nanocomposites were obtained by the masterbatch technique. The effects of modified Ca-MMT introduction into the rubber matrix, via the masterbatch technique, on the properties of the resulting composites were studied. It was found that the vulcanization was hindered by the incorporation of modified Ca-MMT, while mechanical performances, thermal stability and aging resistance were improved. The scorch time and the vulcanization time are increased by the incorporating of modified Ca-MMT. And (Ratnam, 2002; Ratnam et al., 2006) preparation poly(vinyl chloride)/epoxidized natural rubber (PVC/ENR) blends by using Brabender mixing at (50/50). The ENR 50 was irradiated using a 3.0 MeV electron beam accelerator at a dose range of 10-100 kGy in air and at room temperature. The irradiated ENR 50 was then melt blended with PVC using a Brabender at 50 rpm, 150 ºC for 15 min. was found that an upward trend was observed for tensile strength, modulus, hardness, impact strength and gel fraction of the 50/50 PVC/ENR blend with irradiation dose. Such observation indicate that irradiation of the ENR 50 phase contributes to the enhancement in PVC/ENR blend properties. (Ratnam and Zaman, 1999) preparation poly(vinyl chloride)/epoxidized natural rubber (PVC/ENR) blends by using Brabender mixing at 70/30 illustrates the importance of PVC phase stabilization in ensuring the enhancement of PVC/ENR blend properties through irradiation and implies the influence of blend homogeneity in enhancing the properties through irradiation. And results showed that effect of stabilizer on tensile strength inverse elongation at break properties which tribasic lead sulfate (TBLS) stabilizer when amount and time increased that tensile strength increased.

b) Solution blending

Then separate the rubber is removed from the solvent by chemical precipitation with non solvent or allow solvent to evaporate completely. Preparation of rubber compounds by this method has several disadvantages including solvents are expensive and difficult to separate rubber. Dry rubber more energy to keep the costs high. The preparation of rubber can not be made in large quantities. Due to the viscosity of rubber solutions If the amount of rubber have very high melting exceeds 5 percent of the weight of rubber / volume of solvent. Therefore, the rubber compound in the form of a solution often used for research purposes only. (In the case of the little rubber) (Nimsuwan, 2011) This technique was used especially for water soluble polymers, such as poly(vinyl alcohol) (Greenland, 1963; Ogata et al., 1997; Strawhecker et. al., 2000), poly(acrylic acid) (Billingham et. al., 1997), poly(ethylene oxide) (Ogata et al., 1997; Lemmom and Lerner, 1994; Malwitz et. al., 2003; Aranda et al., 1992; Simon et al., 2002), etc., whose polarity probably contributes an enthalpy gain helping intercalation, though examples of preparations carried out with organic solvents and hydrophobic polymers have also been given (Li and Ishida, 2003; Chiu and Chu, 2006; Qu et al., 2002). A solution blending have been reported, including (Magagnini et. al., 2007) preparation of the ethylene-acrylic acid and a montmorillonite clays (EAA/organoclay) composites dissolved under stirring in a solvent such as 1,2,4 trichlorobenzene, chloroform, n-hexane and mixtures of THF and pentane (incomplete precipitation was obtained with pure THF, and mixtures of xylene and benzonitrile, were employed occasionally. (Wang and Wilkiem, 2002) PVC-clay nanocomposites have been prepared by solution blending of the polymer then dissolved in THF for 30 min. This was the followed by evaporation of the solvent, air-drying and drying in a vacuum oven, and then annealing. And (Schjødt-Thomsen et al., 2010) PVC/MMT nanocomposites prepared using the solution blending method. By then dissolved in THF until the solution became homogeneous and afterwards it was poured in plastic moulds, followed by the evaporation of the solvent.

c) Latex blending

Is an effective method because of the blend can take a good dispersion and compatibility thoroughly and use less energy in the mix. But must pay attention to the use of surfactants or soaps. The type and quantity of rubber latex to prevent degradation and an agglomeration process. However, the blending in the form of rubber latex has disadvantages in terms of cost. Because of coagulation dehydration and drying when it is a process that requires high costs. (Nimsuwan, 2011) A latex blending have been reported, elastomers used as epoxidized natural rubber (Chang et al., 2007; Senna et al., 2008), carboxylated nitrile rubber (Das et al., 2000; Das et al., 2000; Ibrahim and Dahlan, 1998) and vulcanized natural rubber (NR). (Dahlan and Zaman, 2002; Ismail and Suryadiansyah, 2002; El-Sabbagh, 2003;) Preparation LDPE and NR latex blends, study the effect of varying the NR latex content on the physical, mechanical and dynamic properties. (Poompradub and Supak, 2011) Study vulcanization of natural rubber latex in presence of styrene-butadiene rubber latex. (Bhardwaj et al., 2005) Study, preparation natural rubber (NR) and carboxylated styrene butadiene rubber (XSBR) lattices and their blends was studied by thermogravimetric methods. (Thomas et al., 2006) and the effect of penetrant size, filler loading and temperature on the diffusion properties were studied. (Thomas et al., 2007)

Classification of polymer blends

Polymer blends can be classified in various ways using different indicators such as compatibility (compatible and incompatible blends), production methods (mechanical blend or chemical blends), nature of polymer architecture (block and graft polymers), number of constituent polymers (binary blends, ternary blends etc.) and the types of constituent polymers. Based on the latest parameter, polymer blends can be broadly classified into three main groups as follows: a) rubber-rubber blends, b) plastic-plastic blends and c) rubber-plastic blends (TPE). (Mohamad, 2005)

The important of rubber-rubber blends become manifest when we realize that nearly every major rubber component in a tire constitutes a blend of two or more of these rubbers, styrene butadiene rubber (SBR), natural rubber (NR), synthetic rubber (IR), poly butadiene rubber (BR), butyl rubber (IIR) and ethylene propylene rubber (EPDM or EPM). The reasons of producing rubber-rubber blend are: (a) the compound cost may be lowered, (b) easy fabricated in the complex shaping, forming and building operations, (c) the final product performance can be modified beneficially.

Polyolefin is the largest group of commercial thermoplastic. They constitute a group of polymer of complex macromolecular structure, wide molecular weight distribution that are diverse in shape, substantial short and long chain branching and high crystallinity. Their density is the lowest among polymers and strongly influences performance characteristics. The characteristic of plastic-plastic blend are: excellent dielectric properties, water repellence, nonpolarity, high melt viscosities that respond weakly to temperature change but strongly to shear rate or stress changes, high melt elasticity and melt strength. Most of the studies on plastic-plastic blending used in production of films, profiles and containers, molding and insulation and jackets for cables.

Rubber-plastic blend or known as thermoplastic elastomer (TPE) blends is a relatively new class of polymer that are processable as a melt at elevated temperature but exhibit properties similar to a vulcanized elastomer at use temperature. Thermoplastic elastomer blends exhibit stress-strain characteristics that fall between the low modulus crosslink elastomers (curve c Figure. 1) and the high modulus yielding materials that undergo a high degree of plastic deformation (curve b, Figure. 1) (Kresge, 1978)

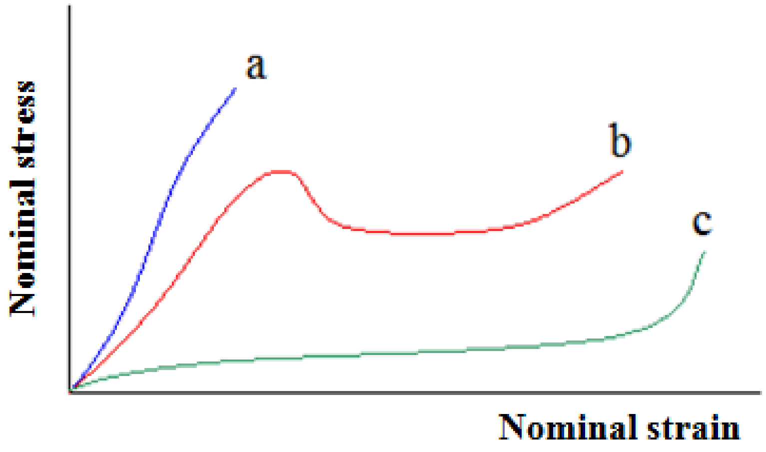


Fig. 1. Stress-strain curve showing behaviour of different polymers; a) high modulus plastic, b) high modulus with yielding and poor recovery on return cycle, c) low-modulus rubbery (Kresge, 1978).

Polymer degradation

Polymer degradation is a change in the properties of tensile strength, color, shape, etc. induced by heat, oxygen, sunlight, high-energy radiation, atmospheric pollutants, mechanical stress, biological reaction, hydrolysis and many other influences. The degradation mechanisms and stabilization processes by use of modern instrumental analytical methods; various spectrometric, chromatographic and thermal analysis techniques in the study of degradation mechanisms. The changes in properties are often termed aging. In general, we can classify mechanisms of polymer degradation is 4 main types. (Chansuvarn, 2011)

Thermal degradation

Thermal degradation of polymers is molecular deterioration as a result of overheating. At high temperatures the components of the long chain backbone of the polymer can begin to molecular scission and react with one another to change the properties of the polymer. Thermal degradation can present an upper limit to the service temperature of plastics as much as the possibility of mechanical property loss. Indeed unless correctly prevented, significant thermal degradation can occur at temperatures much lower than those at which mechanical failure is likely to occur. (Soldi et al., 2002)

Oxidative degradation

Oxidative degradation is reactive oxygen molecules into the polymer, which can occur naturally and slowly. By oxygen and UV light, heat or mechanical force is an important factor. Born compound is hydroperoxide (ROOH).

Photo-degradation

Photodegradation is degradation of a photodegradable molecule caused by the absorption of photons, particularly those wavelengths found in sunlight, such as infrared radiation, visible light, and ultraviolet light. However, other forms of electromagnetic radiation can cause photodegradation.

Hydrolysis degradation

Hydrolysis degradation is degradation of polymers that are functionalized esters or amides, such as starch, polyethylene, polycarbonate and polyurethane. Hydrolysis reactions that occur, generally divided into two types by using catalyst (catalytic hydrolysis), and not the catalyst post (non-catalytic hydrolysis), which is also first type is divided into 2 types is an external catalytic degradation and Internal catalytic degradation.

There are many reports on the thermal degradation of polymer blends. For example, NBR/EVA blend system exhibited a two-step degradation process and the activation energy of degradation for the blends was higher than that of the pure component indicating the enhanced thermal stability (Thomas et al., 2001). The compatibilisation of the two blends usually increases the degradation temperature. The effect of compatibilisation of PP/NBR blend using phenolic modified PP on the thermal degradation has been analysed (Thomas et al., 2000). Lizymol and Thomas compared the thermal behaviour of miscible and immiscible blends (Waldman and De Paoli, 2013). Investigated the thermal, UV-vis and sunlight ageing of thermoplastic elastomeric NR/PE blends. They found that thermal ageing of the blends caused the tensile properties to deteriorate, especially at longer times, or higher temperatures of ageing after an increase of properties in the initial stage. (Bhowmick and White, 2002) Investigated the ageing behavior of IIR/EPDM blends and found that the ageing resistance increased with increase in EPDM content. (Deuri et al., 1993) Study the ageing of different rubber-rubber blends. (Peng and Kong, 2007; 24 Thomas et al., 2001) and (Sulekha et al., 2002) reported that the use of oligomer bound antioxidants was an effective means of protecting non-resistant rubbers against surface cracking.

Thermoplastic Elastomer Blends (TPEs)

Thermoplastic elastomer (TPE) is defined as a polymer or polymers that has properties at its service temperature similar to those of vulcanized rubber but can be processed or reprocessed at elevated temperature like a thermoplastic. (Jiri, 2007) They need no separate vulcanization step. Scrap and rejects of these materials can be recycled without significant inferior effect on the properties. TPEs are capable of being molded like thermoplastics in injection moulding and extrusion at suitable processing temperatures. They are a measure of flexibility and resilience in recovery related to rubber vulcanization at temperatures normal. (De and Bhowmick, 1990) Some advantage and disadvantage of TPEs, such as the following: (Drobny, 2007)

(1) Simpler processing with fewer steps since TPEs use the processing methods for thermoplastics, which are typically more efficient and significantly less costly so the final cost of the finished part is lower.

(2) Shorter fabrication times, which also lead to lower finished part costs. Since molding cycles for TPEs are typically several seconds as opposed to minutes for thermoset rubbers, the productivity of the given equipment is greatly increased.

(3) There is little or no compounding. The majority of TPEs is supplied fully formulated and ready for fabrication.

(4) The possibility of reusing scrap in the same fashion as with thermoplastics. The scrap from thermoset rubbers is very often discarded. Its amount generated may be in some cases comparable to the weight of the molded part. The TPE scrap can be reused as a regrind frequently producing materials having the same properties as the virgin material.

(5) Lower energy consumption due to shorter molding cycles and simpler processing.

(6) Better quality control and closer tolerances of finished parts due to simpler formulations and process.

(7) Lower quality control costs because of greater reproducibility and consistency of properties of TPE resins.

(8) Since most TPEs have lower density than conventional rubber compounds, their volume cost is often lower.

The disadvantages of TPEs in comparison to conventional rubber materials include

(1) Melting at elevated temperatures. This inherent property limits the use of parts from TPEs to service temperatures well below their melting point. A thermoset rubber would be probably suitable for a brief exposure to that temperature;

(2) Limited number of low hardness TPEs. Many TPEs are available at hardnesses about 80 Durometer A or higher. The number of materials softer than 50 Durometer A is still rather limited;

(3) Drying prior to processing. This step is almost never used for conventional rubber materials but is quite common in fabrication of thermoplastics in general.

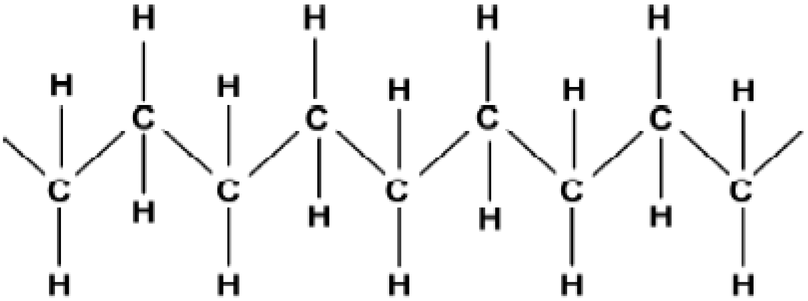
Thermoplastic elastomers are classified into following seven groups: (Drobny, 2007)

(1) styrenic block copolymers (SBCs);
(2) crystalline multiblock copolymers;
(3) miscellaneous block copolymers;
(4) combinations of hard polymer/elastomer;
(5) hard polymer/elastomer graft copolymers;
(6) ionomers; and
(7) polymers with core-shell morphologies.

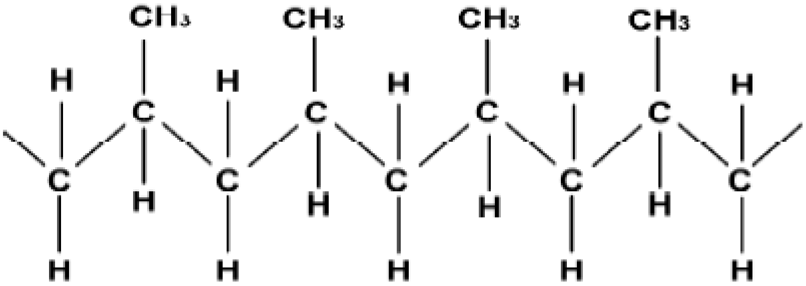
Thermoplastic Elastomer Olefins (TPOs)

Thermoplastic elastomer polyolefin is defined as materials combining polyolefin semi-crystalline thermoplastic and amorphous elastomeric components. They exhibit rubber-like characteristics and can be processed as melts by common thermoplastic processing equipment.(Kresge, 2004)

polyolefins are produced by reaction of an alkene as a monmer with general formula C_nH_{2n}. Polyethylene and polypropylene are produced by long chain polymerization of olefins ethylene and propylene respectively as shown in Figure. 2.



a) Polyethylene



b) Polypropylene

Fig. 2. Chemical structure of different polyolefins. (Amin S. and Amin M.,2011)

The simple blends are prepared by mixing the hard polymer and the elastomer together on high shear compounding equipment, such as internal mixer (e.g., Banbury) or continuous mixer (e.g., single- or twin-screw extruders). A two-dimensional representation of a hard polymer/elastomer blends is in Figure. 3. The viscosities of the two polymers must be matched at the temperature and shear rates of the mixing.

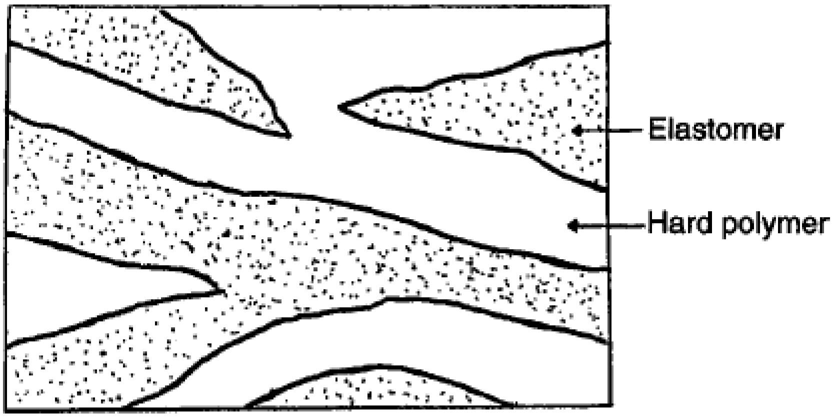


Fig. 3. Morphology of hard polymer/elastomer blends. (Kresge, 2000)

The optimum viscosity match also depends on the proportion of the two components (A and B) and the proportion of these components in the mixture

(Figure. 4). The other important factor is the compatibility of the two components, which is often expressed by the difference between their solubility parameters. If the volumes of the two components are about equal, then for ideal mixing, their viscosities should also be about equal. If the volumes are not equal, then the component with the larger volume should also have the higher viscosity. (Holden, 2000)

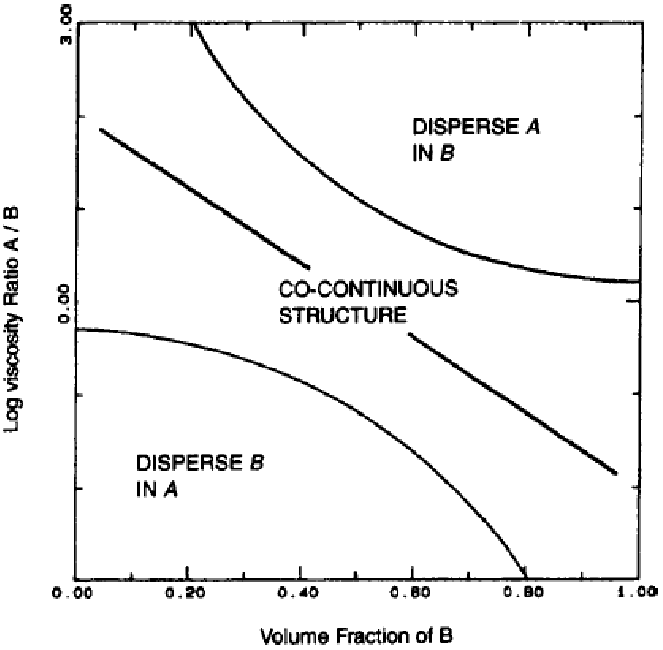


Fig. 4. Relationship between the ratio of the viscosities of two components (A and B) and their proportion in the mixture. (Drobny, 2007)

Thermoplastics

Thermoplastic is a material with becomes soft when heated and hard when cooled. They can be recycled. Thermoplastics are made up of linear molecular chains and can be shaped by flow into articles by molding or extrusion without need of any chemical processing before molding. Themoset useful physical property of a thermoplastic is its glass transition temperature at which it begins to soften. Glass transition temperatures of different thermoplastics. There are three types of thermoplastics crystalline, amorphous and semi-crystalline (Legge et al, 1987). The examples of thermoplastic polymers are polyethylene, polypropylene, polyethylene terephthalate, polystyrene, poly (vinyl chloride) and polyurethane etc.

a) Polyethylene (PE) is the most common plastic, with most having the chemical formula $(C_2H_4)_n$. Polyethylene is classified into three groups are HDPE, LLDPE and LDPE, dissolved at elevated temperatures in aromatic hydrocarbons such as toluene or xylene or in chlorinated solvents. (Kenneth et al, 2005; Sjoqvist et al., 2011)

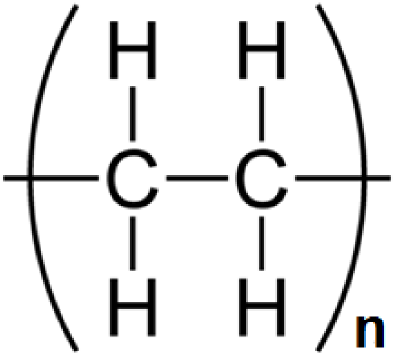


Fig. 5. Structure of Polyethylene (PE)

b) Poly (vinyl chloride) (PVC) is a thermoplastic prepared by free-radical polymerization of vinyl chloride in dispersion (emulsion), bulk, or suspension process. Unmodified PVC is very rigid and requires plasticizers to make it more flexible. The main end forms are rigid PVC and flexible PVC. (Drobny, 2007) The flexible form is often made from plastisols, suspensions of PVC in plasticizers. Flexible form is also obtained when PVC is blended with acrylonitrile butadiene rubber *(*NBR). (Wimolmala et al, 2000*)*

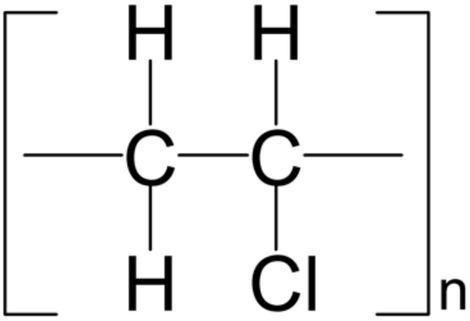


Fig. 6. Structure of Poly (vinyl chloride) (PVC)

Elastomer

Elastomers are rubbery polymers that can be stretched easily to several times their unstretched length and which rapidly return to their original dimensions when the applied stress is released. Elastomers are crosslinked, but have a low cross-link density. The polymer chains still have some freedom to move, but are prevented from permanently moving relative to each other by the crosslinks. To stretch, the polymer chains must not be part of a rigid solid. An elastomer must be above its glass transition temperature, T_g and have a low degree of crystallinity. (Mohamad, 2005) such as natural rubber (NR), synthetic polyisoprene (IR), butyl rubber (IIR), polybutadiene (BR), styrene-butadiene rubber (SBR) and acrylonitrile butadiene rubber (NBR) etc.

a) **Epoxidized natural Rubber** is a modified molecules of natural rubber with chemical name is cis-1, 4 polyisoprene. The restructuring using chemicals such as peroxy acid will reaction with double bonds of the natural rubber molecules to form a ring oxygen is replaced. The reaction epoxidized natural rubber, as shown in Figure 7. In the beginning was the acid used formic acid reaction with hydrogen peroxide. (Teoh, 2006; Ismail et al., 1998) Then the peroxy formic acid as shown in Figure 7(a) And then peroxy formic acid will reaction with double bonds of natural rubber was arranged as a ring epoxide. And formic acid is a product as shown in Figure 7(b).

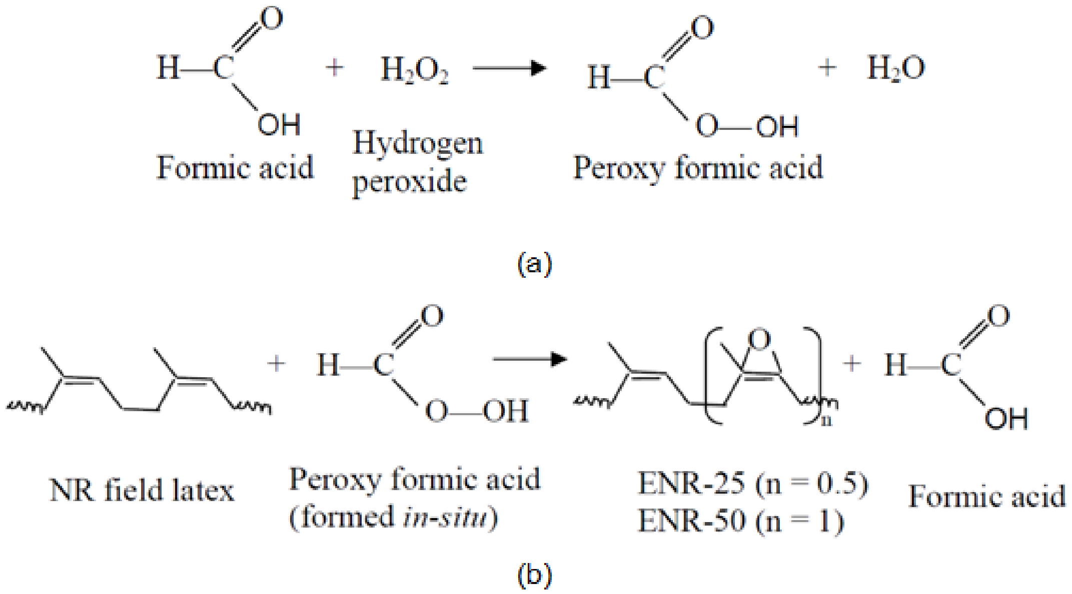


Fig. 7. The reaction epoxidation of natural rubber (Ismail, 2011).

However, only 3 types of ENR were considered as commercial standard. These are ENR-10, ENR-25 and ENR-50 where the integers designate 10, 25 and 50 %mole of epoxide incorporated into the natural rubber chain respectively. (Ismail et al, 1998; Poh et al., 2001)

Besides the proposed commercial uses shown, ENR has the potential to be further exploited for its usage as advanced materials such as in blends, additives and fuel cells applications. (Cheng Hoon, 2006) ENR had been blended with various polymers such as natural rubber (Okwu and Okieimen, 2001; Ismail et al., 2011), styrene butadiene rubber (SBR) (Ismail and Suzaimah, 2000) and poly(vinyl chloride) (PVC). (Ratnam and Zaman, 1999; Ratnam, 2002)

Thermoplastic/Elastomer blends

Over recent years, blends of natural rubber with thermoplastic elastomers have been studied. (Douibi et al, 2012; Ishiaku et al., 1995) The thermoplastic elastomers prepared by blending natural rubber with thermoplastics such as polyethylene (PE), poly(vinyl chloride) (PVC) and polyurethane etc. Properties have been reported for thermoplastic elastomers based on natural rubber and thermoplastic by several workers such as

PE/ Elastomer blends

Polyethylene had been blended with various polymers such as styrene butadiene rubber (SBR) (Khalf and Ward, 2010), natural rubber (Roy Choudhury et al., 1989; White et al., 2001), epoxidised natural rubber (Roy choudhury et al., 1992), acrylonitrile butadiene rubber (NBR) (Thomas, 2000) and ethylene propylene diene terpolymer rubber (EPDM). (Airinei et al., 2013) One of the polymer blends is exemplified with the blending of PE with natural rubber. It was reported that LDPE and NR latex blends were prepared. The effect of varying the NR latex content on the physical, mechanical and dynamic properties. The degree of crystallinity of the LDPE/NR composite films increased with increasing NR latex content up to 7.5 phr, the tensile strength and hardness of the LDPE/NR composite films decreased with increasing NR latex content. (Poompradub and Mahapram, 2006) Study the morphology and properties of thermoplastic/elastomer blends from natural rubber and high-density polyethylene have been studied. Abrasion resistance, flexural modulus, hardness and impact strength have been correlated with the morphological findings. (Akhtar, 1988) and the effects of LNR as a compatibilizer in binary blends of 60/40 NR/LLDPE. It has been observed that increasing LNR content decreases T_m and ΔH_f which are indicators of the crystalline part of the blends. The decrease reflects a reduction in the degree of crystallinity which is due to the interference in the form of NR dissolution into the LLDPE phase. The phenomenon leads to a shift in T_g of the amorphous part of LLDPE to higher temperatures. (Dahlan et al., 2002)

PVC/ Elastomer blends

Poly (vinyl chloride) had been blended with various polymers such as natural rubber (Beppu et al., 2001) nitrile butadiene rubber (NBR) (Pappa et al., 2011; Pasa et al., 2013), epoxidized natural rubber (Ratnam and Zaman, 1999; Ratnam, 2002) and styrene butadiene rubber (SBR) (Chan and Zhu, 1998; Chan et al., 1998) etc. It was reported that study the effects of an epoxidized plasticizer on the mechanical properties and thermo-oxidative ageing behavior of poly (vinyl chloride)/epoxidized natural rubber thermoplastic elastomers (TPEs). It was found thatthe tensile strength is higher when addeddi-2-ethylhexylphthalate (DOP) plasticized. (Ishiaku et al., 1997) Study the melt rheological behavior of poly(vinyl chloride)/epoxidized natural rubber (PVC/ENR) thermoplastic elastomers (TPEs) was studied the effect of dynamic vulcanization it was found that the apparent viscosity decreased with increased in apparent shear rate (Mousa et al., 2000) and temperatures (Mousa et al.,1998) has been studied with respect to sulfur concentration(Mousa et al.,2000) as well as the effect of sulfur content on the melt flow index and the activation energies of the PVC/ENR, the effect of compounding parameters. (Ishiaku et al., 1995) And have reported improve the mechanical properties of poly(vinyl chloride) (PVC) with modification of natural rubber (NR) by graft copolymerization with methyl methacrylate (MMA). It was found that the impact strength of blends was increased with an increase of the graft copolymer product content (Rempel et al., 2004) and it was found that 300% modulus, tensile strength, tear strength, hardness and solvent resistance were increased with increasing MMA content, while the % elongation at break decreased. The physical properties decreased with increasing the PVC content, but solvent resistance increased. (Kaesaman et al., 1996)

Thermoplastic Vulcanizate (TPVs)

A well-established and widely used method to prepare thermoplastic compositions comprising vulcanized elastomer particles in melt-processable matrix is called dynamic vulcanization. The elastomer is vulcanized during its melt-mixing with a suitable molten thermoplastic. (Drobny, 2007) Cross-linking of the elastomer phase which have superior elastic properties (Roy Martinus, 2009), defined as thermoplastic rubber vulcanizate consisting of a blend of a thermoplastic material and a conventional rubber in which the rubber has been crosslinked by the process of dynamic vulcanization during the blending and mixing step. Upon melt mixing of the thermoplastic and rubbery polymers under high shear, the less viscous. (Mohamad, 2007) Crosslinked elastomer particles dispersed in a semi-crystalline thermoplastic matrix (Figure. 8). The dispersion of a large amount of crosslinked rubber into the thermoplastic matrix results in soft and highly elastic products.

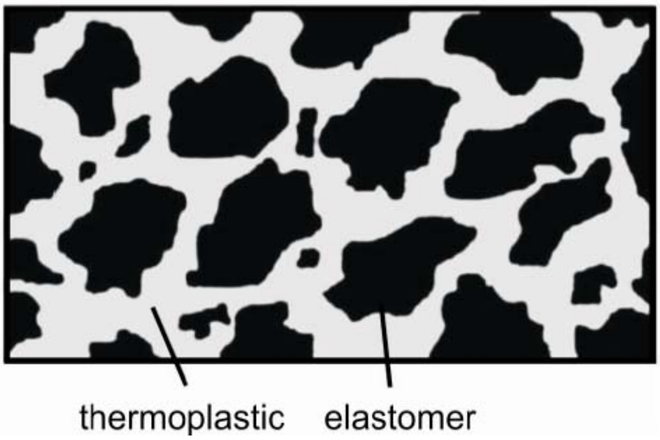


Fig. 8. Schematic representation of the morphology of a TPV. (Roy Martinus, 2009)

Many studies have focused on the morphology of polymer blends during melt. Blending (Avgeropoulos et al, 1976; Martin, et al, 2004; Chuai, et al, 2003) and the influence of crosslinking on phase inversion (Machado and van Duin, 2005; Harrats et al., 2007; Goharpey et al., 2001). Combining the results of these studies leads to the simplified representation of the morphology development during dynamic vulcanization as shown in Figure. 9

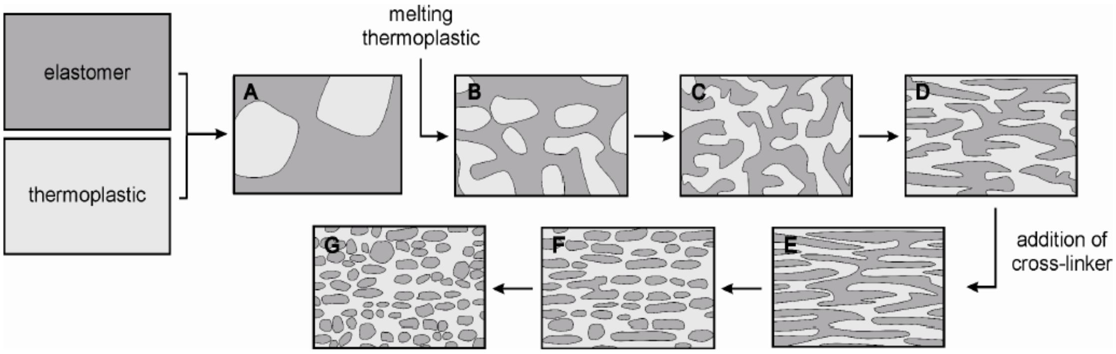


Fig. 9. Schematic representation of the morphology development during dynamic vulcanization of elastomer/thermoplastic blends. (Roy l'Abee, 2009)

The early stage of the mixing process (A) is characterized by the presence of non-molten thermoplastic pellets that 'swim' in the elastomer matrix. After complete melting of the thermoplastic and intimate mixing of the two phases (B) the morphology changes towards co-continuity (C). The combined shear and elongational forces that act on the viscous co-continuous phases during mixing deform the co-continuous morphology. This deformation leads to a refinement of the co-continuous strands, i.e. the strands become thinner but the co-continuity is preserved (D). Crosslinking leads to an increased viscosity of the elastomer phase, which results in a simultaneous increase in the shear and elongational forces acting on the system and, thus, to an increased deformation of the co-continuous structure (E). When a critical stress is achieved, the strands will break up into small particles, which results in a reduction of the stress and in a dispersion of crosslinked elastomer particles in a thermoplastic matrix (F). The dispersed elastomer phase will reach a final particle size (G) that depends on the deformation rate, the type of deformation, the composition, the viscosity (ratio) and the interfacial tension. (Roy l'Abee, 2009, Holden et al, 2004)

Curing method

The crosslinking of the rubber phase in heterogeneous blends consisting of a thermoplastic and a rubber component takes place by introduction of a crosslinking between the mixing process. (Roy l'Abee, 2009) During the crosslinking covalent bonds are formed between network points resisting thermal and chemical stresses.

Commonly used crosslinking agent for rubber vulcanization. Among them are those who require unsaturated double bonds in the molecules to be crosslinked such as: sulfhur, phenolic resins, irradiation and peroxides. (Drobny, 2007)

In addition to vulcanization agents accelerators, such as sulfenamines or thiuram sulfides, in combination with activators, such as zine oxide or stearic acid, are used to shorten curing times and to prevent thermo-oxidative degradation of the polymer. A scheme of the vulcanization process by the classical vulcanization agent sulfur is shown in Figure. 10.

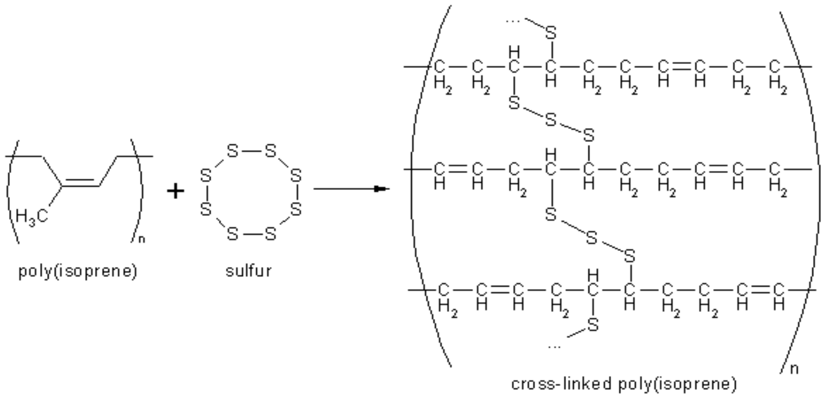


Fig. 10. Scheme of crosslinking reaction with sulphur. (Ballard, 2010)

It is well known that the sulphur vulcanization process as it occurs in the production of natural rubber goods strongly effect on the rubber properties. It was reported that studies on dynamic vulcanization of PP/NBR thermoplastic elastomer blends. It was found that dynamically vulcanized blends have higher tensile strength, elongation at break, solvent and oil resistance. (Nader et al., 1999, Hernandez et al., 2003) Study effect of accelerator/sulphur ratio on the scorch time of ENR. It was found that Mooney scorch time decreases exponentially with increasing temperature for ENR and SMR L and mooney scorch time decreases in the order; N-tert-butyl-2-benzothiazyl sulphenamide (TBBS) > tetramethyhhiuram disulphide (TMTD) > diphenyl guanidine (DPG) > 2-mercaptobenzothiazole (MBT) > zinc dimethvldithiocarbamate (ZDMC). And effect of accelerator/sulfur, it was also found that the influence of accelerator/sulfur ratio becomes less significant as vulcanization temperature increases. (Ishiaku et al., 1998)

Polymer electrolyte membrane fuel cell (PMFC)

Fuel cell is device to cause a electrochemical reaction between oxygen and hydrogen, which hydrogen based fuel in the anode, oxygen in the cathode (Costa et al., 2004) and can change the energy of the fuel directly into electrical energy by without a burning. Polymer electrolyte membrane fuel cell is fuel cells where the electrolyte is made of an organic polymer that has the characteristic of a good proton carrier when in presence of a water solution. (Osta et al., 2004; Roshandel and Parhizgar, 2013) For application as a power source for the car or on places by the fuel cell has the following features that can work at room temperature and low pressure. It also has a special section of the membrane polymer that can be used to exchange protons. Polymers used as polymer electrolytes such as sulfonated monomers (Nafion), polyphenylene oxides (PPO), polysulfones (PES), poly ether ether ketones (PEEK) and epoxidized natural rubber (ENR) etc. It was reported that epoxidized natural rubber can perform as polymer electrolytes just like polyethylene oxide (PE), with an addition of ethylene carbonate (EC) and propylene carbonate (PC), the ionic conductivities of the polymer can be enhanced at ambient temperature. (Linford et al., 2002; Yahya et al., 2008) Study prepared depolymerization of epoxidized natural rubber latex (LEDPNR) mixed with lithium bis (trifluoromethane sulfonyl) imide (LiTFSI) salt. It was found that the ionic conductivity of LEDPNR/LiTFSI mixtures was dependent on epoxy group content and dependent on LiTFSI salt concentration and glass transition temperature (T_g). (Kawahara et al., 2006) Study prepared poly (vinyl chloride)/polystylene blend films were measured at different temperatures and at the different frequencies using LCR meter. It was found that the dielectric constant decreases with the increase of the temperature of blends and it increases with the increase of frequency at constant temperature. (Hasan et al., 2013)

Electrospinning process

Electrospinning is a unique process to prepare electrospun fibers with diameters in the range micrometers to nanometers that depends on the type of polymer and processing conditions. (Jung and Lee, 2011; Lee et al., 2005)

Electrospinning is the process that occurred over 60 years. In the year 1934, Formhals was patented process and used electrical instruments in synthetic fibers. (Sill and von Recum, 2008) In the year 1969, Taylor published work describing the phenomena occurring at the time. Polymer solution is ejected from a metal needle at high voltage power supply. As the electrostatic charge on the droplet overcomes the surface tension, the low molecular weight fluid breaks up into small droplets, named a Taylor cone. (Sill and von Recum, 2008; Kessick et al., 2004)

The electrospinning experimental is represented in Figure. 11. The basic principles of electrospinning are a very simple. There are mainly three components to fulfill the process as follows: a high voltage power supply, syringe with metal needle and collector. A polymer in solution is encapsulated within a syringe, which is connected to an anode that connects to a high-voltage power supply. Because of surface tension, the polymer solution forms a hemispherical drop at the end of the capillary tip. The surface of the liquid is distorted into a conical shape known as the Taylor cone. Once the voltage exceeds a critical value, the electrostatic force overcomes the solution surface tension and a stable liquid jet is ejected from the cone tip. Solvent evaporates as the jet travels through the air, leaving behind ultrafine polymeric fibers collected on an electrically grounded target. The jet often follows a bending or a spiral track resulting from the interaction between the external electric field and the surface charge of the jet. Bending instability of jets not only results in the electrospinning jet being elongated up to ultrafine fibers but also leads to the formation of randomly deposited nonwoven electrospun fiber mats. (Truong et al., 2011; Yuan et al., 2005; Zhu et al., 2010) Electrospun mats have a larger specific surface area and small pore size compared to commercial nonwoven fabrics. They are of interests in a wide variety of applications including tissue engineering, drug delivery system (Chew et al., 2006), wound dressing (Venugopal and Ramakrishna, 2005) membrane (Liu and Hsieh, 2002) and conductive fiber (Diaz-De Leon, 2001; MacDiarmid et al., 2001)

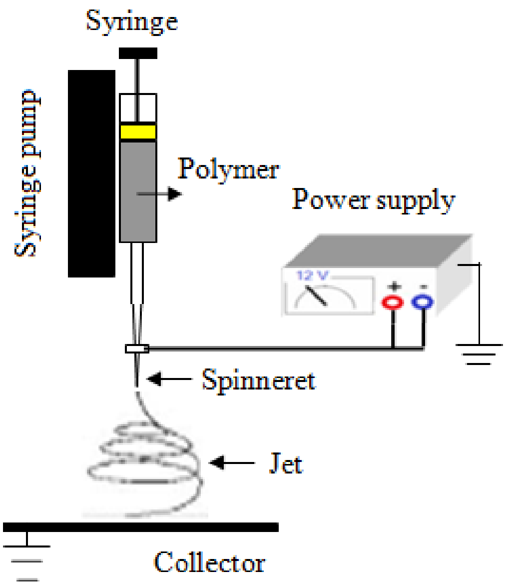


Fig. 11. Schematic of the experimental set-up

Polymer used in electrospinning

There are a wide range of polymers that used in electrospinning and are able to form fine nanofibers within the submicron range and used for varied applications. Electrospun nanofibers have been reported as being from various synthetic polymers, natural polymers were electrospun from solutions. Such as poly (vinyl chloride) (Lee et al., 2002), poly(ethylene-co-vinyl alcohol) (Kenawy et al., 2003), polycarbonates (Krishnappa et al., 2003), nylon-6 (Fong et al., 2002), polyurethane (Demir et al., 2002), polyacrylonitrile (Yang et al., 2003) polylactide (Luu et al., 2004), poly(e-caprolactide) (Yoshimoto et al., 2003) and cellulose acetate. (Liu and Hsieh, 2002)

It was reported that (Wang et al., 2003) prepared of electrospun polyvinyl chloride (PVC)/polyurethane (PU) blended solutions (10/0, 9/1, 8/2, and 7/3 wt%) were prepared by adding PVC and PU in the mixture solvent of THF/DMF (1/9, w/w). It was found that membranes exhibited relatively high tensile strength (9.9 MPa), good air permeability (154.1 mm/s) and excellent abrasion resistance (134 cycles)

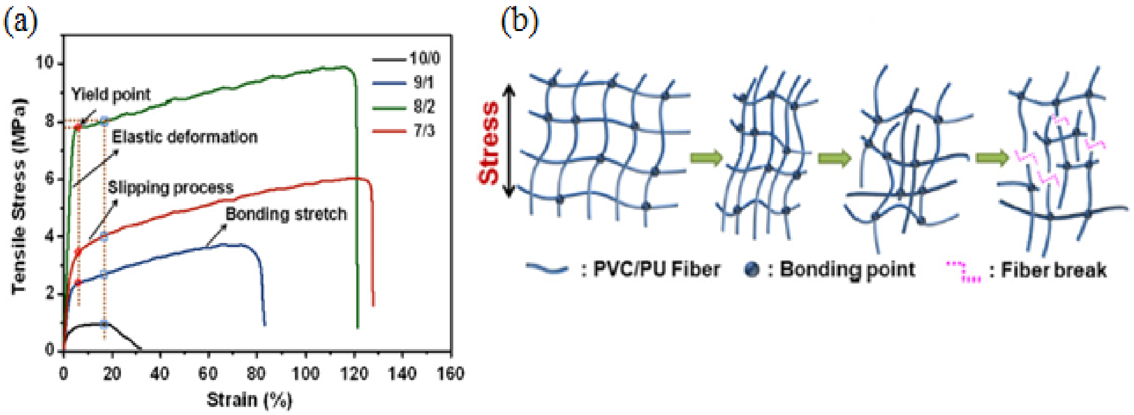


Fig. 12. (a) Stress-strain curves of PVC/PU fibrous membranes fabricated from varied weight ratios. (b) Proposed three-step break mechanism of tensile fracture process upon external stress. (Wang et al., 2003)

As shown in Figure. 12. when an external load is applied, the hydrogen bonding between C=O groups of PU and the α-hydrogen of PVC, and the dipole-dipole-C=O····Cl-C- interactions tend to bear the stress on intermolecular levels, resulting in the elongation less than 6% in the first linear elastic behavior

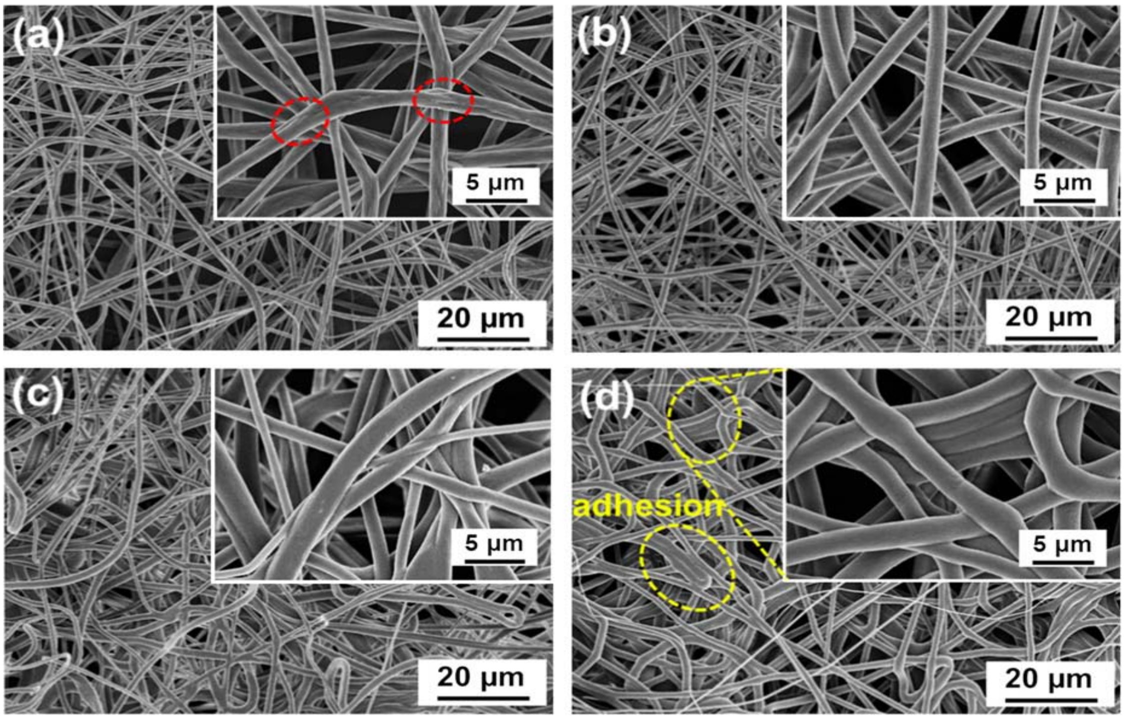


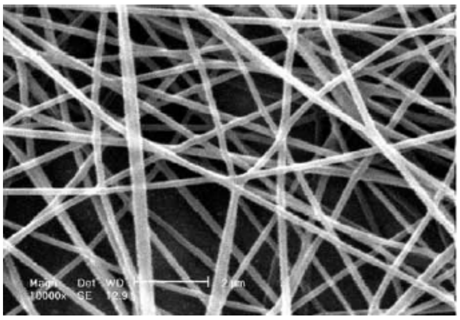
Fig.13. FE-SEM images of PVC/PU membranes fabricated from 10 wt% PVC/PU solutions and varied weight ratios of PVC/PU (a) 10/0, (b) 9/1, (c) 8/2, and (d) 7/3. (Wang et al., 2003)

As seen in Figure. 13a, the fibers formed from 10 wt% PVC solutions exhibited irregular wrinkled microfibrous surfaces. After the introduction of PU, the morphology of the membranes was greatly changed comparing with pure PVC, as shown in Figure. 13b-d. By varying the weight ratios of PVC/PU from 9/1 to 7/3, the average fiber diameter increased from 1.33 to 2.06 μm, which can be contributed to the increased viscosity and decreased conductivity of solutions with increasing the PU content.

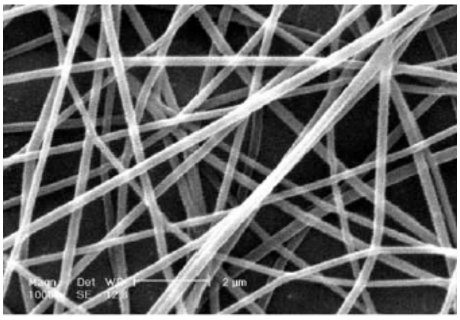
It is well known that the morphology and size of electrospun fibers depends on various processing parameters such as the solution properties, controlled variables, ambient conditions, viscosity and surface tension. With the control of these parameters, optimal nanofibers can be prepared. Electrospinning parameters and their effects on fiber morphology are as follows:

Process parameters

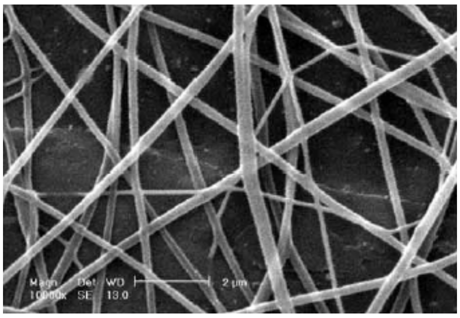
- Applied voltage, decrease in fiber diameter with increase in voltage. But the beads increase, because the voltage affects the Taylor cone. (Demir et al., 2002; Jun et al., 2003; Kim et al., 2005)



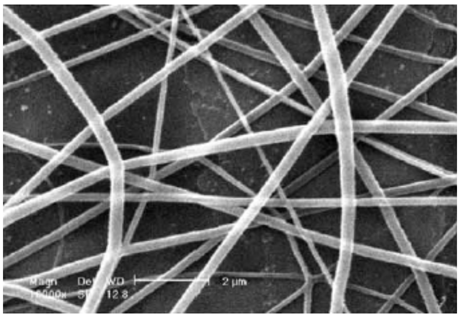
(a) Average 218±20 nm.



(b) Average 243±31 nm.



(c) Average 230±63 nm.



(b) Average 254±76 nm.

Fig. 14. Effect of voltage on morphology and fiber diameter distribution from a 7.4% PVA/water solution (DH = 98%, tip-target distance = 15 cm, flow rate = 0.2 ml/h). Voltage: (a) 5 kV; (b) 8 kV; (c) 10 kV; (d) 13 kV. Original magnification 10 kX. (Zhang et al., 2005)

- Distance between tip and collector, generation of beads with too small and too large distance, minimum distance required for uniform fibers. (Geng et al., 2005; Zhao et al., 2005)

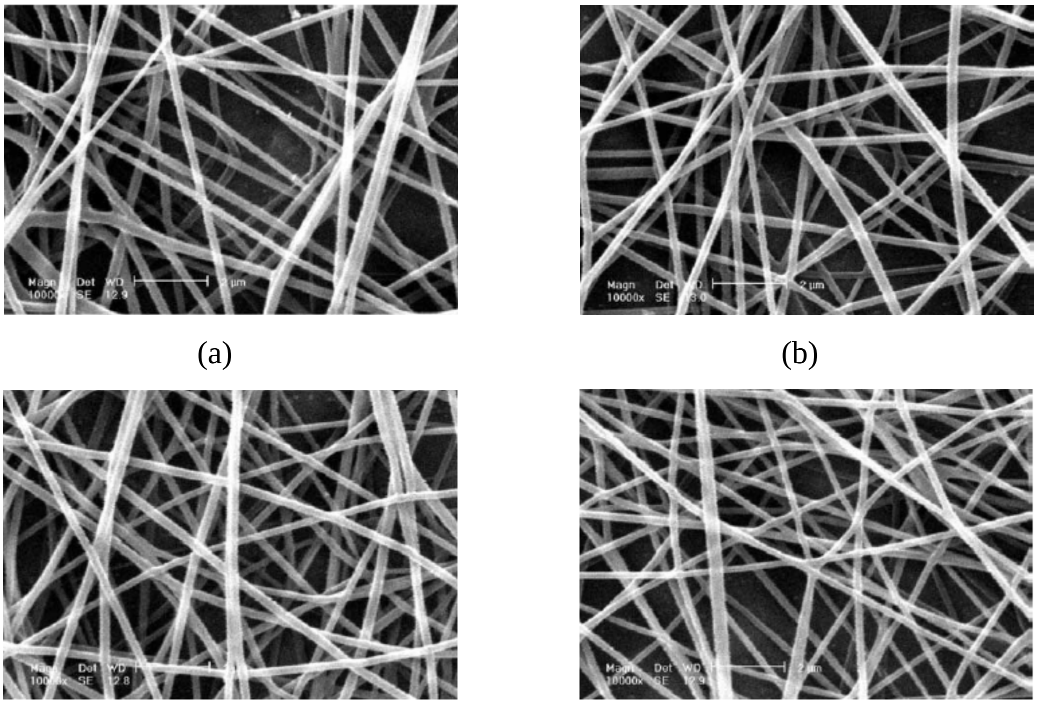
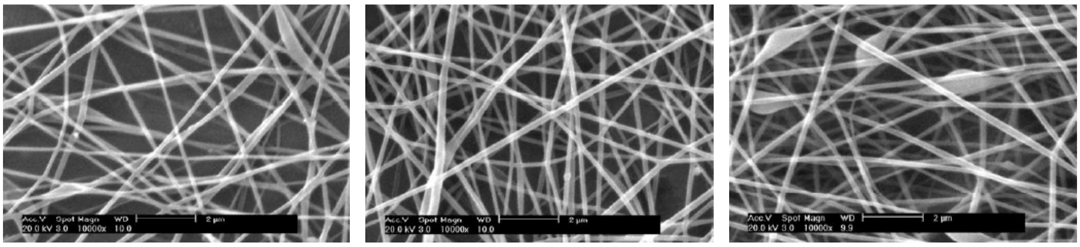

(a)
(b)
(c)
(d)

Fig. 15. Effect of tip-target distance on fiber morphology from a 7.4% PVA/water solution (DH = 98%, voltage = 5 kV, flow rate = 0.2 ml/h). Tip-target distance: (a) 8 cm; (b) 10 cm; (c) 12 cm; (d) 15 cm. Original magnification 10 kX. (Zhang et al., 2005)

- Flow rate, decrease in fiber diameter with decrease in flow rate, generation of beads with too high flow rate. (Zuo et al., 2005; Zhang et al., 2005)



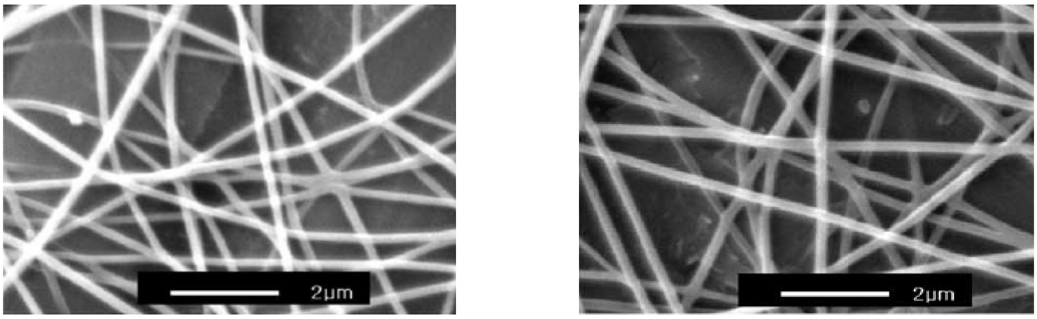
(a) (b) (c)

Fig.16. Effect of flow rate of 7% PVA water solution on fiber morphology (DH = 98%, voltage = 8 kV, tip-target distance = 15 cm). Flow rate: (a) 0.1 ml/h; (b) 0.2 ml/h; (c) 0.3 ml/h. Original magnification 10 kX. (Zhang et al., 2005)

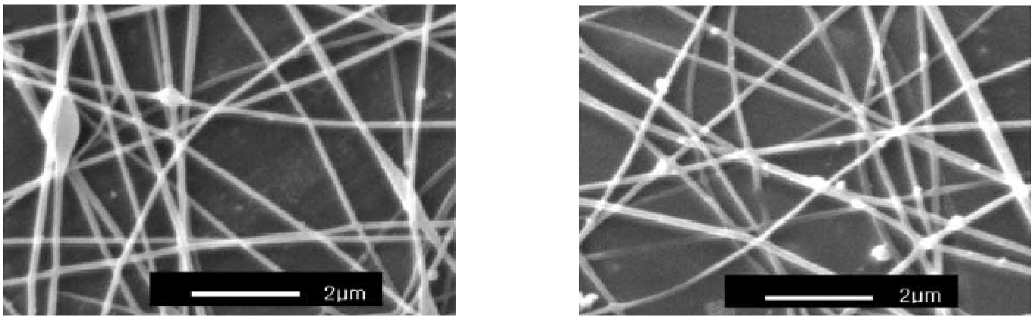
Solution parameters

- Viscosity, low-beads generation, high-increase in fiber diameter, disappearance of beads. (Zhao et al., 2005; Zhang et al., 2005)

- Polymer concentration, increase in fiber diameter with increase of concentration. (Son et al., 2004; Jun et al., 2003)



(a) Average 214±19 nm. (b) Average 190±19 nm.



(c) Average 158±19 nm. (d) Average 159±21 nm.

Fig. 17. Effect of NaCl amount in the PVA solution on fiber morphology (DH = 98%, voltage = 5kV, tip-target distance = 10cm; flow rate = 0.2 ml/h). NaCl amount based on H_2O: (a) 0.05%; (b) 0.10%; (c) 0.15%; (d) 0.2%. Original magnification 10 kX. (Zhang et al., 2005)

- Molecular weight of polymer, reduction in the number of beads and droplets with increase of molecular weight. (Chen and Ma, 2004; Demir et al., 2002)

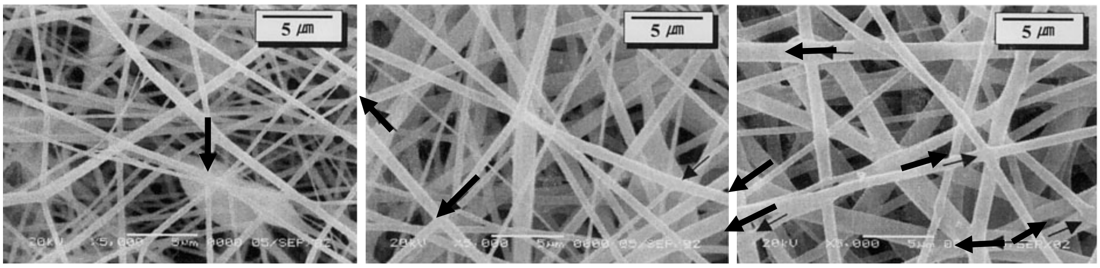
Solvents used for electrospinning

The solvent used in preparing polymer solutions has a significant influence on its spinnability, because the first and foremost step in the electrospinning process is dissolution of polymer in a suitable solvent. Solvents should have some properties such as, good volatility, vapor pressure, boiling point and should maintain the integrity of the polymer solution. Thus for successful electrospinning the selection of an appropriate solvent system is indispensable. (Bhardwaj and Kunda, 2010) It is well known that different solvents may contribute different surface tensions. The solution viscosity is determined by the concentration of the polymer, but the value of surface tension depends on both the polymer and solvent. (Reneker and Chun, 1996; Yang et al., 2004) In table 1, shown different properties of solvents.

Table 1. Properties of different solvents used in electrospinning process. (Bhardwaj and Kunda, 2010)

Solvents	Surface tension (mN/m)	Dielectric constant	Boiling point (°C)	Density (g/ml)
Chloroform	26.5	4.8	61.6	1.498
Dimethyl formamide	37.1	38.3	153	0.994
Hexafluoro isopropanol	16.1	16.7	58.2	1.596
Tetrahydrofuran	26.4	7.5	66	0.886
Acetone	21.1	27	78	1.393
Water	25.2	21	56.1	0.786
Methanol	72.8	80	100	1.000
Acetic acid	22.3	33	64.5	0.791
Formic acid	26.9	6.2	118.1	1.049
Dichloro methane	37	58	100	1.21
Ethanol	27.2	9.1	40	1.326
Tri fluoro acetic acid	21.9	24	78.3	0.789

The ability of the volatility in the solvent.such as reported that study PVC/PU electrospinning by solutions for electrospinning were prepared in a mixed solvent of tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF). It was found that THF is ability of the good volatility and DMF is ability of the poor volatility. Found that when used THF 100% to make the fibers have high porosity and when used DMF 100% to make the fibers are smooth and microtexture fiber. (Lee et al., 2002; Lee et al., 2003)



(a) (b) (c)

Fig. 18. SEM images of fibers electrospun from a 13 wt%. solution of PVC/PU polyblends with an applied voltage of 12 kV and tip-to-collector distance of 12 cm: (a) 100/0, (b) 50/50, and (c) 0/100 (arrow means point bonded structure). (Lee et al., 2003)

OBJECTIVES

This study aimed to prepared polymer electrolyte membrane and improve properties from the blending of natural rubber with thermoplastics (PE and PVC) using hot compression moulding and electrospinning.

RESULTS AND DISCUSSION

Polyethylene Thin Film Coating Preventing the Degradation of Natural Rubber (Paper I)

Oxidative breakdown of natural rubber (NR) was related to reactions between unsaturation and free radicals in the presence of heat which ultimately leads to chain scission. As well as ozone plays a much more important role in the degradation of unsaturated polymers. Ozone degradation destroys the polymer chains and thus changes the properties of materials. The preventing of this degradation was vital to the rubber industry. In the present study, the preventing of membrane degradation by polyethylene (PE) thin film coating was investigated. NR was directly mixed with PE in contents from 15 to 150 part per hundred of rubber (phr) and was vulcanized at 150 ºC. The PE separated and migrated to form a thin film on the rubber surface during the hot compression process. The tensile strength of PE membrane is higher than NR membrane while the tensile strength of blend membrane is slightly increased when compared with NR membrane. In addition, the tensile properties of composite film were rising with increasing the PE concentration as well as the ozone aging properties. The sulfur cross-linking in rubber molecule was determined cover photon energy range of 2460 to 2490 eV. The S K-edge XANES absorption peak area is increased and shifts towards lower photon energy at 2472.0±0.2 eV with increasing the PE concentration corresponds with the mechanical properties of membrane. The surface topography of the composite film was examined by using scanning electron microscopy (SEM). The SEM images showed that the PE was migrated to create a barrier film and formed micro-pore at the bottom surface of blend membrane after extraction with xylene and present to the ozone resistance. The surface of PE coated membrane formed lamellae crystallites which crystalline size and number depend on ozone aging time. The results revealed that the PE coating layer formed crystalline lamellae to improve the ozone aging of membrane and increasing of tensile properties.

TPNR Membrane Reinforcing with Cotton Fibre Spun (Paper II)

The emergence of thermoplastic natural rubber (TPNR) is one of the most important developments in the area of polymer science and technology. TPNR are a new class of material that combines the properties of vulcanized rubbers with the ease of processability of thermoplastics. TPNR can be prepared by blending thermoplastic with NR (natural rubber). To improve their conductions, it can simply be done by incorporation with conductive materials such as carbon black, fiber, cellulose and chitosan. In this work, TPNR was prepared by mixing NR with thermoplastic (polyethylene; PE) using 2-roll mills before compressed on cotton fiber spun and vulcanized at 150 ºC. The mechanical properties and morphology of the membrane were investigated using DMTA (dynamic mechanical thermal analyzer) and SEM (scanning electron microscopy), respectively. The tensile strength of NR was increased from 10 to 18 MPa after reinforcing with cotton fiber spun. The distribution of vulcanized NR was increased with increasing PE component from 30 to 90 phr by tensile strength changed from 12 to 30 MPa. The membrane was immersed in xylene to remove PE phase and found that the tensile strength was decreased while the elongation at break was not changed due to inserting cotton fibre spun sheet. The SEM micrographs of the cotton fiber reinforced NR and TPNR demonstrated that the cotton fiber layer was inserted in the polymer matrix. It is clear that, the increasing of PE component resulted in PE cover the spun of cotton fibre and formed film on the film surface. To investigate the membrane mechanical properties, DMTA thermogram were measured. The storage modulus (*E’*) is found to decrease with adding PE for 90 phr below the glass transition temperature (T_g) and indicated that PE blending has improved the softness of the TPNR during the transition from the glassy to the rubber state. The damping property (*tan*δ) was corresponding to T_g of the polymer matrix which decreased when adding PE. The dielectric property of cotton fiber reinforced NR and TPNR were increased. The dielectric constant of NR is increased when blending with PE for 30 phr and decreased with adding PE at higher concentration for more than 90 phr. The sharp decrease in dielectric loss in lower frequency range of TPNR with 150 phr PE is attributed to the decrease in contribution of both interfacial polarization and conductivity. This data conclude that the reinforcing of NR with cotton fiber spun is not only to improve the mechanical properties but also increase the dielectric properties due to the polarity of cotton fiber. NR is miscibility blends with PE at the composition (90:100) increased the mechanical properties and vulcanized NR might be dispersed in PE matrix.

In Situ Coating of Natural Rubber Film with Poly (vinyl chloride) Resin (Paper III)

Natural rubber (NR) blend represents very important field in processing of new materials, which has better properties in comparison with the net polymers. Basically, from the thermodynamic point of view there are two types of polymer blends: miscible and immiscible. Most NR blends show immiscible systems, as the formation of two or more distinct separated phases. Many articles were devoted to studying in NR modification to increase the compatibility. For example, the compatibility of epoxidized liquid natural rubber (ELNR)/poly (vinyl chloride) (PVC) blend was observed by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). In this research, Film formation of poly (vinyl chloride) resin (rPVC) coating on natural rubber (NR) surface in solid state was prepared and then investigated for immiscible effect of PVC/NR blend. The tensile strength of PVC/NR blend is increased when mixing with rPVC for 5 phr and rapidly decreased with adding more rPVC content. The SEM image showed that rPVC particles were accumulated and dispersed on top and bottom surface of the blend film. In a high addition of rPVC, it was immiscible blend with NR and exist in two distinct separated. The experimental results obtained from atom force microscopy (AFM) showed that the surface of NR/5rPVC is roughness covered with rPVC particle. The blend film composed of aggregates of particles and arranged particles with sharp spherical contours. Then, the surface roughness average (R_a) and root mean square (R_q) of NR and NR/rPVC blend films were calculated and the data are presented that the roughness of the NR/rPVC blend film is slight broader than NR film. Furthermore, the effect of rPVC concentration on the dielectric constant for the blend NR/rPVC was measured. The dielectric property of the blend changed with rPVC concentration which increasing in small amount of rPVC and lower dielectric constant in more than 50 phr of rPVC due to heterogeneous of the polymer blend. The addition of 10 phr of rPVC in blend provides the sharp increase in dielectric loss factor attributed to the increase in contribution of both interfacial polarization and conductivity. This data conclude that small amount of rPVC migrated to the surface and form a thin film coating on NR surface along with improve in physical and dielectric properties of the NR/PVC blend, conversely with over 50 phr rPVC blending.

Preparation and Properties of Electrospun PVC Nanofiber. (Paper IV)

The low thermal stability of poly (vinyl chloride) (PVC) is considered as one of the most serious industrial problems. The developing PVC nanofiber was attended to improve material properties. Ultrafine PVC fibers cannot be produced by ordinary spinning techniques. Electrospinning is one of the methods to prepare nanofibers of polymer or polymer composite materials. In this article, the effects of electrospinning condition including electric voltage, tip-to-collector distance and polymer solution concentration such as PVC concentration and mixed solvent of THF and DMF were studied on the morphological and physical properties of PVC nanofibrous. The morphology of nanofibrous was observed under field emission scanning electron microscope (FE-SEM) and the images demonstrate that morphological variation depends on PVC concentration and electrospinning conditions. The low concentration of PVC (10%) led to the formation of beads on the fiber. Therefore, in this study, PVC nanofibrous were prepared from PVC solution at 15% by weight with applied voltage 12 kV and distance between the syringe tip and collector plat is 15 cm. The thermal properties of membranes were performed using differential thermal analysis (DTA). The membrane prepared from PVC dissolved in THF is harder than that from DMF and mixed solvents. THF was evaporated very fast led to high crystalline membrane indicated with high exothermal peak at -30^{o}C. In contrast, DMF was evaporated to decreasing of melting temperature of the membrane. The mixed solvents between THF and DMF enhanced the membrane properties. Additionally, dielectric constant of the membrane prepared from PVC dissolved in DMF pure solvent enhanced the dielectric properties due to its charge compared to THF. PVC dissolved in mixed solvent between DMF and THF found that the dielectric properties decreased depends on the amount of added THF. The result suggest that smooth surface of electrospun PVC nanofiber can be prepared by using high concentration of

PVC in mixed solvent between DMF and THF with applied voltage 12 kV and 15 cm of tip to collector distance. PVC nanofiber had a high ionic conductivity and their thermal properties were improved comparing with PVC sheet.

Electrospun Epoxidized Natural Rubber with Poly(vinyl chloride) (ENR-PVC) nanofibrous for PEMFC Applications. (Paper V)

Blending to achieve a microheterogeneous mixture of two or more polymers is a well-known method to improve the mechanical, environmental and rheological properties of polymers. Epoxidized natural rubber (ENR) blending with poly (vinyl chloride) (PVC) for improving some properties is currently important topic. In this research, a series of polymer blends of ENR/PVC was prepared by electrospinning technique and characterized. The effects of electrospinning condition including electric voltage, tip-to-collector distance and polymer solution concentration were studied on the morphological and physical properties of ENR/PVC nanofibrous. Various concentration of ENR solution in *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were directly added to PVC solution for plasticization of the electrospun nanofibrous. The SEM images showed that the morphological structure of ENR/PVC nanofibrous was changed by changing the ENR concentration. For ENR blending with PVC, it clearly shows the beads on the fiber be disappear, which increasing ENR composition can be attributed to higher viscosity and surface tension. The PVC nanofiber prepared from 10% by weight is more rigid than that from 15% by weight which correspond with DTA thermogram. The thermal properties of nanofibers were improved after mixing PVC with ENR. The mixture of PVC with high ENR content gave more flexible nanofiber with lower glass transition temperture (Tg). The nanofiber spun from high concentration of PVC (15%) is high viscous and was not easily to mix with ENR solution need to optimized the electrospinning condition. Studies also revealed that the membrane prepared from 10% PVC mixed with high ENR content reduced the dielectric constant due to dense of ENR phase. The dielectric properties of 15% PVC mixed with ENR was not changed with ENR contents due to the prepared nanofibrous membrane were dense. This data conclude that the smooth surface ENR/PVC nanofibrous membrane can be prepared from electrospinning method with applied voltage 12 kV and distance between the syringe tip and collector plate is 15 cm. The increasing ENR composition can result in higher viscosity and surface tension and the thermal properties of the ENR/PVC nanofibrous results indicate that the ENR/PVC membrane has a good thermal stability.

.

CONCLUDING REMARKS

NR with PE blending by using hot compression moulding, it was found that PE phase separated from NR phase and formed thin film coating on the membrane and was found that the PE form lamellar crystallites on the rubber interface after ozone treatment resulted in preventing rubber oxidation reaction and improvement of membrane strength. NR with PE blending using 2-roll mills before compressed on cotton fiber. It was found that the membrane strength was increased from 10 MPa to 18 MPa after reinforced with cotton fibre spun as well as the increasing of dielectric constant. The membrane was immersed in xylene to remove PE phase before characterization of membrane properties. Next, PVC with NR were compressed and found that the PVC was migrated and coated on the NR surface as same as NR with PE blends. The tensile strength of blend is increased with adding the PVC for 5 phr and rapidly decreased with increasing PVC content and higher dielectric constant than uncoated NR films.

The results, study ENR with PVC blending was prepared by electrospinning technique. Various concentration of epoxidized natural rubber (ENR) solution in N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) were directly added to PVC solution for plasticization of the electrospun nanofibrous was found that ENR/ PVC the eletrospinning condition ENR/ PVC nanofibrous were prepared from PVC solution at 10 wt% by weight with applied voltage 12 kV and distance between the syringe tip and collector plate is 15 cm. Dielectric constant of the membrane prepared from 10 wt% PVC mixed with high ENR content reduced the dielectric constant due to dense of ENR phase and The thermal properties of the ENR/PVC nanofibrous results indicate that the ENR/PVC membrane has a good thermal stability.

Further studies should be conducted using natural rubber with a polar properties mixing with thermoplastics with a polar properties for use polymer electrolyte membrane instead of conductive polymer commercial.

REFERENCES

Aflori, M., Stelescu, D. M., Airinei, A., Homocianu, M., Fifere, N. and Timpu, D. (2013). Structural characteristics of some high density polyethylene/EPDM blends. Polymer Testing. 32(2): 187-196.

Akhtar, S. (1988). Morphology and properties of blends of high-density polyethylene with natural rubber. European Polymer Journal, Volume. 24(7): 651-655.

Aranda, P. and Ruiz-Hitzky, E. (1992). Poly(ethylene oxide)-silicate intercalation materials. Chemistry of Materials. 4: 1395-1403.

Amin, S. and Amin, M. (2011). Thermoplastic elastomer (TPE) materials and their use in outdoor electrical insulation. Reviews on advanced materials science. 29: 15-30.

Avgeropoulos, G. N., Weissert, F. C., Biddison, P. H. and Bohm, G. G. A. (1976). Heterogeneous blends of polymers. Rheology and morphology. Rubber Chemistry and Technology. 49(1): 93-104.

Bajsić, E. G., Šmit, I. and Leskovac, M. (2007). Blends of thermoplastic polyurethane and polypropylene. I. Mechanical and phase behavior. Journal of Applied Polymer Science, 104(6): 3980-3985.

Ballard, D. (2008). WIPO Patent No. 2008134371. Geneva, Switzerland: World Intellectual Property Organization.

Beppu, M. M., Altenhofen da Silva, M., Adeodato Vieira, M. G. and Gomes Maçumoto, A. C. (2011). Polyvinylchloride (PVC) and natural rubber films plasticized with a natural polymeric plasticizer obtained through polyesterification of rice fatty acid. Polymer Testing. 30(5): 478-484.

Bhardwaj, Y. K., Chaudhari, C. V., Patil, N. D., Dubey, K. A., Kumar, V. and Sabharwal, S. (2005). Radiation-induced vulcanisation ofnatural rubber latex in presence ofstyrene-butadiene rubber latex. Radiation Physics and Chemistry 72: 613-618

Bhardwaj, N., & Kundu, S. C. (2010). Electrospinning: a fascinating fiber fabrication technique. Biotechnology Advances. 28(3): 325-347.

Bhowmick, A. K. and White, J. R. (2002). Thermal, uv and sunlight ageing of thermoplastic elastomeric natural rubber-polyethylene blends. Journal of Material Science. 37: 5141-5151.

Billingham, J., Breen, C. and Yarwood, J. (1997). Adsorption of polyamine, polyacrylic acid and polyethylene glycol on montmorillonite: an in situ study using ATR-FTIR. Vibration Spectroscopy. 14: 19-34.

Chan, C. M. and Zhu, S. (1998). Transition of phase continuity induced by crosslinking and interfacial reaction during reactive processing of compatibilized PVC/SBR blends. Polymer. 39(26): 7023-7032.

Chan, C. M., Zhu, S. H. and Cheung, M. K. (1998). Interfacial characterization of compatibilized PVC/SBR blends by solid-state NMR and TEM. Polymer. 39(24): 6099-6108.

Chang, Y. W., Mishra, J. K. and Kim, D. K. (2007). Green thermoplastic elastomer based on polycaprolactone/epoxidized natural rubber blends as a heat shrinkable. Materials Letters. 61: 3551-3554.

Chansuvarn, W. (2011). Chemical Applications. Rajamangala University of Technology Phra Nakhon, Science and Technology, Thailand.

Chen, V. J. and Ma, P. X. (2004). Nano-fibrous poly (L-lactic acid) scaffolds with interconnected spherical macropores. Biomaterials. 25: 2065-2073.

Chew, S. Y., Wen, Y., Dzenis, Y., & Leong, K. W. (2006). The role of electrospinning in the emerging field of nanomedicine. Current Pharmaceutical Design. 12(36): 4751-4770.

Chuai, C. Z., Almdal, K., and Lyngaae-Jørgensen, J. (2003). Phase continuity and inversion in polystyrene/poly (methyl methacrylate) blends. Polymer. 44(2): 481-493.

Chiu, F. C. and Chu, P. H. (2006). Characterization of solution-mixed polypropylene/clay nanocomposites without compatibilizers. Journal of Polymer Research.13: 73-78.

Costa, R. A., Camacho, J. R., Guimarães Jr, S. C., & Salerno, C. H. (2004). The polymer electrolyte membrane fuel cell as electric energy source, steady state and dynamic behavior. Fundação Educacional de Barretos, School of Electrical Engineering.

Dahlan, H. M., Khairul Zaman, M. D. and Ibrahim, A. (2002). The morphology and thermal properties of liquid natural rubber (LNR)-compatibilized 60/40 NR/LLDPE blends. Polymer Testing. 21(8): 905-911.

Dahlan, H. M., Zaman, M. D., and Ibrahim, A. (2002). Liquid natural rubber (LNR) as a compatibilizer in NR/LLDPE blends. II. The effects of electron-beam (EB) irradiation. Radiation Physics and Chemistry. 64: 429-436.

Das C. K., Chowdhury, S. R. and Mishra, J. K.(2000). Structure, shrink ability and thermal property correlations of ethylene vinyl acetate (EVA)/carboxylated nitrile rubber (XNBR) polymer blends. Polymer Degradation and Stability. 70(2): 199-204.

Das C. K., Raychowdhury, S. and Mishra, J. K. (2000). Effect of interchain crosslinking on the shrink ability of the blends consisting of grafted low-density polyethylene and carboxylated nitrile rubber. Materials Letters. 46(4): 212-218.

Davis, V. A., Radhakrishnan, V. K. and Davis, E. W. (2010). Influence of initial mixing methods on melt-extruded single-walled carbon nanotube-polypropylene nanocomposites. Polymer Engineering and Science. 50(9): 1831-1842.

De, S. K. and Anil Bhowmick, K. (1990). Thermoplastic elastomers from rubber-plastic blends. London: Ellis Horwood. 1-268.

Demir, M. M., Yilgor, I., Yilgor, E. E. A. and Erman, B. (2002). Electrospinning of polyurethane fibers. Polymer. 43(11): 3303-3309.

Deuri, A. S., Adhikari, A. and Mukhopadhyay, R. (1993). Ageing studies on EPDM/SBR blends. Polymer Degradation and Stability. 41: 145-164.

Díaz-de León, M. J. (2001). Electrospinning nanofibers of polyaniline and polyaniline/ (polystyrene and polyethylene oxide) blends. In Proceeding of The National Conference on Undergraduate Research (NCUR), University of Kentucky: 15-17.

Douibi, A., Merabet, S. and Merabet, S. (2012). The physical modification of a natural rubber-polypropylene thermoplastic elastomer blend by azobisformamide blowing agent. Polymer Science. 2012.

Drobny, J. G. (2007). Handbook of thermoplastic elastomers. Access Online via Elsevier.

El-Sabbagh, S.H. (2003). Compatibility study of natural rubber and ethylene-propylene diene rubber blends. Polymer Testing. 22(1): 93-100.

Fong, H., Liu, W., Wang, C. S. and Vaia, R. A. (2002). Generation of electrospun fibers of nylon 6 and nylon 6-montmorillonite nanocomposite. Polymer. 43(3): 775-780.

Geng, X., Kwon, O. H. and Jang, J. (2005). Electrospinning of chitosan dissolved in concentrated acetic acid solution. Biomaterials. 26(27): 5427-5432.

Goharpey, F., Katbab, A. A. and Nazockdast, H. (2001). Mechanism of morphology development in dynamically cured EPDM/PP TPEs. I. Effects of state of cure. Journal of Applied Polymer Science. 81(10): 2531-2544.

Govorčin Bajsić, E., Pustak, A., Šmit, I., & Leskovac, M. (2010). Blends of thermoplastic polyurethane and polypropylene. II. Thermal and morphological behavior. Journal of Applied Polymer Science. 117(3): 1378-1384.

Greenland, D. J. (1963). Adsorption of polyvinyl alcohols by montmorillonite. Journal Colloid Science. 18: 647-64.

Harrats, C., Thomas, S. and Groeninckx, G. (2007). Micro-and nanostructured multiphase polymer blend systems: phase morphology and interfaces. Macromolecular Chemistry and Physics. 208(2): 233-233.

Hasan, B. A., Hasan, A. A. and AUmran, D. (2013). Ac electrical conductivity analysis of (PVC-PS) blend films. International Journal of Application or Innovation in Engineering & Management (IJAIEM). 2(11): 86-95.

Hernández, M., González, J., Albano, C., Ichazo, M. and Lovera, D. (2003). Effects of composition and dynamic vulcanization on the rheological properties of PP/NBR blends. Polymer Bulletin. 50(3): 205-212.

Holden, G. (2004). Understanding Thermoplastic Elastomers, Hanser Gardner Publishers. 56.

Holden, G.; Kricheldorf, H.R. and Quirk, R.P. (2004). Thermoplastic Elastomers. Carl Hanser Verlag, Munich. 80: 574.

Ibrahim, A. and Dahlan, M. (1998). Thermoplastic natural rubber blends. Progress in Polymer Science. 23(4): 665-706.

Ishiaku, U. S., Nasir, M. and Ishak, Z. A. (1995). Rheological properties of poly (vinyl chloride)/epoxidized natural rubber blends. Part I: Composition dependence and the effect of compounding conditions. Journal of Vinyl Technology, 1(3): 142-147.

Ishiaku,U. S., Poh, B. T., Mohd lshak, A. and Ng, D. (1996). Mechanical and thermo-oxidative properties of blends of poly(viny1 chloride) with epoxidized natural rubber and acrylonitrile butadiene rubber in the presence of an antioxidant and a base. Polymer International. 39: 67-76.

Ishiaku, U. S., Shaharum, A., Ismail, H. and Mohd. Ishak Z. A. (1997). The effect of an epoxidized plasticizer on the thermo-oxidative ageing of poly(vinyl chloride)/ epoxidized natural rubber thermoplastic elastomers. Polymer International 45(1): 83-91.

Ismail, H., Sadequl, A. M., Ishiaku, U. S. and Poh, B. T. (1998). Effect of accelerator/sulphur ratio on the scorch time of epoxidized natural rubber. European Polymer Journal. 34(1): 51-57

Ismail, H. and Suzaimah, S. (2000). Styrene butadiene rubber/epoxidized natural rubber blends: dymamic properties, curing characteristics and swelling studies. Polymer Testing. 19(8): 879-888.

Ismail, H. and Suryadiansyah, S. (2002). Thermoplastic elastomer based on polypropylene/natural rubber and polypropylene/recycle rubber blends. Polymer Testing. 21(4): 389-395.

Ismail H., Shaari, S. M. and Othman, N., (2011). The effect of chitosan loading on the curing characteristics mechanical and morphological properties of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) compounds. Journal of Polymer Testing. 30: 784-790.

Jensen, W. B. (2008). Ask the Historian: The origin of the polymer concept. Journal of Chemical Education. 88: 624-625.

Jun, Z., Hou, H., Schaper, A., Wendorff, J. H., Greiner, A. (2003). Poly-L-lactide nanofibers by electrospinning - influence of solution viscosity and electrical conductivity on fiber diameter and fiber morphology. e-Polymer. 9: 1-9.

Jung, H. R. and Lee, W. J. (2011). Electrochemical characteristics of electrospun poly (methyl methacrylate)/polyvinyl chloride as gel polymer electrolytes for lithium ion battery. Electrochimica Acta. 58: 674-680.

Kaesaman, A., Prasassarakich, P. and Wongvisetsirikul, N. (1996). Preparation of natural rubber-g-methyl methacrylate/poly (vinyl chloride) blends. Master. Science Polymer Science, Chulalongkorn University. Bangkok. (Thailand). Graduate School.

Kenawy, E. R., Layman, J. M., Watkins, J. R., Bowlin, G. L., Matthews, J. A., Simpson, D. G. and Wnek, G. E. (2003). Electrospinning of poly (ethylene-co-vinyl alcohol) fibers. Biomaterials. 24(6): 907-913.

Kenneth, S., Whiteley, Geoffrey Heggs, T., Koch, H., Mawer, L. R. and Immel, W (2005). Polyolefins in Ullmann's Encyclopedia of Industrial Chemistry. Wiley Online Library.

Kessick R, Fenn J. and Tepper G. (2004). The use of AC potentials in electrospraying and electrospinning process. Polymer. 45(9): 2981-2984.

Khalf, A. I. and Ward, A. A. (2010). Use of rice husks as potential filler in styrene butadiene rubber/linear low density polyethylene blends in the presence of maleic anhydride Materials & Design, 31(5): 2414-2421.

Kim, B., Park, H., Lee, S. H. and Sigmund, W. M. (2005). Poly (acrylic acid) nanofibers by electrospinning. Materials Letters. 59(7): 829-832.

Klinklai, W., Kawahara, S., Marwanta, E., Mizumo, T., Isono, Y. and Ohno, H. (2006). Ionic conductivity of highly deproteinized natural rubber having various amount of epoxy group mixed with lithium salt. Solid State Ionics. 177(37): 3251-3257.

Kresge, E. N. (1978). Rubbery thermoplastic blends. Polymer blends. Volume 2: Chapter 20.

Kresge, E.N. (2000) Rubber Chemistry Technology. Hanser Gardner Publishers. 64(3): 469

Kresge, E.N. (2004). Thermoplastic Elastomers. 3rd edition (Holden, G., Kricheldorf, H. R. and Quirk, R. P., Eds.), Hanser Gardner Publishers. 93

Krishnappa, R. V. N., Desai, K. and Sung, C. (2003). Morphological study of electrospun polycarbonates as a function of the solvent and processing voltage. Journal of Materials Science. 38(11): 2357-2365.

Lee, K. H., Kim, H. Y., La, Y. M., Lee, D. R. and Sung, N. H. (2002). Influence of a mixing solvent with tetrahydrofuran and N, N-dimethylformamide on electrospun poly (vinyl chloride) nonwoven mats. Journal of Polymer Science Part B: Polymer Physics. 40(19): 2259-2268.

Lee K. H., Kim H. Y., Ryu Y. J., Kim K. W. and Choi S. W., 2003. Mechanical Behavior of Electrospun Fiber Mats of Poly(vinyl chloride)/Polyurethane Polyblends. Journal of Polymer Science: Part B: Polymer Physics. 41(11): 1256-1262.

Lee, K., Lee, B., Kim, C., Kim, H., Kim, K., & Nah, C. (2005). Stress-strain behavior of the electrospun thermoplastic polyurethane elastomer fiber mats. Macromolecular Research. 13(5): 441-445.

Legge, N. R., Holden. G. and Schroeder, H. E. (1987). Thermoplastic elastomers: A comprehensive review, Carl Hanser Verlag, Munich. 80: 574.

Lemmon, J. P. and Lerner, M. M. (1994). Preparation and characterization of nanocomposites of polyethers and molybdenum disulfide. Chemistry of Materials. 6: 207-210.

Li, Y. and Ishida, H. (2003). Solution intercalation of polystyrene and the comparison with poly(ethyl methacrylate). Polymer. 44: 6571-6577.

Linford, R. G., Glasse, M. D., Idris, R., Latham, R. J. and Schlindwein, W. S. (2002). Polymer electrolytes based on modified natural rubber. Solid State Ionics. 147(3): 289-294.

Liu, H. and Hsieh, Y. L. (2002). Ultrafine fibrous cellulose membranes from electrospinning of cellulose acetate. Journal of Polymer Science Part B: Polymer Physics. 40(18): 2119-2129.

Luu, Y. K., Kim, K., Hsiao, B. S., Chu, B. and Hadjiargyrou, M. (2003). Development of a nanostructured DNA delivery scaffold via electrospinning of PLGA and PLA–PEG block copolymers. Journal of Controlled Release. 89(2): 341-353.

MacDiarmid, A. G., Jones, W. E., Norris, I. D., Gao, J., Johnson, A. T., Pinto, N. J., Hone, J., Han, B., Ko, F. K., Okuzaki, H. and Llaguno, M. (2001). Electrostatically-generated nanofibers of electronic polymers. Synthetic Metals. 119: 27-30.

Machado, A.V. and van Duin, M. (2005). Dynamic vulcanization of EPDM/PP-based thermoplastic vulcanizates studied along the extruder axis. Polymer. 46: 6575-6586.

Magagnini, P., Filippi, S., Maneli, E. and Marazzato, C. (2007). Comparison of solution-blending and melt-intercalation for the preparation of poly(ethylene-co-acrylic acid)/organoclay nanocomposites. European Polymer Journal. 43(5): 1645-1659.

Malwitz, M. M., Lin-Gibson, S., Hobbie, E. K., Butler, P. D. and Schmidt ,G. (2003). Orientation of platelets in multilayered nanocomposite polymer films. Journal of Polymer Science Part B: Polymer Physics. 41: 3237-3248.

Martin, P., Maquet, C., Legras, R., Bailly, C., Leemans, L., van Gurp, M. and van Duin, M. (2004). Conjugated effects of the compatibilization and the dynamic vulcanization on the phase inversion behavior in poly(butylene terephthalate)/epoxide-containing rubber reactive polymer blends. Polymer. 45(15): 5111-5125.

McCrum, N. G., Buckley, C. P. and Bucknall, C. B. (1997). Principles of polymer engineering. 2nd edition oxford; New York: Oxford University Press. Chapters 0-6.

Michael, M. C. and Paul, C. P. (1995). Hydrogen bonded polymer blends. Progress in Polymer Science. 20(1): 1-59.

Mitupatham, C., Udomkichdecha, W. and Euapermkiati, A. (1996). Structure and property relationship of semi-interpenetrating polymer networks of polyurethane and poly (vinyl chloride), Master. Science (Applied Polymer Science and Textile Technology), Chulalongkorn University. Bangkok. (Thailand). Graduate School. 45(36).

Mohamad, Z., Ismail, H. and Ratnam, C. T. (2005). Characterization of epoxidized natural rubber/ethylene vinyl acetate (ENR-50/EVA) blend: Effect of blend ratio. Journal of Applied Polymer Science. 99(5): 1504-1515.

Mousa, A., Ishaiku, U. S. and Mohd Ishak, Z. A. (1998). Oil resistance studies of dynamically vulcanized PVC/ENR thermoplastic elastomers, Journal of Applied Polymer Science, 69(7): 1357-1366.

Mousa, A., Ishiaku, U. S. and Mohd Ishak, Z. A. (2000). Rheological properties of dynamically vulcanized poly (vinyl chloride)/epoxidized natural rubber thermoplastic elastomers: effect of processing variables. Polymer Testing, 19(2): 193-204.

Mousa, A., Ishiaku, U. S. and Mohd Ishak, Z. A. (2000). Rheological properties of dynamically vulcanized poly (vinyl chloride)/epoxidized natural rubber thermoplastic elastomers: effect of processing variables. Polymer Testing, 19(2): 193-204.

Naderi, G., Nouri, M. R., Mehrabzadeh, M. and Bakhshandeh, G. R. (1999). Studies on dynamic vulcanization of PP/NBR thermoplastic elastomer blends. Iranian Polymer Journal, 8: 37-42.

Nakason, C., Pichaiyut, S., Kummerlöwe C. and Vennemann, N. (2012). Thermoplastic elastomer based on epoxidized natural rubber/thermoplastic polyurethane blends: influence of blending technique. Polymers for Advanced Technologies. 23(6): 1011-1019.

Nimsuwan, C. (2011). Rubber technology: technical problems and methods, Journal for the development of Thailand rubber industry. Research and Development Centre for Thai Rubber Industry, MTEC National Science and Technology Development Agency. 3-12.

Ogata, N., Kawakage, S. and Ogihara, T. (1997). Poly (vinyl alcohol)-clay and poly(ethylene oxide)-clay blends prepared using water as solvent. Journal of Applied Polymer Science. 66: 573-581.

Okwu, U. N. and Okieimen (2001). Preparation and properties of thioglycolic acid modified epoxidized natural rubber and its blends with natural rubber. European Polymer Journal. 37(11): 2253-2258.

Palanivelu, K., Sivaraman, P. and Reddy, M. D. (2002). Studies on thermoplastic polyurethane toughened poly(butylene terephthalate) blends. Polymer Testing. 21(3): 345-351.

Pappa, A., Mikedi, K., Agapiou, A., Karma, S., Pallis, G. C., Statheropoulos, M. and Burke, M. (2011). TG–MS analysis of nitrile butadiene rubber blends (NBR/PVC). Journal of Analytical and Applied Pyrolysis, 92(1): 106-110.

Pasa, V. M. V., Maciel, A. V., Machado, J. C. and Maria, V. (2013). The effect of temperature on the properties of the NBR/PVC blend exposed to ethanol fuel and different gasolines. Fuel. 13: 679-689.

Peng, Z. and Kong, L. X. (2007). A thermal degradation mechanism of polyvinyl alcohol/silica nanocomposites. Polymer Degradation and Stability. 92(6): 1061-1071**.**

Pichaiyut, S., Nakason, C. and Vennemann, N. (2012). Thermoplastic elastomers-based natural rubber and thermoplastic polyurethane blends. Iranian Polymer Journal. 21(1): 65-79.

Pita, V. J. R. R., Sampaio, E. E. M. and Monteiro, E. E. C. (2002). Mechanical properties evaluation of PVC/plasticizers and PVC/thermoplastic polyurethane blends from extrusion processing. Polymer Testing. 21(5): 545-550

Plastic & thermoplastic elastomer materials, online technical report (Minnesota Rubber and QMR Plastics, section 5, 2003).

Poh, B. T., Ismail, H. and Quah, E. H. (2001). Fatigue, resilience and hardness properties of unfilled SMR L/ENR 25 and SMR L/SBR blends, Polymer Testing. 20(4): 389-394.

Poompradub, S. and Mahapram, S. (2011). Preparation of natural rubber (NR) latex/low density polyethylene (LDPE) blown film and its properties. Polymer Testing. 30(7): 716-725.

Pötschke, P., Bhattacharyya, A. R., Janke, A., Sven, P., Leonhardt, A., Täschner, C., Ritschel, M., Roth, S., Hornbostel, B. and Cech, J. (2005). Melt mixing as method to disperse carbon nanotubes into thermoplastic polymers. Fullerenes, Nanotubes and Carbon Nanostructures. 13: 211-224**.**

Purushothaman, E., Al Minnath, M. and Unnikrishnan, G. (2011). Transport studies of thermoplastic polyurethane/natural rubber (TPU/NR) blends. Journal of Membrane Science, 379(1): 361-369.

Qu, B., Qiu, L. and Chen, W. (2006). Morphology and thermal stabilization mechanism of LLDPE/MMT and LLDPE/LDH nanocomposites. Polymer. 47: 922-930.

Ratnam, C. T. (2002). Enhancement of PVC/ENR blend properties by electron beam irradiation: effect of stabilizer content and mixing time. Polymer Testing. 21(1): 93-100.

Ratnam, C. T. and Zaman, K. (1999). Stabilization of poly(vinyl chloride)/epoxidized natural rubber (PVC/ENR) blends. Polymer Degradation and Stability. 65(1): 99-105.

Ratnam, C. T. and Zaman, K. (1999). Enhancement of polyvinyl chloride (PVC)/epoxidised natural rubber (ENR) blend properties by electron beam irradiation: effect of antioxidants. Polymer Degradation and Stability. 65(3): 481-490.

Ratnam, C. T., Kamaruddin, S., Sivachalam, Y., Talib, M. and Yahya, N. (2006). Radiation crosslinking of rubber phase in poly(vinyl chloride)/epoxidized natural rubber blend: Effect on mechanical properties. Polymer Testing. 25: 475-480.

Rempel, G. L., Arayapranee, W. and Prasassarakich, P. (2004). Blends of poly (vinyl chloride)(PVC)/natural rubber-g-(styrene-co-methyl methacrylate) for improved impact resistance of PVC. Journal of applied polymer science, 93(4): 1666-1672.

Reneker, D. H. and Chun, I. (1996). Nanometre diameter fibres of polymer, produced by electrospinning. Nanotechnology. 7(3): 216.

Robeson, L. M. (2007). Polymer blends: A comprehensive review. New York: Hanser Gardner Publishers.

Roshandel, R. and Parhizgar, T. (2013). A new approach to optimize the operating conditions of a polymer electrolyte membrane fuel cell based on degradation mechanisms. Energy Systems. 4: 219-237.

Roy Choudhury, A., De, P. P., Bhowmick, A. K. and De, S. K. (1992). Self-crosslinkable ternary blend of chlorosulphonated polyethylene, epoxidized natural rubber and carboxylated nitrile rubber. Polymer. 33(22): 4737-4740.

Roy Choudhury, N., Chaki, T. K., Dutta, A. and Bhowmick, A. K. (1989). Thermal, X-ray and dynamic mechanical properties of thermoplastic elastomeric natural rubber-polyethylene blends. Polymer. 30(11): 2047-2053.

Roy Martinus, A. (2009). Thermoplastic vulcanizates ;The rubber particle size to control the properties-processing balance, the Laboratory of Polymer Technology (SKT) within the Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, The Netherlands.

Sadequl, A. M., Ishiaku, U. S., Ismail, H. and Poh, B. T. (1998). The effect of accelerator/sulphur ratio on the scorch time of epoxidized natural rubber. European polymer journal. 34(1): 51-57.

Schjødt-Thomsen, J., Madaleno, L. and Pinto, J. C. (2010). Morphology, thermal and mechanical properties of PVC/MMT nanocomposites prepared by solution blending and solution blending-melt compounding. Composites Science and Technology. 70: 804-814.

Senna, M. H., Abdel-Fattah, A. and Abdel-Monem, Y. K. (2008). Spectroscopic analysis and mechanical properties of electron beam irradiated polypropylene/epoxidized natural rubber (PP/ENR) polymer blends. Nuclear Instruments and Methods in Physics Research Section B. 266(11): 2599-2606.

Sill, T. J. and von Recum, H. A. (2008). Electrospinning: applications in drug delivery and tissue engineering. Biomaterials. 29(13): 1989-2006.

Simon, G. P., Shen, Z. and Cheng, Y. B. (2002). Comparison of solution intercalation and melt intercalation of polymer-clay nanocomposites. Polymer. 43: 4251-4260.

Sjoqvist, M. and Boldizar, A. (2011). Molecular modification and compatibilization of collected polyethylene. Journal Polymer Environment. 19: 335-340.

Soldi, M. S., Villetti, M. A., Crespo, J. S., Pires, A. T. N., Borsali, R. and Soldi, V. (2002) Thermal degradation of natural polymers. Journal of Thermal Analysis and Calorimetry. 67: 295-303.

Son, W. K., Youk, J. H., Lee, T. S. and Park, W. H. (2004). The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly (ethylene oxide) fibers. Polymer. 45(9): 2959-2966.

Strawhecker, K. E. and Manias, E. (2000). Structure and properties of poly(vinyl alcohol)/Na^+ montmorillonite nanocomposites. Chemistry of Materials. 12: 2943-2949.

Sulekha, P.B., Joseph, R., Madhusoodanan, K. N. and Thomas, K.T. (2002). New oligomer-bound antioxidants for improved flex crack resistance and ozone resistance. Polymer Degradation and Stability. 77(3): 403-416.

Teoh, C. H. (2006). Epoxidized natural rubber (ENR-50) stabilized gold and platinum organosols, Thesis submitted in fulfillment of the requirements for the degree of Master of Science. Universiti Sains Malaysia.

Thomas, S., George, J. and Varughese, K. T. (2000). Dynamically vulcanised thermoplastic elastomer blends of polyethylene and nitrile rubber. Polymer. 41(4): 1507-1517.

Thomas, S., Stephen, R., Joseph, K. and Oommen, Z. (2000). Molecular transport of aromatic solvents in isotactic polypropylene/ acrylonitrile-co-butadiene rubber blends. Polymer, 41(2): 579-594.

Thomas, S., Stephen, R., Joseph, K. and Oommen, Z. (2006). Thermal stability and ageing properties of sulphur and gamma radiation vulcanized natural rubber (NR) and carboxylated styrene butadiene rubber (XSBR) latices and their blends. Polymer Degradation and Stability. 91(8): 1717-1725.

Thomas, S., Stephen, R., Joseph, K. and Oommen, Z. (2007). Molecular transport of aromatic solvents through microcomposites of natural rubber (NR), carboxylated styrene butadiene rubber (XSBR) and their blends. Composites Science and Technology. 67(6): 1187-1194.

Thomas, S., Varghese H. and Bhagawan S. S. (2001). Thermogravimetric analysis and thermal ageing of crosslinked nitrile rubber/poly(ethylene-co-vinyl acetate) blends. Journal of Thermal Analysis & Calorimetry. 63: 749-763.

Truong, Y. B., Wong, L. and Shen, W. (2011). Investigation of electrospun and film-cast PVC membranes incorporated with aliquat 336 for efficient Cd extraction: A comparative study. Journal of Applied Polymer Science. 121(1): 327-335.

Ulcnik-Krump, M. (2006). Study of morphology influence on rheological properties of compatibilized TPU/SAN blends. Journal of Applied Polymer Science. 100(3): 2303-2316.

Ulcnik-Krump M. and De Lucca Freitas, L. (2004). The study of morphology, thermal and thermo-mechanical properties of compatibilized TPU/SAN blends. Polymer Engineering & Science. 44(5): 838-852.

Utracki, L. A. (1989). Polymer alloys and blends. New York: Hanser Gardner Publishers.

Utrack, L.A. and Lyngaae-Jorgensen, J. (2003). Structuring polymer blends with bicontinuous phase morphology. Part II. Tailoring blends with ultralow critical volume fraction. Polymer. 44: 1661-1669.

Utracki, L. A and Shi G, Z, H, (2002). Compounding polymer blends. Polymer blends handbook. Dordrecht: Kluwer Academic. Chapter 10.

Venugopal, J. and Ramakrishna, S. (2005). Applications of polymer nanofibers in biomedicine and biotechnology. Applied Biochemistry and Biotechnology. 125(3): 147-157.

Versteegen, R. M. (2003). Well-defined thermoplastic elastomers : reversible networks based on hydrogen bonding. Universiteitsdrukkerij, Technische Universiteit Eindhoven

Waldman, W. R. and De Paoli. M-A. (2013). Influence of compatibilizer on blends degradation during processing. Polímeros. 23(1): 7-13.

Wang, D. and Wilkie, C. (2002). Preparation of PVC/Clay nanocomposites by solution blebding. Journal of Vinyl and Additive Technology. 8(4): 238-245.

Wang, N., Raza, A., Si, Y., Yu, J., Sun, G. and Ding, B. (2013). Tortuously structured polyvinyl chloride/polyurethane fibrous membranes for high-efficiency fine particulate filtration. Journal of Colloid and Interface Science. 398: 240-246.

Wang, X., Tan, J., Luo, Y. and Jia, D. (2012). Rubber/clay nanocomposites by combined latex compounding and melt mixing: A masterbatch process. Materials and Design. 34: 825-831.

White, J. R., Heslop, J. and Bhowmick, A. K. (2001). Effect of stabilizers in photodegradation of thermoplastic elastomeric rubber-polyethylene blends-a preliminary study. Polymer Degradation and Stability. 74(3): 513-521.

Wimolmala, E., Wootthikanokkhan, J. and Sombatsompop, N. (2000). Preparation and characterization of poly (vinyl chloride) acrylic rubber blends, Master. Engineering (Material Technology), King Mongkuts University of Technology Thonburi. Bangkok (Thailand). Graduate School.

Work, W. J., Horie, K., Hess, M. and Stepto, R. F.T. (2004). Definitions of terms related to polymer blends composites and multiphase polymeric materials. Pure and Applied Chemistry 76: 1985-2007.

Yahya, M. Z. A., Mohamed, S. N., Johari, N. A., Ali, A. M. M. and Harun, M. K. (2008). Electrochemical studies on epoxidised natural rubber-based gel polymer electrolytes for lithium-air cells. Journal of Power Sources. 183(1): 351-354.

Yang, Q., Li, Z., Hong, Y., Zhao, Y., Qiu, S., Wang, C. E. and Wei, Y. (2004). Influence of solvents on the formation of ultrathin uniform poly (vinyl pyrrolidone) nanofibers with electrospinning. Journal of Polymer Science Part B: Polymer Physics. 42(20): 3721-3726.

Yang, Q. B., Li, D. M., Hong, Y. L., Li, Z. Y., Wang, C., Qiu, S. L. and Wei, Y. (2003). Preparation and characterization of a PAN nanofibre containing Ag nanoparticles via electrospinning. Synthetic metals. 137: 973-974.

Yang, Y. and Ma, H. (2008). Rheology, morphology and mechanical properties of compatibilized poly (vinylidene fluoride) (PVDF)/thermoplastic polyurethane (TPU) blends. Polymer Testing. 27(4): 441-446

Yoshimoto, H., Shin, Y. M., Terai, H. and Vacanti, J. P. (2003). A biodegradable nanofiber scaffold by electrospinning and its potential for bone tissue engineering. Biomaterials. 24(12): 2077-2082.

Yuan, X., Zhang, C., Wu, L., Han, Y. and Sheng, J. (2005). Study on morphology of electrospun poly (vinyl alcohol) mats. European Polymer Journal. 41(3): 423-432.

Zhao, Z., Li, J., Yuan, X., Li, X., Zhang, Y. and Sheng, J. (2005). Preparation and properties of electrospun poly (vinylidene fluoride) membranes. Journal of applied polymer science. 97(2): 466-474.

Zuo, W., Zhu, M., Yang, W., Yu, H., Chen, Y. and Zhang, Y. (2005). Experimental study on relationship between jet instability and formation of beaded fibers during electrospinning. Polymer Engineering & Science. 45(5): 704-709.

Zhu, X., Jiang, X., Cheng, S., Wang, K., Mao, S., & Fan, L. J. (2010). Preparation of high strength ultrafine polyvinyl chloride fibrous membrane and its adsorption of cationic dye. Journal of Polymer Research. 17(6): 769-777.

APPENDICES

Paper I

Phatcharasit, K. and Taweepreda, W. 2011. Polyethylene Thin Film Coating Preventing the Degradation of Natural Rubber. Engineering Journal, 16(3):53-58.

ENGINEERING JOURNAL

Article

Polyethylene Thin Film Coating Preventing the Degradation of Natural Rubber

Wirach Taweepreda* and Kritsada Phatcharasit

Membrane Science and Technology Research Center, Department of Materials Science and Technology,
Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90110, Thailand
E-mail: wirach.t@psu.ac.th*

Abstract. In this research, natural rubber (NR) was directly mixed with polyethylene (PE) and was compressed at 150°C. The PE was then separated and migrated to form a thin film on the rubber surface during the vulcanization process. The tensile properties of composite film were rising with increasing the PE contents from 15 to 150 phr as well as the ozone aging properties. The surface topography of the composite film was examined by using scanning electron microscopy (SEM) and was found that the PE form lamellar crystallites on the rubber interface after ozone treatment. The effect of PE on NR cross-linking was also investigated using S K-edge XANES Spectroscopy.

Keywords: Natural rubber, degradation, coating, polyethylene.

ENGINEERING JOURNAL Volume 16 Issue 3
Received 23 November 2011
Accepted 30 April 2012
Published 1 July 2012
Online at http://www.engj.org/
DOI:10.4186/ej.2012.16.3.53

This paper is based on the poster presentation at the German-Thai Symposium on Nanoscience and Nanotechnology 2011—Green Nanotechnology of the Future, GTSNN 2011, in Nakhon Ratchasima, Thailand, 13-16 September 2011.

DOI:10.4186/ej.2012.16.3.53

1. Introduction

Natural rubber (NR) has excellent mechanical properties but it likes any other polymers which are composed with highly unsaturated chain that is susceptible to oxidative degradation [1]. The double bond of NR molecule will be attacked by peroxy free radicals initiated scission reaction when the rubber is placed under strain in air at high temperature [2]. As well as ozone degradation which is the cause of surface cracking when the rubber is placed under strain in an ozone environment. These degradations are serious problem to shorten the serviceable life of rubber article. It is necessary to add antioxidants either natural or synthetic in rubber compound to prevent this oxidative reaction [3-5]. However, chemical antioxidants and antiozonants are very expensive and have many limitations when applied with rubber.

In this study, a study of phase morphology with blend ratio and its effects on ozone resistance properties will be investigated, and the resulting degradation of sulfur bonding will be studied accordingly.

2. Methodology

2.1. Compounding and Making Thin Film

Standard Thai Rubber (STR20) was milled and mixed with spindle oil using 2-rolls mill before adding the polyethylene (PE) powder with following ratios: 100:15, 100:30, 100:90, and 100:150 by weight of NR:PE at an ambient temperature. For compounding was also directly mixed with chemicals followed Table 1. The rubber compound was compressed and vulcanized at 150°C for 5 minutes to formed membrane with thickness not over than 0.4 mm, in approximately.

Table 1. Formulation of NR compound (phr = part per hundred of rubber).

Ingredient	**phr**
STR20	100.0
Spindle oil	200.0
Sulfur	15.0
MBT	10.5
ZnO	7.5
Stearic acid	3.0
Winstay L	3.0
PE Powder	vary

2.2. Characterization

The mechanical properties of membrane were carried out on a LLOYD instrument tensile tester. The samples were cut into dumbbell shape with dimension according to ASTM D412 (die C). Aging of the dumbbell specimens were carried out by placing under strain in an ozone environment at 75 pphm for 8, 16, and 24 hours. Tensile properties were operated at a cross-head speed of 500 mm/min.

The XANES measurement was carried out at the beamline 8 of the Synchrotron Light Research Institute (SLRI) in Thailand [6]. The measurements were performed in a fluorescence mode using a 5-grid ionization Lytle fluorescence detector. The photon energy scan was carried out using the Si(111) double crystal monochromator to cover the *K*-edge of sulfur. For the energy calibration, the maximum of the absorption peak (white line) of zinc sulfate ($ZnSO_4$) powder was used as the reference energy of 2481.4±0.1 eV [7]. Surface morphology of membrane was studied using scanning electron microscope (SEM), JEOL JSM-5800 LV.

3. Results and Discussion

The membrane of PE, NR, and their blends has mechanical properties as shown in Fig. 1. The tensile strength of PE membrane is higher than NR membrane while the tensile strength of membrane from their blends is slightly increased when compared with NR membrane.

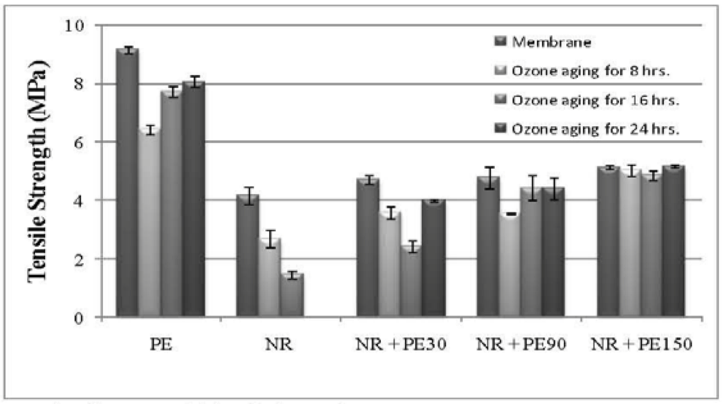


Fig. 1. Tensile strength of pure and blended membranes.

The tensile strength of PE membrane is dramatically decreased after ozone ageing for 8 hrs due to oxidative reaction while longer ozone ageing of PE membrane results in increasing of tensile strength. The PE scission chains might be oriented and formed crystalline structure to increases the tensile strength. On the other hand, the NR membrane is degraded with increasing ozone aging period until the rubber is broken down with ozone aging for 24 hr. The aging property of rubber blend membrane is improved with increasing the PE concentration because PE phase is separated and migrated to form thin film coating on the membrane surface during hot compression process.

The S K-edge absorption spectra of NR and their blends membrane as illustrated in Fig. 2. The sulfur cross-linking in rubber molecule was investigated cover photon energy range of 2460 to 2490 eV with the accuracy of photon energy up to within 0.2 eV. The S K-edge absorption peak would shift depending on sulfur environment. In this case the peak of S K-edge absorption was found at 2472.0±0.2 eV for polysulfidic crosslink. The position of the peak in the absorption spectra shifts towards lower photon energy may be used as the indicator for the type of the σ^* resonance [8, 9]. The absorption peak area is increased and shifts towards lower photon energy with increasing the PE concentration corresponds with the mechanical properties of membrane.

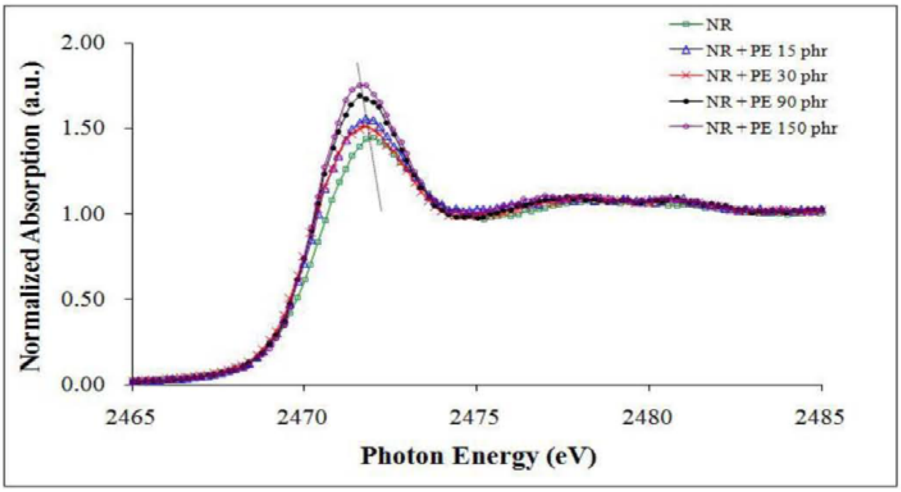


Fig. 2. XANES spectra of NR and their blends membrane.

DOI:10.4186/ej.2012.16.3.53

The SEM images in Fig. 3 clearly showed that PE migrated to the surface and created a barrier film at bottom surface because PE was removed after immersing the membrane in xylene. The membrane is consisted of micro-pores at the bottom surface and cross-section after removing PE. This effect is similar to wax blooming which will carry chemical antiozonants to the surface of the rubber, improving their performance. In this study, the membrane prepared from NR blending with PE for 150 phr created highest thickness of the film and contribute to the ozone resistance.

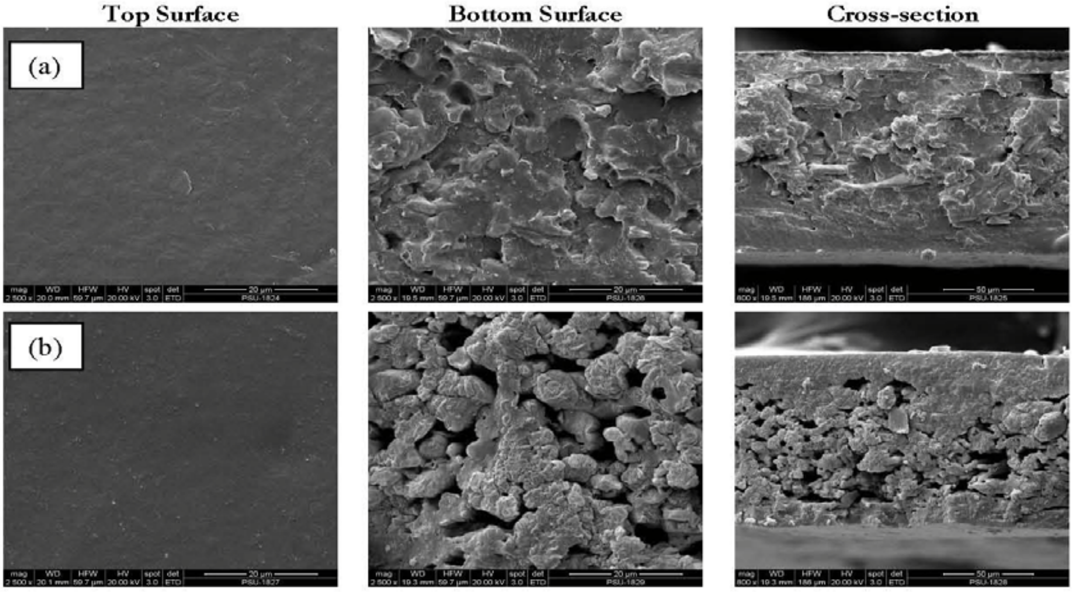


Fig. 3. SEM images of the membrane from NR blending with PE 150 phr before (a) and after (b) extraction with xylene.

The surface of NR membrane is cracked after ozone aging as shown in Fig. 4 while the PE coated membrane formed lamellae crystallites on the surface as shown in Fig. 5. Coated PE layer was oriented and the crystalline lamellae were grown in submicrometer size after ozone treatment. The crystalline size and number depend on ozone aging time. The increasing of crystalline lamellae corresponds with the tensile strength of PE coated membrane.

4. Conclusions

PE phase separated from NR phase to formed thin film coating on the membrane. The coating improved the ozone aging of the membrane without adding any antiozonants. The coating layer formed crystalline lamellae after treated the membrane with ozone resulted in preventing rubber oxidation reaction and improvement of membrane strength.

Acknowledgement

This work was supported by the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission. KP would like to thank Prince of Songkla University for supporting PhD. Scholarship under National Research University Program.

DOI:10.4186/ej.2012.16.3.53

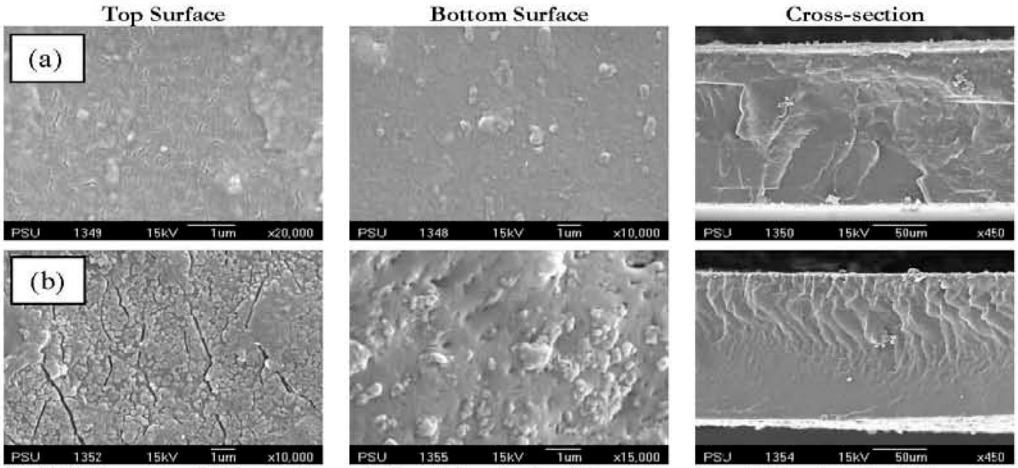


Fig. 4. SEM images of NR membrane before (a) and after (b) ozone aging at 75 pphm for 16 hrs.

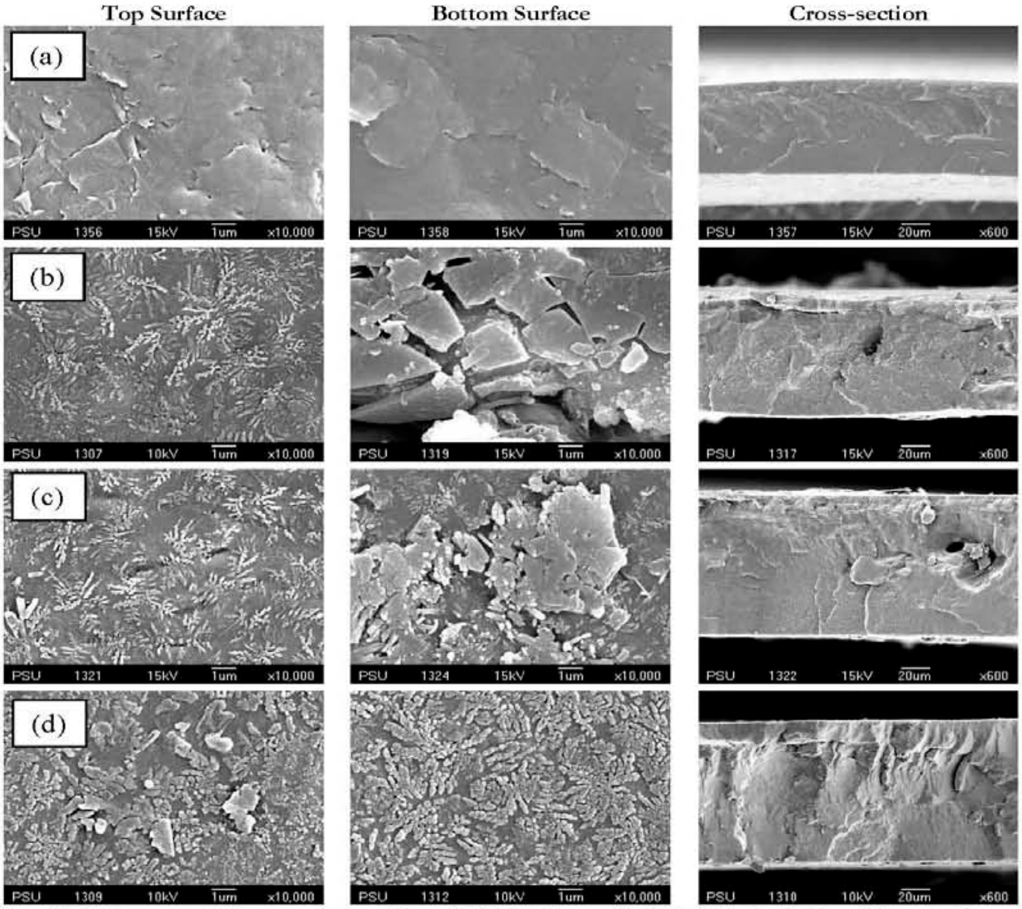


Fig. 5. SEM images of the membrane from NR blending with PE 150 phr before (a) and after ozone aging at 75 pphm for 8 hrs (b) 16 hrs (c) and 24 hrs (d).

DOI:10.4186/ej.2012.16.3.53

References

[1] C. Sirisinha, S. Baulek-Limcharoen, and J. Thunyarittikorn, "Relationships among blending conditions, size of dispersed phase, and oil resistance in natural rubber and nitrile rubber blends," *J.Appl.Polym.Sci.*, vol. 82, pp. 1232-1237, 2001.

[2] S. Al-Malaika, "Mechanisms of antioxidant action and stabilization technology-the Aston experience," *Polym.Degrad.Stab.*, vol. 34, pp. 1-36, 1991.

[3] L. V. Abad, L. S. Relleve, C. T. Aranilla, A. K. Aliganga, C. M. San Diego, and A. M. dela Rosa, "Natural antioxidants for radiation vulcanization of natural rubber latex," *Polym.Degrad.Stab.*, vol. 76, pp. 275-279, 2002.

[4] P. B. Sulekha, R. Joseph, and K. E. George, "Study on polyisobutylene bound paraphenylene diamine antioxidant in natural rubber," *Polym.Degrad.Stab.*, vol. 63, pp. 225-230, 1999.

[5] Y. Li, Z. Zheng, C. Xu, C. Ren, Z. Zhang, and Z. Xie, "Synthesis of iron-containing polysilazane and its antioxidation effect on silicone oil and rubber," *J.Appl.Polym.Sci.*, vol. 90, pp. 306-309, 2003.

[6] W. Klysubun, P. Sombunchoo, N. Wongprachanukul, P. Tarawarakarn, S. Klinkhico, J. Chaiprapa, and P. Songsiriritthigul, "Commissioning and performance of X-ray absorption spectroscopy beamline at the Siam Photon Laboratory," *Nucl Instum Meth. A*, vol. 582, pp. 87–89, 2007.

[7] B. Ravel and M. Newville, "*ATHENA*, *ARTEMIS*, *HEPHAESTUS*: data analysis for X-ray absorption spectroscopy using *IFEFFIT*", *J. Synchrotron Rad.*, vol. 12, pp. 537–541, 2005.

[8] J. Hormes and M. Modrow, "Industrial use of synchrotron radiation: a very subjective overview," *Nucl Instum Meth. A*, vol. 467-468, pp. 1179-1191, 2001.

[9] W. Taweepreda, R. Nu-Mard, W. Pattanasiriwisawa, and P. Songsiriritthigul, "Model compound vulcanization studied by XANES," *J. of Phys.: Conference Series*, vol. 190, p. 012150, 2009.

Paper II

Phatcharasit, K., Taweepreda, W. and Saesia, W. 2012. TPNR Membrane Reinforcing with Cotton Fibre Spun. Journal of Chemistry and Chemical Engineering, 6:799-802.

J. Chem. Chem. Eng. 6 (2012) 799-802

TPNR Membrane Reinforcing with Cotton Fibre Spun

Wirach Taweepreda[1*], Kritsada Phatcharasit[1] and Wipa Saesia[2]

1. Membrane Science and Technology Research Center, Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Songkhla 90110, Thailand

2. Surgical Nursing Department, Faculty of Nursing, Prince of Songkla University, Songkhla 90110, Thailand

Received: August 20, 2012 / Accepted: September 14, 2012 / Published: September 25, 2012.

Abstract: Reinforcement of TPNR (thermoplastic natural rubber) with cotton fibre spun was prepared by using hot compression moulding. The TPNR was prepared by mixing NR (natural rubber) with PE (polyethylene) using 2-roll mills before compressed on cotton fibre spun and vulcanized at 150 °C. The mechanical properties and morphology of the membrane were investigated using DMTA (dynamic mechanical thermal analyzer) and SEM (scanning electron microscopy), respectively. The membrane strength was increased from 10 MPa to 18 MPa after reinforced with cotton fibre spun as well as the increasing of dielectric constant. The membrane was immersed in xylene to remove PE phase before characterization of membrane properties.

Key words: TPNR, natural rubber, cotton fibre spun, reinforcement, PE.

1. Introduction

NR (natural rubber) is used extensively in industry because of its excellent mechanical properties and heat build-up but poor oxidation resistance [1] and conductor of electricity [2]. The important way to improve the conductivity of polymer is the incorporation of conductive materials such as carbon black [3, 4], fibre [5, 6], cellulose [7], and chitosan [8], etc.. TPNR (thermoplastic natural rubber) which is prepared by blending NR with thermoplastic combines the physical properties of NR with the ease processing characteristic of thermoplastics. The process which the rubber phase is vulcanized during the mixing process at high temperature is known as in-situ dynamic vulcanization process [9]. PE (polyethylene) powder is selected in this work to blend with NR due to its low melting temperature of about 110 °C and low glass transition temperature. The influence of NR composition with PE and reinforced cotton fiber spun on mechanical and dielectric properties was investigated.

2. Experiment

2.1 Sample Preparation

STR5L (standard Thai rubber) was milled and mixed with spindle oil using 2-rolls mill before adding PE at different concentration. The compounding with chemicals followed Table 1.

The rubber compound was compressed with inserting cotton fibre spun sheet and vulcanized at 150 °C for 5 min to formed membrane.

Table 1 Formulation of NR compound (phr = part per hundred of rubber).

Ingredient	phr
STR5L	100.0
Spindle oil	150.0
Sulfur	10.0
MBT	10.0
ZnO	2.5
Stearic acid	1.0
Winstay L	1.0
PE powder	vary

---

[*] **Corresponding author:** Wirach Taweepreda, Ph.D., research fields: polymer science and technology. E-mail: wirach.t@psu.ac.th.

2.2 Characterization

The mechanical properties of thin films were carried out on a LLOYD instrument tensile tester. The samples were cut into dumbbell shape with dimension according to ASTM D412 (die C). The dynamic mechanical properties of vulcanized LNR and TPNR/cotton fibre spun composites were performed using DMTA (dynamic mechanical thermal analyser; Model-V, supplied by Rheometric Scientific). The shape of test sample was rectangular, 25 mm long, 10 mm wide and 1.5 mm thick. The single cantilever mode of deformation was used under the test temperature range from -100 °C to 70 °C with a heating rate of 3 °C/min, the test frequency being 1 Hz. The cooling process was achieved through liquid nitrogen. The results were presented in terms of loss tangent (*tanδ*) and glass transition temperature (T_g). In this work, loss tangent (*tanδ*) was the ratio of loss modulus (E'') to storage modulus (E') whereas T_g was obtained from the loss modulus peak. Surface morphology of membrane was studied using SEM (scanning electron microscope), FEI Quanta 400. Dielectric measurements were carried out in the frequency range 75 kHz up to 30 MHz by using precision LCR meter (Agilent 4285A).

3. Results and Discussion

The NR and TPNR reinforcing with cotton fiber spun have mechanical properties as shown in Fig. 1. The tensile strength of NR was increased from 10 to 18 MPa after reinforcing with cotton fiber spun. Blending of NR with PE for 30 phr was found that the tensile strength was decreased to 12 MPa while adding more amount of PE to 90 phr increased the tensile strength to 30 MPa. This indicated that vulcanized NR might be dispersed phase in PE matrix and distribution of vulcanized NR was increased with increasing PE component from 30 to 90 phr. The PE matrix was removed after xylene immersing and found that the tensile strength was decreased while the elongation at break was not changed due to inserted layer of cotton fiber spun.

The morphological characterization of cotton fiber reinforced NR and TPNR is illustrated in Fig. 2. The SEM image indicated that the cotton fiber layer was inserted in the polymer matrix. The increasing of PE components was found that PE covered the spun of cotton fiber and formed film on the film surface. The SEM images of the cotton fiber reinforced TPNR after removed the PE phase as shown in Fig. 3. Fig. 3b confirms the film formation of PE phase on the film surface at both sides and dynamically vulcanized of NR that occurred during the hot compression process.

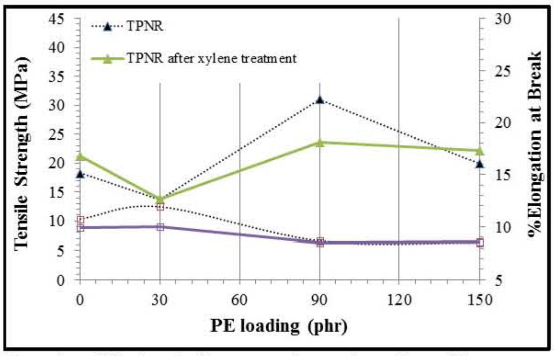


Fig. 1 Mechanical properties of cotton fiber spun reinforced TPNR by blending NR with PE at various compositions before and after xylene treatment.

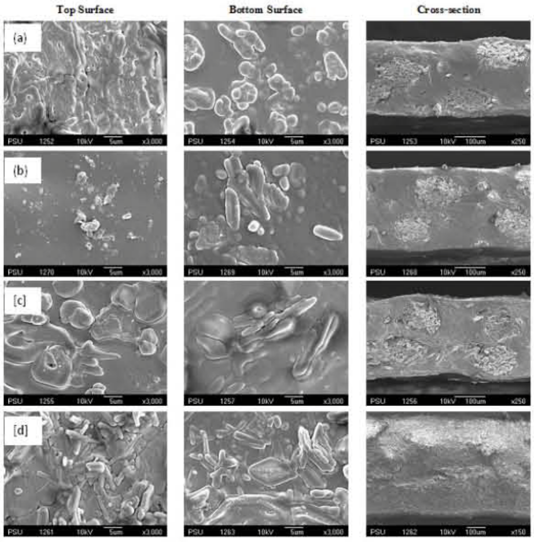


Fig. 2 SEM images of composited cotton fiber spun NR: (a) blending with PE (b) 30 (c) 90 and (d) and 150 phr.

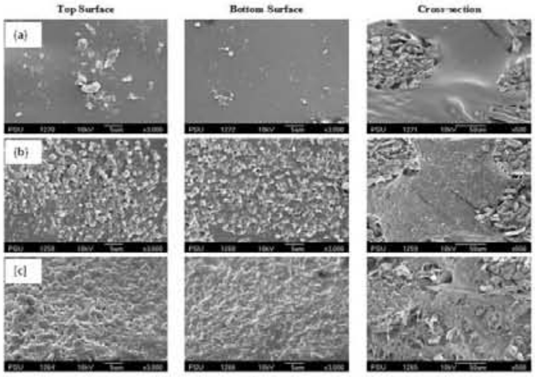


Fig. 3 SEM images of xylene etching surface of composited film blending with PE: (a) 30 (b) 90 and (c) 150 phr.

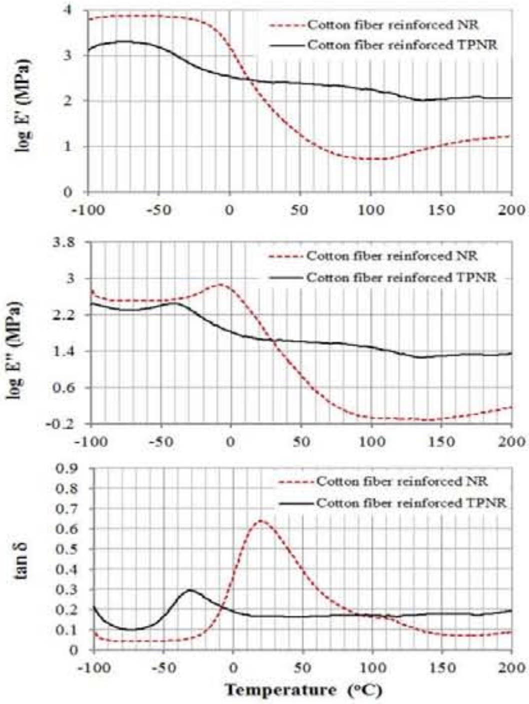


Fig. 4 DMTA thermogram of cotton fiber spun reinforced NR and TPNR.

The properties obtained from the dynamic mechanical thermal analysis are the storage modulus (E'), loss modulus (E''), and loss tangent ($tan\delta$) that is recorded as a function of temperature from -100 °C to 200 °C and shown in Fig. 4. The storage modulus is found to decrease with adding PE for 90 phr below the glass transition temperature (T_g). This indicates that PE blending has improved the softness of the TPNR during the transition from the glassy to the rubber state which occur around 20 °C. The damping property ($tan\delta$) is the ratio of the dynamic loss modulus to the dynamic storage modulus, correspond to T_g of the polymer matrix is found to decrease with adding PE from 20 °C to 30 °C. It can be replied that NR is miscibility blends with PE and vulcanized NR might be dispersed in PE matrix.

The permittivity and dielectric loss of cotton fiber reinforced NR and TPNR films were measured over the frequency range from 75 kHz up to 30 MHz at room temperature. The dielectric property of cotton

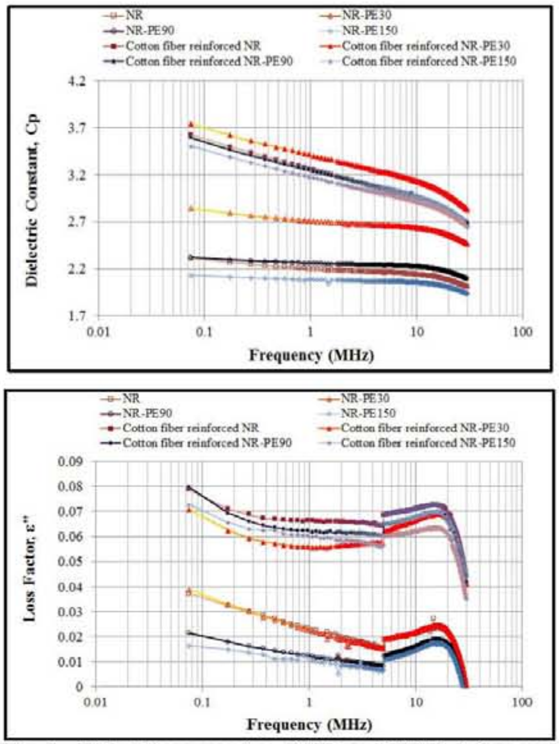


Fig. 5 Dielectric properties of NR and TPNR before and after reinforcing with cotton fiber spun.

fiber reinforced NR and NR blending with PE were increased as shown in Fig. 5. The dielectric constant of NR blending with PE for 30 phr was increased due to phase separation of PE from NR during the compression process. Most of PE covered the spun of cotton fiber and formed thin film that leads to increased capacitance of material. Blending of NR with PE at higher concentration for more than 90 phr lowered dielectric constant due to dynamic vulcanized NR in PE matrix. The sharp decrease in dielectric loss in lower frequency range of TPNR with 150 phr PE is attributed to the decrease in contribution of both interfacial polarization and conductivity.

4. Conclusions

The reinforcing of NR with cotton fiber spun is not only to improve the mechanical properties but also increase the dielectric properties due to the polarity of cotton fiber. Blending of PE with NR at the composition (90:100) increased the mechanical properties and it was found that vulcanized NR dispersed in PE matrix with average size 2 m similar with the properties of TPNR. This is the first report on new method to prepare TPNR by using 2-rolls mill and hot compression molding.

Acknowledgments

This work was supported by the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission. Author would like to thank the Higher Education Research Promotion and National Research University Project of Thailand, CHE (Office of the Higher Education Commission) for supporting his Ph.D. scholarship.

References

[1] Sirisinha, C.; Baulek-Limcharoen, S.; Thunyarittikorn, J. Relationships among Blending Conditions, Size of Dispersed Phase, and Oil Resistance in Natural Rubber and Nitrile Rubber Blends. *J. Appl. Polym. Sci.* **2001,** *82(5),* 1232-1237.

[2] Suksawad, P.; Kosugi, K.; Yamamoto, Y.; Akabori, K.; Kuroda, H.; Kawahara, S. Polymer Electrolyte Membrane with Nanomatrix Channel Prepared by Sulfonation of Natural Rubber Grafted with Polystyrene. *J. Appl. Polym. Sci.* **2011,** *122(4),* 2403-2414.

[3] Azura, A. R.; Ghazali, S.; Mariatti, M. Effects of the Filler Loading and Aging Time on the Mechanical and Electrical Conductivity Properties of Carbon Black Filled Natural Rubber. *J. Appl. Polym. Sci.* **2008,** *110(2),* 747-752.

[4] Tian, H.; Tian, M.; Zou, H.; Dang, Z.; Zhang, L. Special Electrical Conductivity of Carbon Black-Filled Two-Phased Thermoplastic Vulcanizates. *J. Appl. Polym. Sci.* **2010,** *117(2),* 691-699.

[5] Chang, W.; Ma, G.; Yang, D.; Su, D.; Song, G.; Nie, J. Electrospun Ultrafine Composite Fibers from Organic-Soluble Chitosan and Poly(Ethylene Oxide). *J. Appl. Polym. Sci.* **2010,** *117(4),* 2113-2120.

[6] Saad, A. L. G.; Younan, A. F. Rheological, Mechanical and Electrical Properties of Natural Rubber-White Filler Mixtures Reinforced with Nylon 6 Short Fibers. *Polymer Degradation and Stability* **1995,** *50(2),* 133-140.

[7] Ortiz-Serna, P.; Díaz-Calleja, R.; Sanchis, M. J.; Riande, E.; Nunes, R.; Martins, A.; et al. Dielectric Spectroscopy of Natural Rubber-Cellulose II Nanocomposites. *Journal of Non-Crystalline Solids* **2011,** *357(2),* 598-604.

[8] Johns, J.; Nakason, C. Dielectric Properties of Natural Rubber/Chitosan Blends: Effects of Blend Ratio and Compatibilization. *Journal of Non-Crystalline Solids* **2011,** *357(1),* 1816-1821.

[9] Lewis, C. K.; Misaen, B.; Changchum, S. Effect of Process and Formulation Variables on Properties of Extrude EPDM Foam. *Songklanakarin J. Sci. Technol.* **1999,** *21(3),* 16-25.

Paper III

Phatcharasit, K. and Taweepreda, W. 2012. In Situ Coating of Natural Rubber Film with Poly(vinyl chloride) Resin. Procedia Chemistry, 4: 232-237.

Available online at www.sciencedirect.com
SciVerse ScienceDirect
Procedia Chemistry 4 (2012) 232 – 237
Procedia Chemistry

In Situ Coating of Natural Rubber Film with Poly(vinyl chloride) Resin

W. Taweepreda[a,*], K. Phatcharasit[a]

[a]*Membrane Science and Technology Research Center, Department of Materials Science and Technology, Faculty of Science,*
Prince of Songkla University, Hat-Yai, Songkhla 90110, Thailand

---

Abstract

Film formation of poly(vinyl chloride) resin (rPVC) coating on natural rubber (NR) surface in solid state was prepared and investigated. The mixtures of rPVC with NR were compressed at 170 °C for 15 min and found that the rPVC was migrated and coated on the NR surface which was proved by the images from Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM). The coated NR films with rPVC loading 5 and 10 phr are stronger and higher dielectric constant than uncoated NR film. Very high loading of rPVC for 50 and 100 phr result in decreasing of tensile strength and dielectric constant.

Keywords: Natural rubber; surface coating; PVC; film formation.

---

1. Introduction

Natural rubber (NR) blending with thermoplastics are extensively interest in materials research and development due to their properties limitation. The blend properties are improved by two phase system occurs during the melt mixing stage [1]. Generally, polymer blends can be divided into 2 categories: miscible and immiscible blends. Most NR blends are immiscible, as the formation of two or more distinct separated phases. Several studies have been reported in NR modification to increase the compatibility for example epoxidized liquid natural rubber (ELNR) blending with poly(vinyl chloride) (PVC) [2]. It is well known that epoxidized oils are used as PVC plasticizers [3]. The compatibility of blend was usually observed from differencial scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). PVC/ELNR blend is commercially important with a wide range of properties development [4-8]. There are hard polymer domain and soft rubbery phase. Matsuo *et al.* reported the NBR/PVC blend is

---

[*] Corresponding author. Tel.: +66-74-288367; fax: +66-74-446925
E-mail address: wirach.t@psu.ac.th

1876-6196 © 2012 Published by Elsevier Ltd.
doi:10.1016/j.proche.2012.06.032

semi-compatible at 20% acrylonitrile (AN) content and almost homogeneous at 40% [9]. Such novel polymer blends that undergo thermally induced crosslinking have been termed "self-crosslinkable polymer blend", and some examples include PVC/epoxidized natural rubber (ENR).

In this present work was to study the effect of immiscible of PVC/NR blends on the formation of thin film coating during hot compression molding of PVC/NR blend.

2. Experiment

2.1. Compounding and making thin film

Standard Thai Rubber (STR5L) was milled and mixed with PVC resin (rPVC) using 2-rolls mill. For compounding was also directly mixed with chemicals followed Table 1. The rubber compound was compressed and vulcanized at 170 °C for 15 min to formed thin film with thickness not over than 0.8 mm, in approximately.

Table 1. Formulation of NR compound (phr = part per hundred of rubber)

Ingredient	phr
STR5L	100.0
Sulfur	5.0
MBT	3.5
ZnO	2.5
Stearic acid	1.0
Winstay L	1.0
rPVC	vary

2.2. Characterization

The mechanical properties of thin films were carried out on a LLOYD instrument tensile tester. The samples were cut into dumbbell shape with dimension according to ASTM D412 (die C).

Surface morphology of membrane was studied using scanning electron microscope (SEM), JEOL JSM-5800 LV and atomic force microscopy (AFM). The AFM measurements (True Non-Contact Mode^{TM}, Park System XE70) were conducted under ambient condition. The silicon nitride cantilever probe vibrates near resonant frequency of piezoelectric modulator passes over a film surface which was placed on a pre-cleaned mica substrate, and correlate changes in the cantilever's vibrations to topographical features. The surface roughness average (R_a) and root mean square (R_q) were calculated from Nanoscope software by using the following equations:

$$R_a = \frac{1}{n}\sum_{j=1}^{n}\left|Z_j\right| \qquad (1)$$

$$R_q = \sqrt{\frac{1}{n}\sum_{j=1}^{n} Z_i^2} \qquad (2)$$

where Z_j is the difference between the height and the mean plane current, and n is number of points.

Dielectric measurements were carried out in the frequency range 75 kHz up to 30 MHz by using precision LCR meter (Agilent 4285A).

3. Results and Discussion

The NR/rPVC blends have mechanical properties as shown in Figure 1. The tensile strength of blend is increased with adding the rPVC for 5 phr and rapidly decreased with increasing rPVC content. rPVC might be migrated to the NR surface during hot compression molding process due to immiscible blend and formed thin film coating on NR surface during vulcanization process. The thin film might be interacts with NR surface enhanced the film properties. The micrographs in Figure 2 clearly showed that rPVC particles were formed aggregate structure and dispersed on both sides of the blend film. For high loading of rPVC, rPVC was immiscible blend with NR and exist in two distinct separated.

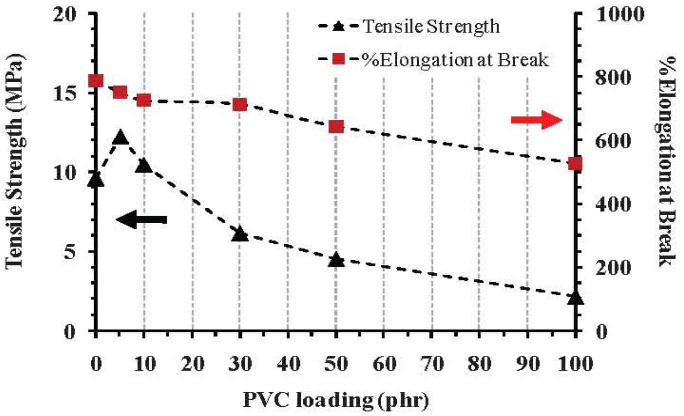


Fig. 1. Mechanical properties of NR and NR blending with rPVC at various compositions

The surface morphology of NR and NR blending with rPVC for 5 phr (NR/5rPVC) were investigated by AFM and found that the surface of NR/5rPVC is roughness covered with rPVC particle as shown in Figure 3. The blend film composed of aggregates of particles and arranged particles with sharp spherical contours. The surface roughness average (R_a) and root mean square (R_q) of NR and NR/rPVC blend films were calculated and the data are presented in Table 2.

Table 2. Surface roughness average (R_a) and root mean square (R_q) values of NR and NR/rPVC blend films on mica substrate

Film	R_a (nm)		R_q (nm)		Surface area (μm^2)
	X-axis	Y-axis	X-axis	Y-axis	
NR	24.6	10.5	31.2	12.9	25.9
NR/5rPVC blend	29.6	32.0	36.6	41.0	1609.4

From Table 2, the roughness of longitudinal rugged NR films, compose of aggregates of particles, is smaller than that of vertical axis. On one hand, the rPVC covering on NR film, rPVC, arrays of orderly arranged particles with sharp spherical contours. The roughness of the NR/rPVC blend film is slight broader than NR film.

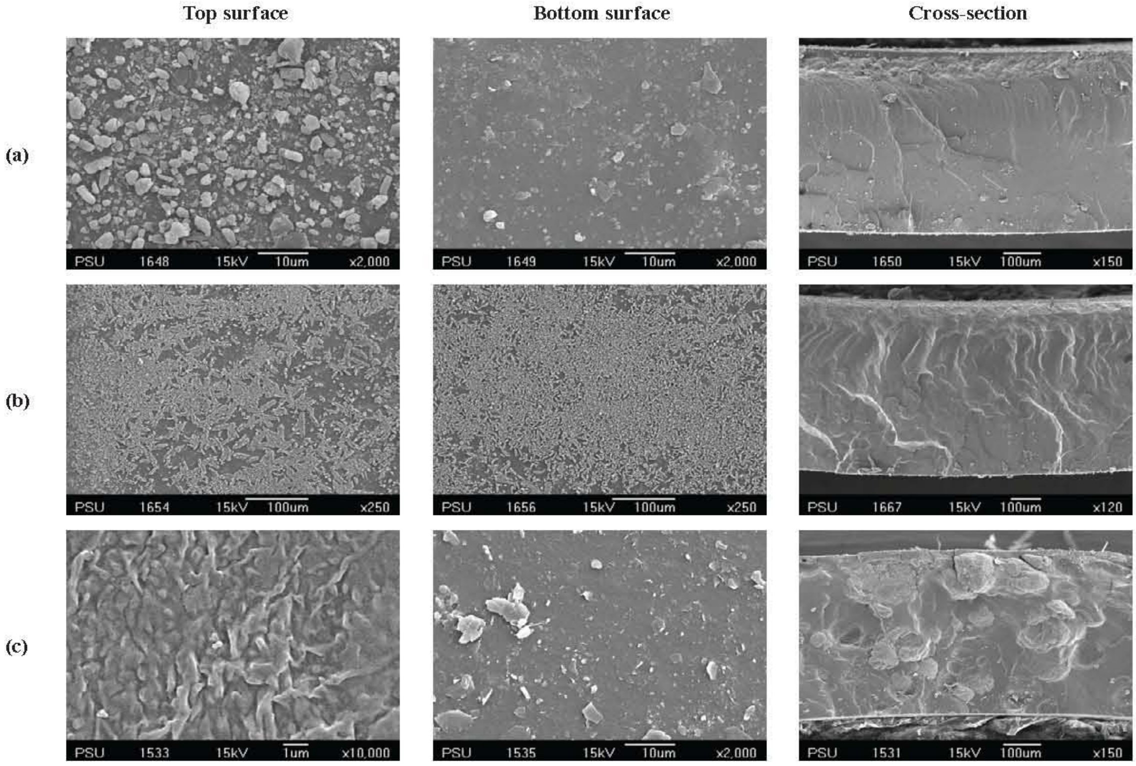
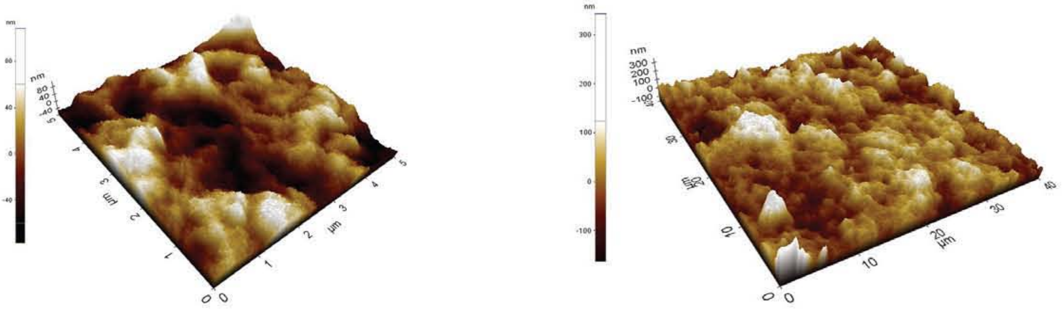


Fig. 2. Top surface, bottom surface and cross section SEM images of (a) NR film; (b) NR film coated with 5 phr rPVC; and (c) with 100 phr rPVC



(a) (b)

Fig. 3. AFM images of (a) NR and (b) NR/5rPVC blend film

The permittivity and dielectric loss of NR and NR/rPVC blend films were measured over the frequency range from 75 kHz up to 30 MHz at room temperature. The dielectric property of NR is changed with concentration of added rPVC. Dielectric constant of the blend film of NR with small amount of rPVC was increased as shown in Figure 4. The formation of rPVC thin film leads to increased capacitance of material. Blending of rPVC with NR at higher concentration for more than 50 phr which is exit in two distinct separated phase lower dielectric constant due to heterogeneous of the polymer blend. The sharp increase in dielectric loss ε" in lower frequency range of NR blending with 10 phr rPVC is attributed to the increase in contribution of both interfacial polarization and conductivity.

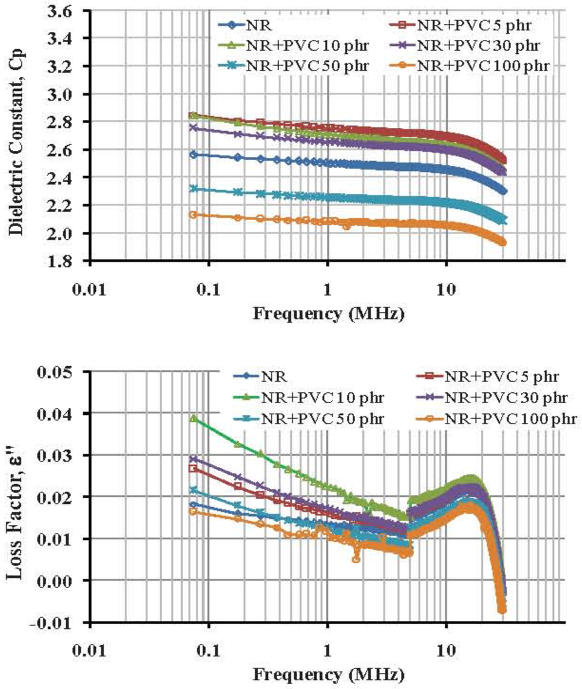


Fig. 4. Effect of rPVC concentration on the dielectric constant for the blend NR/rPVC

4. Conclusion

Natural rubber (NR) is easily blending with poly(vinyl chloride) resin (rPVC) in solid state using hot compression molding. Only small amount of rPVC migrated to the surface and form a thin film coating on NR surface which can be clarify by SEM and AFM images. Not only the physical properties of the blend film improved but also the dielectric properties. NR blending with high concentration of rPVC over 50 phr, the two phases was distinct separated with poorer physical and dielectric properties.

Acknowledgement

This work was supported by the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission.

References

[1] Elliot D.J., Tinker A.J., *Blends of natural rubber with thermoplastics*, in: Roberts, A.D. (Ed.), Natural Rubber Science and Technology, Oxford University Press, Oxford, 1990; 327-358.

[2] Margaritis A.G., Kalfoglou N.K., *Polymer* 1987; **28**(3): 497-502.

[3] da Silva M.A., Vieira M.G.A., Maçumoto A.C.G., Beppu M.M., *Polym. Testing* 2011; **30**: 478-484.

[4] Egharevba O., Okieimen F.E., Okwu U.N., Malomo D., *Mater. Sci. Appl.* 2011; **2**: 196-199.

[5] Radhakrishnan Nair, M.N., Biju P.K., Thomas G.V., Gopinathan Nair M.R., *J. Appl. Polym. Sci.* 2008; **111**(111): 48-56.

[6] Radhakrishnan Nair M.N., Thomas G.V., Nair M.R.G., *Polym. Degrad. Stability* 2006; **11**(2): 14-18.

[7] Biju P.K., Radhakrishnan Nair M.N.,Thomas, G.V., Nair M.R.G., *Mater. Sci. Poland* 2007; **25**(4): 919-932.

[8] Ishiaku U.S., Poh B.T., Mohd Ishak Z.A., Ng D., *Polym. Intl.* 1996; **39**: 67-76.

[9] Manoj N.R., De P.P., *Polymer* 1998; **39**(3): 733-741.

[10] Ho C.C., Khew M.C., *Langmuir* 2000; **16**: 2436-2449.

Paper IV

Phatcharasit, K., Taweepreda, W., Boonkerd, K. and J. K., Kim. 2013. Preparation and Properties of Electrospun PVC Nanofiber. Advanced Materials Research, 770:193-196.

Advanced Materials Research Vol. 770 (2013) pp 193-196
© (2013) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/AMR.770.193

PREPARATION AND PROPERTIES OF ELECTROSPUN PVC NANOFIBER

Kritsada Phatcharasit[1], Wirach Taweepreda[1,2]*, Kanoktip Boonkerd[3], and Jin-Kuk Kim[4]

[1]Membrane Science and Technology Research Center, Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90110, THAILAND
[2]Centre of Excellence in Nanotechnology for Energy (CENE), Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90110, THAILAND
[3]Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10300, Thailand
[4]School of Nano and Advanced Materials Engineering, Gyeongsang National University, Gyeongnam, Jinju 660-701, South Korea
wirach.t@psu.ac.th

Keywords: Electrospinning; PVC; Nanofibrous; Membrane

Abstract. Nanofibrous membranes based on poly(vinyl chloride) (PVC) were prepared by electrospinning. The morphology of nanofibrous was observed under field emission scanning electron microscope (FE-SEM) and effects of instrument parameters including electric voltage, tip to collector distance, and solution parameters such as PVC concentration and mixed solvent of THF and DMF (50:50) were evaluated. The beads on the fiber were formed with low concentration of PVC. The dielectric constant, thermal properties and crystallinity of the electrospun membranes were characterized by precision LCR meter, and differential thermal analysis (DTA), respectively. It was found that smooth surface of electrospun PVC nanofiber had a high ionic conductivity and their thermal properties were improved comparing with PVC sheet.

Introduction

Poly (vinyl chloride) (PVC) is an important commercial thermoplastic. PVC is hard and stiff material which can be immensely modified with plasticizer for flexibility [1]. Important disadvantage in the manufacture and use of PVC is its low thermal stability. At high temperatures well below its decomposition temperature, PVC loses hydrogen chloride and becomes mottled. Because of these changes are accompanied by deterioration on some of the useful properties of the polymer [2]. Ultrafine PVC fibers cannot be produced by ordinary spinning techniques. Through the processes, such as melt spinning, dry spinning and wet spinning, fibers with diameters ranging from 5 μm to 50 μm are usually obtained. Electrospinning is the process in which a polymer solution is ejected from a syringe that has a directly attached to a high power supply [3]. This power source generates a high voltage difference, usually selected between 5–30 kV, which support the ejection of a liquid jet followed by solvent evaporation and the formation of a dry polymer fiber, which deposits on a grounded cathode-connected metallic collector. Under the appropriate conditions, a single jet may undergo solution instability and splay or split, resulting in smaller diameter fibers. Therefore, by controlling the electrospinning parameters, optimal nanofibers can be prepared.

In this research, the effects of electrospinning condition including electric voltage, tip-to-collector distance and polymer solution concentration were studied on the morphological and physical properties of PVC nanofibrous.

Experimental Procedure

Poly(vinyl chloride) (PVC) was kindly supplied by Thai Plastic and Chemicals Co., Ltd. The solvent *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were used as received. PVC was dissolved in a mixed solvent of DMF/THF (at weight ratio 5:5) by varying the PVC concentration for

10% and 15% by weight at 50°C. The nanofibrous membranes were prepared by eS-robot electrospinning capable of generating voltages up to 30 kV at room temperature. Electrospinning was performed at a flow rate 0.5 mL/h with applied voltage between 12 and 15 kV. The distance between the syringe tip and collector plate was varied from 12 to 18 cm. A nanofibrous was then deposited on the collector plate and formed thin film with thickness around 0.1 mm.

Characterization

The membrane was carbon sputtered using a Joel JFC-1100 fine coater before studied the surface morphology using a Philips XL30 field emission scanning electron microscope (FESEM, Japan). The thermal properties of membranes were performed using differential thermal analysis (DTA) (TA Instruments Q200, USA) under nitrogen gas with a flow rate of 50 ml/min. The samples were put in alumina pans and were heated from -90 °C to 350 °C with heating rate of 20 °C/min. Dielectric measurements were carried out in the frequency range 75 kHz up to 30 MHz by using Precision LCR meter (Agilent 4285A).

Results and Discussion

Scanning Electron Microscopy. The picture of PVC nanofibrous obtained from SEM shows the morphological variation depends on PVC concentration and electrospinning conditions as illustrated in Fig. 1. The surface instabilities induced by electrospun jet motion and charge interaction. At PVC low concentration led to the formation of beads on the fiber to disruption the jet into beads. In this studied, PVC nanofibrous were prepared from PVC solution at 15% by weight with applied voltage 12 kV and distance between the syringe tip and collector plate is 15 cm.

Thermal properties. Fig. 2 shows the thermal properties of the PVC nanofibrous membrane. The membrane prepared from PVC dissolved in THF is harder than that from DMF and mixed solvents. THF was evaporated very fast led to high crystalline membrane indicated with high exothermal peak at -30 °C. On the other hand, DMF was evaporated too decreasing of melting temperature of the membrane. The mixed solvents between THF and DMF enhanced the membrane properties.

Dielectric properties. The permittivity and dielectric loss of PVC nanofibrous membrane were measured over the frequency range from 75 kHz up to 30 MHz at room temperature. Dielectric constant of the membrane prepared from PVC dissolved in DMF pure solvent enhanced the dielectric properties due to its charge compared to THF. PVC dissolved in mixed solvent between DMF and THF found that the dielectric properties decreased depend on the amont of added THF as illustrated in Fig. 3.

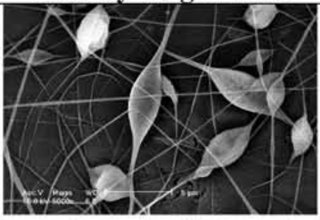
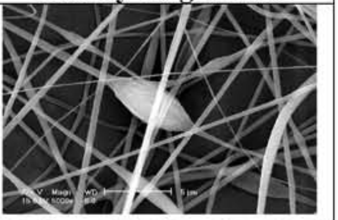
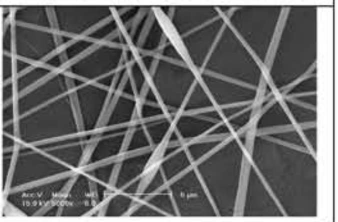
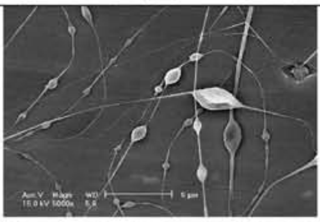
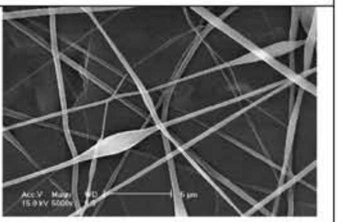
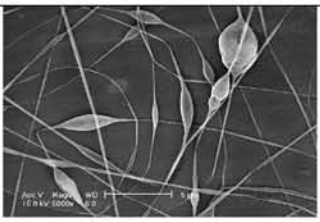
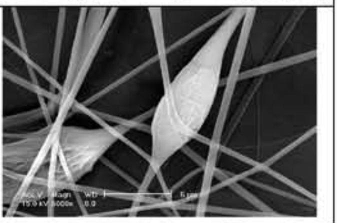
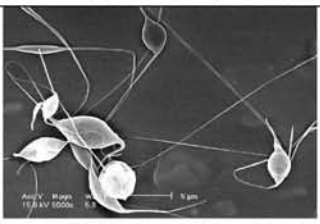
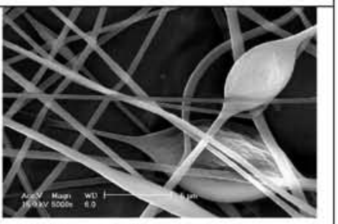
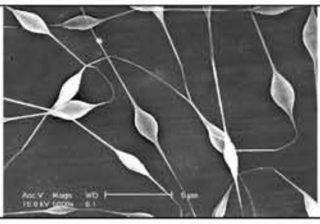
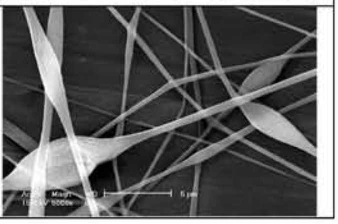
Electrospinning Conditions	10% by weight PVC	15% by weight PVC
Voltage: 12 kV Tip to collector: 12 cm.		
Voltage: 12 kV Tip to collector: 15 cm.		
Voltage: 12 kV Tip to collector: 18 cm.		
Voltage: 15 kV Tip to collector: 12 cm.		
Voltage: 15 kV Tip to collector: 15 cm.		
Voltage: 15 kV Tip to collector: 18 cm.		

Fig. 1 SEM images of PVC nanofibers.

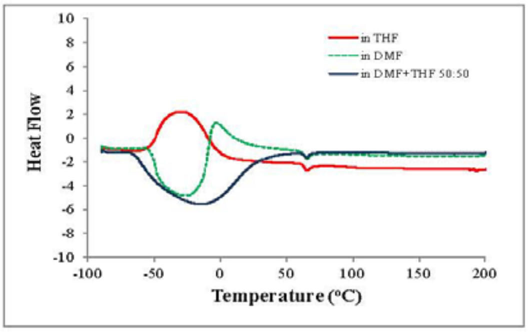


Fig. 2 DTA thermogram of PVC nanofibrous in difference solvent.

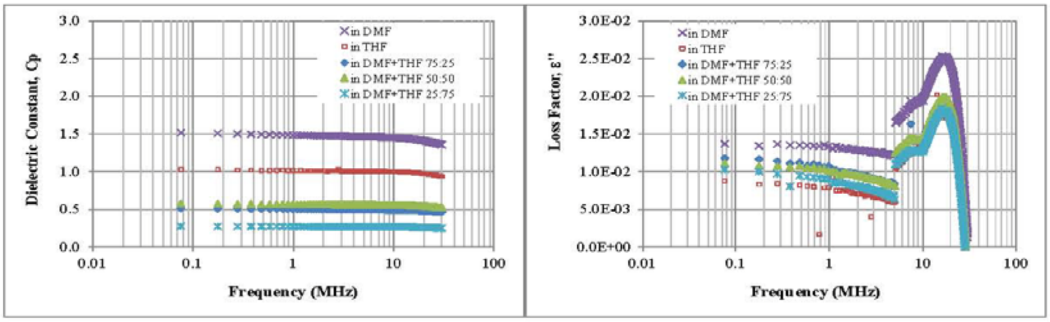


Fig. 3 Dielectric properties of PVC nanofibrous in difference solvent.

Conclusions

The PVC nanofibrous membrane can be prepared from electrospinning method by choosing high concentration of PVC in mixed solvent between DMF and THF. The eletrospinning conditions with applied voltage 12 kV and distance between the syringe tip and collector plate is 15 cm gave smooth surface PVC nanofibrous and desired properties.

Acknowledgements

This work was supported by the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission. KP would like to thank Prince of Songkla University for supporting PhD. Scholarship under National Research University Program.

References

[1] M.A. *da* Silva, M.G.A. Vieira, A.C.G. Maçumoto, M.M. Beppu, Polym. Testing 30(2011) 478-484.

[2] H. Bockhorn, A. Hornung, U. Hornung, J. Anal. Appl. Pyrolysis 50(1999) 77-101.

[3] Z. Zhong, Q. Cao, B. Jing, X. Wang, X. Li, H. Deng, Mat. Sci. Eng. B 177(2012) 86-91.

Paper V

Phatcharasit, K., Taweepreda, W., Boonkerd, K. and J. K., Kim. 2014. Electrospun Epoxidized Natural Rubber with Poly(vinyl chloride)(ENR-PVC) nanofibrous for PEMFC Applications. Advanced Materials Research, 844:507-510..

Advanced Materials Research Vol. 844 (2014) pp 507-510
Online available since 2013/Nov/15 at www.scientific.net
© (2014) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/AMR.844.507

Electrospun Epoxidized Natural Rubber with Poly(vinyl chloride) (ENR-PVC) nanofibrous for PEMFC Applications

Kritsada Phatcharasit[1], Wirach Taweepreda[1]*, Kanoktip Boonkerd[2], and Jin-Kuk Kim[3]

[1]Membrane Science and Technology Research Center, Department of Materials Science and Technology, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90110, THAILAND
[2]Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok 10300, Thailand
[3]School of Nano and Advanced Materials Engineering, Gyeongsang National University, Gyeongnam, Jinju 660-701, South Korea

wirach.t@psu.ac.th

Keywords: Electrospinning; PVC; ENR; Membrane; Dielectric Properties

Abstract. Various electrospun epoxized natural rubber / poly(vinyl chloride) (ENR/PVC) blend nonwoven membranes were prepared by electrospinning technique. Various concentration of epoxidized natural rubber (ENR) solution in N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) were directly added to PVC solution for plasticization of the electrospun nanofibrous. Differencial thermal analysis (DTA), thermogravimetry analysis (TGA) and scanning electron microscopy (SEM) were used to characterize the pristine and plasticized nanofibrous. DTA results indicated that the addition of ENR resulted in the shifting of glass transition temperature (Tg) towards lower temperatures. The blending of PVC with ENR is thermodynamically incompatible.

Introduction

Epoxidized natural rubber (ENR) has good properties with low glass transition temperature, Tg, soft elastomer characteristics at room temperature and good elasticity. Blending ENR with another polymer, such as poly(vinyl chloride) (PVC) which is an important commercial polymer, for improve some properties of blends as well as good thermal stability is currently one of important topics. PVC is hard, stiff material, although, mechanical properties, notably the flexibility, can be extensively modified with plasticization. [1] A number of publications [1-4] deal with incorporation of ENR with PVC. It also gives excellent contact between an electrolytic layer and an electrode in batteries [5]. For fuel cell such as proton exchange membrane fuel cell have advantage as a viable option due to their high energy efficiency and environmental friendly [2]. Polymer electrolyte membrane is interesting of researchers because it is a new source of electrical power generation and energy storage systems, such as displays, sensors, electric windows, super capacitors and rechargeable batteries. Unlike conventional fiber spinning techniques (wet spinning, dry spinning, melt spinning, gel spinning), which are capable of producing polymer fibers with diameters down to the micrometer range, electrostatic spinning, or electrospinning is a process capable of producing polymer fibers in the nanometer diameter range. [3] Electrospinning is the process in which a polymer solution is ejection from a syringe that has a directly attached to a high power supply. This power source generates a high voltage difference, usually selected between 5–30 kV, which support the ejection of a liquid jet followed by solvent evaporation and the formation of a dry polymer fiber, which deposits on a grounded cathode-connected metallic collector. Under the appropriate conditions, a single jet may undergo solution instability and splay or split, resulting in smaller diameter fibers. Therefore, by controlling the electrospinning parameters, optimal nanofibers can be prepared.

In this research, the effects of electrospinning condition including electric voltage, tip-to-collector distance and polymer solution concentration were studied on the morphological and physical properties of ENR/PVC nanofibrous.

Experimental Procedure

Polyvinyl chloride (PVC) with *K*-value of 580 was kindly supplied by Thai Plastic and Chemicals Co., Ltd. The solvent *N, N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were used as received. PVC was dissolved in a mixed solvent of DMF/THF (at weight ratio 5:5) by varying the PVC concentration for 10% and 15% by weight at 50°C. ENR was dissolved in the same solvent mixtures as PVC solution. The ENR solution was directly mixed with PVC solution at room temperature. The nanofibrous membranes were prepared by eS-robot electrospinning capable of generating voltages up to 30 kV at room temperature. Electrospinning was performed at a flow rate 0.5 mL/h with applied voltage between 12 and 15 kV. The distance between the syringe tip and collector plate was varied from 12 to 18 cm. The nanofibrous was then deposited on the collector plate and formed thin film with thickness around 0.1 mm.

Characterization

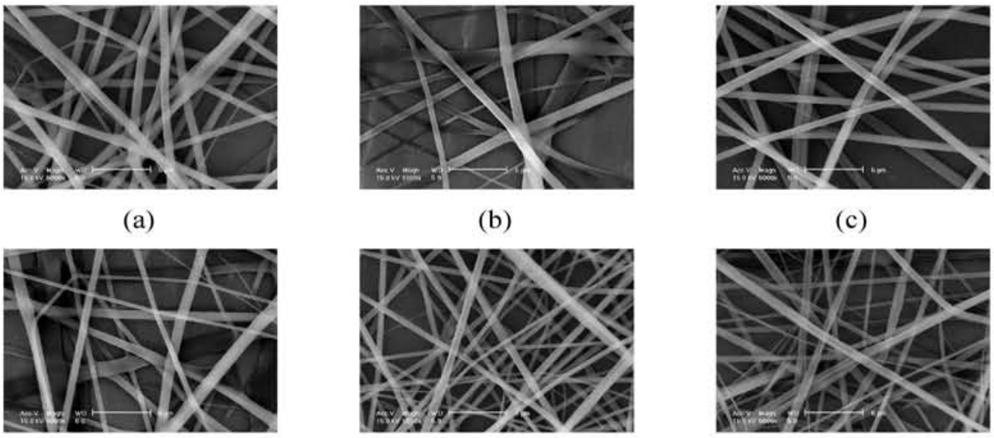
The membrane was carbon sputtered using a Joel JFC-1100 fine coater before studied the surface morphology using a Philips XL30 field emission scanning electron microscope (FESEM, Japan). The thermal properties of membranes were performed using differential thermal analysis (DTA) (TA Instruments Q200, USA) under nitrogen gas with a flow rate of 50 ml/min. The samples were put in alumina pans and were heated from -90 °C to 350 °C with heating rate of 20 °C/min. and thermal stability was studied by using a thermogravimetric analyzer (TGA) (TA Instruments Q600, USA) under nitrogen atmosphere at a heating rate of 20 °C/min. Dielectric measurements were carried out in the frequency range 75 kHz up to 30 MHz by using Precision LCR meter (Agilent 4285A).

Results and Discussion

Scanning Electron Microscopy. The morphological structure of ENR/PVC nanofibrous was changed by changing the ENR concentration. ENR blending with PVC, it clearly shows the beads on the fiber be disappear, which ENR composition can be attributed to higher viscosity and surface tension with increasing ENR composition. Viscosity and surface tension play an important role in determining the fiber formability and diameter. The morphological structure of ENR/PVC nanofibrous as shown in Figure 1

Thermal properties. The thermal properties of the PVC nanofibrous and PVC plasticized with ENR nanofibers. The PVC nanofiber prepared from 10% by weight is rigid than that from 15% by weight which correspond with DTA thermogram. The 10% PVC has high exothermal peak at 30 °C and 275 °C while the 15% PVC shows endothermal peak. The thermal properties of nanofibers were improved after mixing PVC with ENR. The mixture of PVC with high ENR content gave more flexible nanofiber with lower glass transition temperture (Tg). For higher concentration of PVC (15% PVC) is high viscous and was not easily to mixed with ENR solution results in difference DTA thermogram. The nanofiber spun from high concentration of PVC mixed with ENR which was heterogeneous solution need to optimized the electrospinning condition. The TG curve of the PVC membrane has two obvious decompositions, which is basically according with the reported TG curve. The thermal properties of the 15% PVC with ENR nano fibers are shown in Figure 2.

Dielectric properties. Figure 3. shows the permittivity of PVC nanofibrous was measured over the frequency range from 75 kHz up to 30 MHz at room temperature. Dielectric constant of the membrane prepared from 10% PVC mixed with high ENR content reduced the dielectric constant due to dense of ENR phase. The dielectric properties of 15% PVC mixed with ENR were not changed with ENR contents due to the prepared nanofibrous membrane were dense.



(a) (b) (c)

(d) (e) (f)

Figure 1 SEM images of electrospun nanofiber from ENR blending with PVC for (a) 67, (b) 100, (c) 156, (d) 233, (e) 600, and (f) 900 phr.

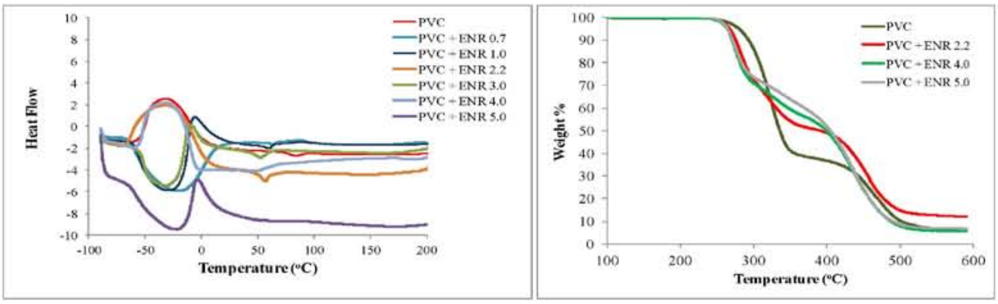
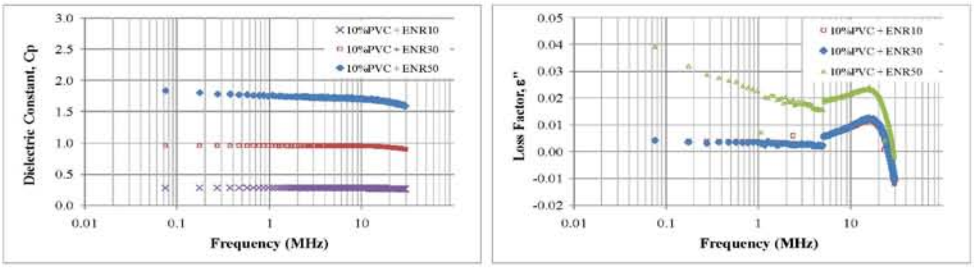


Figure 2 DTA and TG thermogram of ENR/PVC nanofibrous in difference ratio.



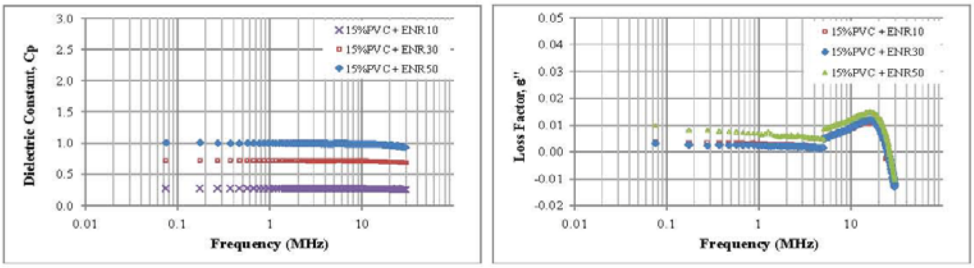


Figure 3 Dielectric properties of ENR/PVC nanofibrous

Conclusions

The ENR/PVC nanofibrous membrane can be prepared from electrospinning method. The eletrospinning condition with applied voltage 12 kV and distance between the syringe tip and collector plate is 15 cm gave smooth surface ENR/PVC nanofibrous and desired properties. ENR blending with PVC, it clearly shows the beads on the fiber be disappear, which ENR composition can be attributed to higher viscosity and surface tension with increasing ENR composition. Viscosity and surface tension play an important role in determining the fiber formability and diameter and the thermal properties of the ENR/PVC nanofibrous results indicate that the ENR/PVC membrane has a good thermal stability.

Acknowledgements

This work was supported by the Higher Education Research Promotion and National Research University Project of Thailand, Office of the Higher Education Commission. KP would like to thank Prince of Songkla University for supporting PhD. Scholarship under National Research University Program.

References

[1] Lee, K.H.; Kim, H.Y.; Ryu, Y.J.; Kim, K.W.; Choi, S.W., J. Polym. Sci. B: Polym. Phys. 2003; 41: 1256-1262.
[2] Pedicini, A.; Farris J.R., J. Polym. 2003; 44: 6857–6862.
[3] Frenot, A.; Chronakis, I.S., Current Opinion in Colloid and Interface Science 8. 2003: 64–75.
[4] Zhang, Y.; Xia, Z.; Huang, H.; Chen, H., J. Anal. Appl. Pyrolysis. 2009; 84: 89–94.
[5] Zhong, Z.; Cao, Q.; Jing, B.; Wang, X.; Li, X.; Deng, H., *Mat. Sci. Eng. B* 2012, **177**:86-91.

Patent

กระบวนการผลิตนาโนไฟเบอร์จากสารละลายยางธรรมชาติอิพ๊อกไซด์ ด้วยเทคนิคอิเล็กโทรสปินนิ่ง

แบบสป/สผ/อสป/001-ก

หน้า 1 ของจำนวน 2 หน้า

คำขอรับสิทธิบัตร/อนุสิทธิบัตร

☐ การประดิษฐ์

☐ การออกแบบผลิตภัณฑ์

☑ อนุสิทธิบัตร

ยื่นทางไปรษณีย์

ข้าพเจ้าผู้ลงลายมือชื่อในคำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้ ขอรับสิทธิบัตร/อนุสิทธิบัตร ตามพระราชบัญญัติสิทธิบัตร พ.ศ.2522 แก้ไขเพิ่มเติมโดยพระราชบัญญัติสิทธิบัตร (ฉบับที่ 2) พ.ศ.2535 และพระราชบัญญัติสิทธิบัตร (ฉบับที่ 3) พ.ศ.2542

สำหรับเจ้าหน้าที่

วันรับคำขอ 16 ก.พ. 2557	เลขที่คำขอ
วันยื่นคำขอ ๒๗ มค ๕๗	1403000141
สัญลักษณ์จำแนกการประดิษฐ์ระหว่างประเทศ	
ใช้กับแบบผลิตภัณฑ์ ประเภทผลิตภัณฑ์	
วันประกาศโฆษณา	เลขที่ประกาศโฆษณา
วันออกสิทธิบัตร/อนุสิทธิบัตร	เลขที่สิทธิบัตร/อนุสิทธิบัตร
ลายมือชื่อเจ้าหน้าที่	

1. ชื่อที่แสดงถึงการประดิษฐ์/การออกแบบผลิตภัณฑ์

กระบวนการผลิตนาโนไฟเบอร์จากสารละลายยางธรรมชาติอิพ็อกไซด์ด้วยเทคนิคอิเล็กโทรสปินนิ่ง

2. คำขอรับสิทธิบัตรการออกแบบผลิตภัณฑ์นี้เป็นคำขอสำหรับแบบผลิตภัณฑ์อย่างเดียวกันและเป็นคำขอลำดับที่ ในจำนวน คำขอ ที่ยื่นในคราวเดียวกัน

3. ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร และที่อยู่ (เลขที่ ถนน ประเทศ)

มหาวิทยาลัยสงขลานครินทร์ 15 ถนนกาญจนวณิชย์ อำเภอหาดใหญ่ จังหวัดสงขลา 90110

3.1 สัญชาติ ไทย

3.2 โทรศัพท์ 0-7428-9322

3.3 โทรสาร 0-7428-9339

3.4 อีเมล์ jittiyut.y@psu.ac.th

4. สิทธิในการขอรับสิทธิบัตร/อนุสิทธิบัตร

☐ ผู้ประดิษฐ์/ผู้ออกแบบ ☑ ผู้รับโอน ☐ ผู้ขอรับสิทธิโดยเหตุอื่น

5. ตัวแทน (ถ้ามี) ที่อยู่ (เลขที่ ถนน จังหวัด ประเทศ รหัสไปรษณีย์)

นายจิตติยุทธ เยี่ยมยกกุล ศูนย์ทรัพย์สินทางปัญญา อุทยานวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์ 15 ถนนกาญจนวณิชย์ อำเภอหาดใหญ่ จังหวัดสงขลา 90110

5.1 ตัวแทนเลขที่ 2266

5.2 โทรศัพท์ 074-289322

5.3 โทรสาร 074-289339

5.4 อีเมล์ jittiyut.y@psu.ac.th

6. ผู้ประดิษฐ์/ผู้ออกแบบผลิตภัณฑ์ และที่อยู่ (เลขที่ ถนน ประเทศ)

1. ผศ. ดร. วิรัช ทวีปรีดา และ 2. นายกฤษฎา พัชรสิทธิ์

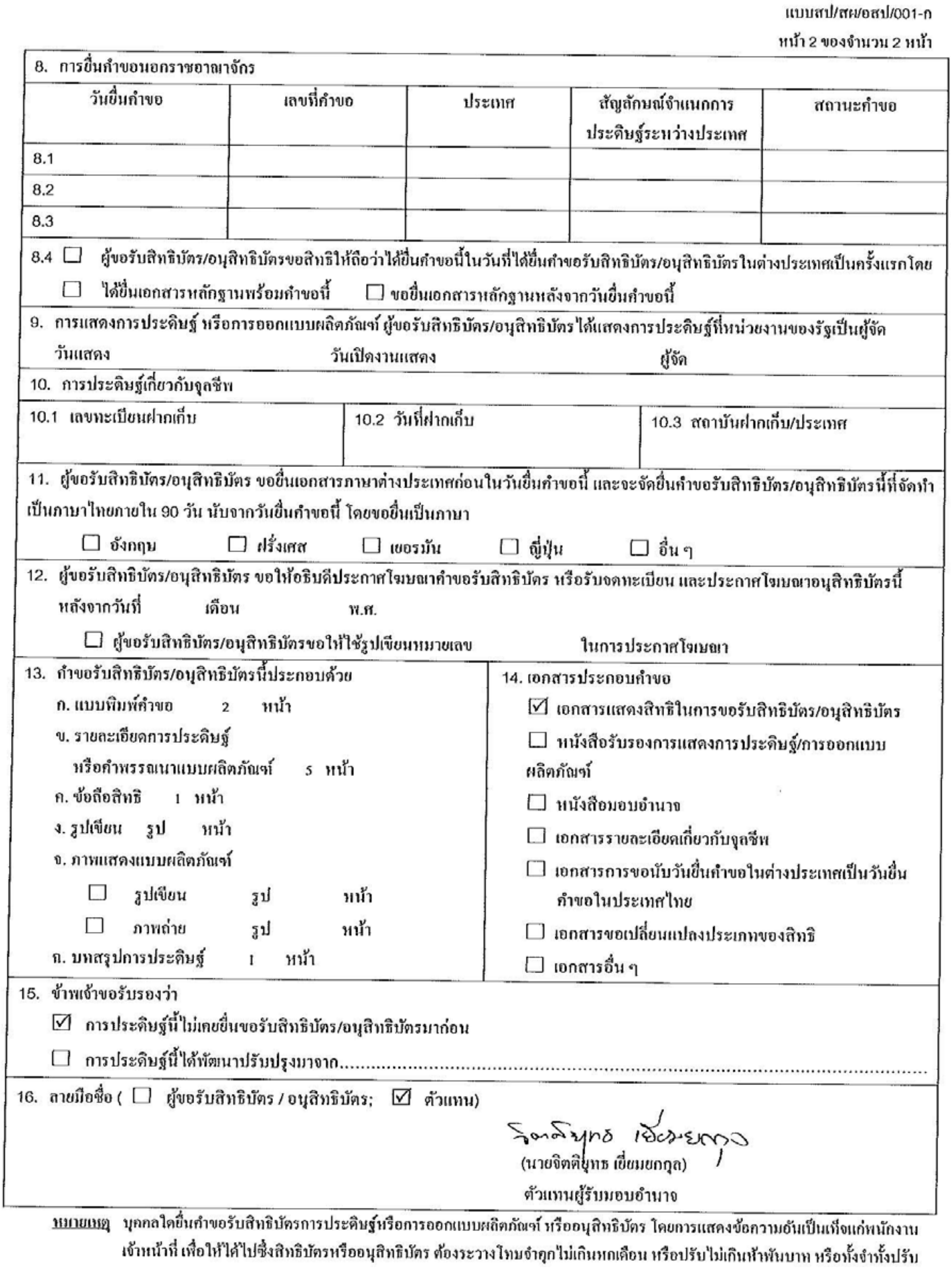
คณะวิทยาศาสตร์ มหาวิทยาลัยสงขลานครินทร์ อ.หาดใหญ่ จ. สงขลา 90110

7. คำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้แยกจากหรือเกี่ยวข้องกับคำขอเดิม

ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตรขอให้ถือว่าได้ยื่นคำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้ในวันเดียวกับคำขอรับสิทธิบัตรเลขที่ วันยื่น เพราะคำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้แยกจากหรือเกี่ยวข้องกับคำขอเดิมเพราะ

☐ คำขอเดิมมีการประดิษฐ์หลายอย่าง ☐ ถูกคัดค้านเนื่องจากผู้ขอไม่มีสิทธิ ☐ ขอเปลี่ยนแปลงประเภทของสิทธิ

__หมายเหตุ__ ในกรณีที่ไม่อาจระบุรายละเอียดได้ครบถ้วน ให้จัดทำเป็นเอกสารแนบท้ายแบบพิมพ์นี้ โดยระบุหมายเลขกำกับข้อและหัวข้อที่แสดงรายละเอียดเพิ่มเติมดังกล่าวด้วย



แบบสป/สผ/อสป/001-ก

หน้า 2 ของจำนวน 2 หน้า

8. การยื่นคำขอนอกราชอาณาจักร

วันยื่นคำขอ	เลขที่คำขอ	ประเทศ	สัญลักษณ์จำแนกการประดิษฐ์ระหว่างประเทศ	สถานะคำขอ
8.1				
8.2				
8.3				

8.4 ☐ ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตรขอสิทธิให้ถือว่าได้ยื่นคำขอนี้ในวันที่ได้ยื่นคำขอรับสิทธิบัตร/อนุสิทธิบัตรในต่างประเทศเป็นครั้งแรกโดย

☐ ได้ยื่นเอกสารหลักฐานพร้อมคำขอนี้ ☐ ขอยื่นเอกสารหลักฐานหลังจากวันยื่นคำขอนี้

9. การแสดงการประดิษฐ์ หรือการออกแบบผลิตภัณฑ์ ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตรได้แสดงการประดิษฐ์ที่หน่วยงานของรัฐเป็นผู้จัด

วันแสดง วันเปิดงานแสดง ผู้จัด

10. การประดิษฐ์เกี่ยวกับจุลชีพ

10.1 เลขทะเบียนฝากเก็บ	10.2 วันที่ฝากเก็บ	10.3 สถาบันฝากเก็บ/ประเทศ

11. ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร ขอยื่นเอกสารภาษาต่างประเทศก่อนในวันยื่นคำขอนี้ และจะจัดยื่นคำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้ที่จัดทำเป็นภาษาไทยภายใน 90 วัน นับจากวันยื่นคำขอนี้ โดยขอยื่นเป็นภาษา

☐ อังกฤษ ☐ ฝรั่งเศส ☐ เยอรมัน ☐ ญี่ปุ่น ☐ อื่น ๆ

12. ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตร ขอให้อธิบดีประกาศโฆษณาคำขอรับสิทธิบัตร หรือรับจดทะเบียน และประกาศโฆษณาอนุสิทธิบัตรนี้

หลังจากวันที่ เดือน พ.ศ.

☐ ผู้ขอรับสิทธิบัตร/อนุสิทธิบัตรขอให้ใช้รูปเขียนหมายเลข ในการประกาศโฆษณา

13. คำขอรับสิทธิบัตร/อนุสิทธิบัตรนี้ประกอบด้วย

ก. แบบพิมพ์คำขอ 2 หน้า

ข. รายละเอียดการประดิษฐ์ หรือคำพรรณนาแบบผลิตภัณฑ์ 5 หน้า

ค. ข้อถือสิทธิ 1 หน้า

ง. รูปเขียน รูป หน้า

จ. ภาพแสดงแบบผลิตภัณฑ์

☐ รูปเขียน รูป หน้า

☐ ภาพถ่าย รูป หน้า

ฉ. บทสรุปการประดิษฐ์ 1 หน้า

14. เอกสารประกอบคำขอ

☑ เอกสารแสดงสิทธิในการขอรับสิทธิบัตร/อนุสิทธิบัตร

☐ หนังสือรับรองการแสดงการประดิษฐ์/การออกแบบผลิตภัณฑ์

☐ หนังสือมอบอำนาจ

☐ เอกสารรายละเอียดเกี่ยวกับจุลชีพ

☐ เอกสารการขอนับวันยื่นคำขอในต่างประเทศเป็นวันยื่นคำขอในประเทศไทย

☐ เอกสารขอเปลี่ยนแปลงประเภทของสิทธิ

☐ เอกสารอื่น ๆ

15. ข้าพเจ้าขอรับรองว่า

☑ การประดิษฐ์นี้ไม่เคยยื่นขอรับสิทธิบัตร/อนุสิทธิบัตรมาก่อน

☐ การประดิษฐ์นี้ได้พัฒนาปรับปรุงมาจาก..

16. ลายมือชื่อ (☐ ผู้ขอรับสิทธิบัตร / อนุสิทธิบัตร; ☑ ตัวแทน)

(นายจิตติยุทธ เยี่ยมยกกุล)

ตัวแทนผู้รับมอบอำนาจ

__หมายเหตุ__ บุคคลใดยื่นคำขอรับสิทธิบัตรการประดิษฐ์หรือการออกแบบผลิตภัณฑ์ หรืออนุสิทธิบัตร โดยการแสดงข้อความอันเป็นเท็จแก่พนักงานเจ้าหน้าที่ เพื่อให้ได้ไปซึ่งสิทธิบัตรหรืออนุสิทธิบัตร ต้องระวางโทษจำคุกไม่เกินหกเดือน หรือปรับไม่เกินห้าพันบาท หรือทั้งจำทั้งปรับ

VITAE

Name Mr. Kritsada Phatcharasit

Student ID 5510230022

Educational Attainment

Degree	Name of Institution	Year of Graduation
Bachelor of Science B.Sc. (Polymer science)	Prince of Songkla University	2008
Master of Science M.Sc. (Polymer science and Technology)	Prince of Songkla University	2010

Scholarship Awards during Enrolment

Research Assistance, Faculty of Science, Prince of Songkla University

Graduate School Prince of Songkla University Scholarships

National Research University Project of Thailand, Prince of Songkla University (November, 2010 - October, 2013)

List of Publication and Proceedings Publication:

Publication:

Phatcharasit, K., Taweepreda, W., Boonkerd, K. and J. K., Kim. 2014. Electrospun Epoxidized Natural Rubber with Poly(vinyl chloride)(ENR-PVC) nanofibrous for PEMFC Applications. Advanced Materials Research, 844: 507-510.

Phatcharasit, K., Taweepreda, W., Boonkerd, K. and J. K., Kim. 2013. Preparation and Properties of Electrospun PVC Nanofiber. Advanced Materials Research, 770: 193-196.

Phatcharasit, K. and Taweepreda, W. 2012. In Situ Coating of Natural Rubber Film with Poly(vinyl chloride) Resin. Procedia Chemistry, 4: 232-237.

Phatcharasit, K., Taweepreda, W. and Saesia, W. 2012. TPNR Membrane Reinforcing with Cotton Fibre Spun. Journal of Chemistry and Chemical Engineering, 6: 799-802.

Phatcharasit, K. and Taweepreda, W. 2012. Self-assembled nanometric spacer on surface of natural rubber composited with TiO_2. World Journal of Engineering 9(4): 349-354

Phatcharasit, K. and Taweepreda, W. 2011. Polyethylene Thin Film Coating Preventing the Degradation of Natural Rubber. Engineering Journal, 16(3): 53-58.

Proceedings:

Phatcharasit, K.; Taweepreda, W.; Boonkerd K. and Kim J. K. 2013. Electrospun Epoxidized Natural Rubber with Poly(vinyl chloride) (ENR-PVC) nanofibrous for PEMFC Applications, The Asia Pacific Rubber Conference (APRC2013), 5th-6th September, Prince of Songkla University, Surat Thani Campus, Thailand.

Phatcharasit, K; Taweepreda, W.; Boonkerd K. and Kim J. K. 2013. Thermal Properties of Electrospun Poly(vinyl chloride) Nanofibrous Plasticized with Polyurethane, Polychar 21: World Forum on Advanced Materials, 11st-15th March, Gwangju, Republic of Korea.

Phatcharasit, K; Taweepreda, W.; Boonkerd K. and Kim J. K. 2013. Preparation and Properties of Electrospun PVC Nanofiber, International Conference on Applied Physics and Material Applications (ICAPMA 2013), 20th-22th February, Golden Beach Cha-Am, Cha-Am, Thailand.

Taweepreda, W.; **Phatcharasit, K**. 2012. Gas permeation in crosslinked natural rubber-molecular sieve mixed matrix membranes, International Rubber Conference (IRC2012), 21st-24th May, Jeju, Korea.

Phatcharasit, K; Taweepreda, W. 2012. TPNR Membrane Reinforcing with Cotton Fibre Spun, Asian International Conference on Materials, Minerals, and Polymer (MAMIP2012), 23rd-24th March, Penang, Malaysia.

Taweepreda, W.; **Phatcharasit, K**. 2012. Film Formation of Nanocomposited Natural Rubber Latex with TiO_2 by Sol-Gel Method, Nanomaterials Technology Specialized Conference 2012, 6th-7th March, Johor Bahru, Malaysia.

Taweepreda, W.; **Phatcharasit, K**. 2012. PVC Film Coating Natural Rubber Surface Investigated Using XANES Spectroscopy, 6th Asia-Oceania Forum for Synchrotron Radiation Research (AOFSRR2012), 8th-12th August, Bangkok, Thailand.

Taweepreda, W.; **Phatcharasit, K**. 2011. In Situ Coating of Natural Rubber Film with Poly(vinyl chloride) Resin, Innovation in Polymer Science and Technology 2011 (IPST2011), 28th November-1st December, Bali, Indonesia.

Phatcharasit, K; Taweepreda, W. 2011. Self-Assembled Nanometric Spacer on Surface of Natural Rubber Composited with TiO_2, 19th Annual International Conference on Composites or Nano Engineering (ICCE-19), 24th-30th July, Shanghai, China.

Phatcharasit, K; Taweepreda, W. 2011. Polyethylene Thin Film Coating Preventing the Degradation of Natural Rubber, German-Thai Symposium on Nanoscience and Nanotechnology (GTSNN2011), 13th-16th September, Nakhon Ratchasima, Thailand.

Taweepreda, W.; **Phatcharasit, K**; Srikong, L. 2010. Nanostructure and Properties of Cross-linked Natural Rubber Latex Composited with TiO_2, NanoThailand 2010 “Nanotechnology for a Sustainable World”, 18th-20th November, Pathumthani, Thailand.

Taweepreda, W.; **Phatcharasit, K**. 2010. Membrane for Gas Separation from Micro Composites of Natural Rubber with TiO_2, Siam Physics Congress 2010: Physics for Creative Society, 25th-27th March, Kanchanaburi, Thailand.

Training experiences:

Scholarship under The Commission on Higher Education Research Promotion and National Research University Project of Thailand for The Joint PhD. Program to conduct the research on “Preparation of Electrospun Epoxidized Natural Rubber with Thermoplastic” at Department of Polymer Science and Engineering Gyeongsang National University, South Korea. (July 5-September 4, 2012)

The short term training course of “Seagate and Synchrotron Light Research Institute (SLRI) debut The 6th Siam Photon Science Camp” on October 19-23, 2009. Synchrotron Light Research Institute (Public Organization), Nakorn Ratchasima, Thailand.

The term training course “The Program of Industrial Production Process Improvement with Cleaner Technology” on February 14-March 24, 2007. Prince of Songkla University and National Science and Technology Development Agency, Thailand.