THE EFFECT OF AMINO FUNCTIONAL STARCH ON THE MECHANICAL AND DEGRADATION PROPERTIES OF CARBOXYLATED NITRILE BUTADIENE RUBBER LATEX FILMS

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by

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In the name of Allah, the most gracious and the most merciful,

"Corruption has appeared on land and sea because of what the ***Hands*** *of men have earned****,*** *that He (Allah) may make them* ***Taste*** *a part of that which they have done, in order that they may* ***Return****" – Ar-Rum (30 : 41).*

Based on the revelation from the holy Quran, we know that, all the corruption on earth is manmade. This is true when it comes into pollution and solid waste disposal. According to the World Bank data, if immediate actions are not taken, by the year 2025, 2.2 billion metric tons of solid waste are expected to be generated by the world's major city. 10 % from this accumulation is contributed by plastics and rubber products; of which being dominated by the latex based products. As a result, global environmental instability occurred as a "**Taste**" for what we has done. To cater the problem, Allah S.W.T had specifically given an instruction in the quoted holy verse. The word "**Return**" hold the key to solve the problem and significantly led the journey to finish this research.

By referring to the Oxford dictionary, the word "Return" means; "go back to" or in the extended definition is; "go back to (a specific place or state or origin)". As this revelation was applied in the context of solving the solid waste (specifically latex based products) disposal problem, a concept of reversion of the solid waste into its elemental compound is transpiring. In academics, this concept is known as the process of degradation/retro-gradation/regression. Thus, by degrading the complex macromolecules of latex based products into its elemental cycle, it could help to restore the environmental problems created. As the latex based products usually end up in the landfill, a process of microbial facilitated degradation or biodegradation process could be manipulated where the by-products is expected to be a simple element or compound.

Thus, by holding the “Key” as instructed by the Almighty God, I finished this research as part of my duty as a believed servant to contribute a little, but significant knowledge as a legacy to our children and for a future betterment, as quoted from Mahatma Gandhi’s saying; “We did not inherit this world from our forefathers, but we borrow it from our children”. With that, I would like to thank my wise supervisor, Associate Professor Dr. Azura A. Rashid, and my co – supervisor, Dr. Zuratul Ain Abd Hamid, for giving a significant advice and assistance as well as trust for me to complete this research.

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Muhammad Afiq Misman, 1 May 2017.

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LIST OF SYMBOLS

n	Number of designated carbon atom
mol	Mol
mol/AGU	Mol of substances with respect to anhydroglucose unit
R_p	Rates of polymerization
K_n, n = 1, 11, 12, 2, 22	Polymerization constant
k_n, n = 1, 11, 12, 2, 22, 4, 5	Polymerization constant
R_i	Rates of initiation
k_p	Polymerization constant
pH	Acidity/alkalinity constant
α	Confidence level
µm	Micrometer
$\%.\mu m^{-2}$	Percentage over area
mV	milivolts
R^2	Coefficient of correlation
cm^{-1}	Per centimeter
%T	Percentage of transmission
M_V	Viscosity average molecular weight
dL/g	Deciliter over grams
K	Kelvin
V_S	Particle’s settling velocity
G	Gravitational constant
ρ_s	Density of the particles
ρ_l	Density of the fluid

d_p	Particle radius in equivalent sphere
MPa	Mega Pascal
N/mm	Newton per millimeter
T_{max}	Maximum degradation temperature
ºC	Degree Celsius
ΔT	Temperature difference
T_o	Onset temperature
pN nm^{-1}	Pico Newton per nanometer
nm	Nanometer
M100	Modulus at 100 % elongation
M300	Modulus at 300 % elongation
M500	Modulus at 500 % elongation
$molcm^{-3}$	Mol per centimeter cubic

LIST OF ABBREVIATIONS

AGU	Anhydroglucose unit
ANS	Amino functional starch
ASTM	American standard for testing materials
CS	Control starch
DMSO	Dimethyl sulfoxide
DMSO-d_6	Dimethyl sulfoxide deuterated
DS	Degree of substitution
DS/SA	Specific degree of substitution
DTG	Derivative thermal analysis
EA	Elemental analysis
EB	Elongation at break
FTIR	Fourier transform infra-red
^{1}H-NMR	Proton nuclear magnetic resonance
MFFT	Minimum film formation temperature
phr	Part per hundred rubber
ppm	Part per million
TGA	Thermo-gravimetric analysis
XNBR	Carboxylated nitrile butadiene rubber

KESAN PENAMBAHAN KANJI BERFUNGSI AMINO KE ATAS SIFAT-SIFAT MEKANIKAL DAN DEGRADASI FILEM LATEKS GETAH NITRIL BUTADIENA TERKARBOKSIL

ABSTRAK

Lateks getah nitril butadiena terkarboksil (XNBR) telah dicampurkan dengan kanji berfungsi amino (ANS) dan filem getah nipis telah dihasilkan melalui teknik pencelupan berkoagulan. Sebelum proses tersebut, ANS telah disintesiskan dengan kepekatan akrilonitril yang berbeza untuk mengkaji kesan kepekatan akrilonitril ke atas tahap penggantian (DS) dan kestabilan partikel ANS di dalam lateks XNBR. ANS yang dihasilkan dicirikan dengan menganalisa keputusan nuklear proton resonans magnetik (^{1}H-NMR), analisis unsur (EA), dan infra merah terubah fourier (FTIR). Kelikatan produk dan berat molekul berdasarkan purata kelikatan ditentukan dengan viskometer 'Ubbelohde' dan kestabilan partikel ditentukan melalui analisa potensi zeta. Kajian mengenai kesan jumlah pembebanan ANS (0, 5, 10, 15, 20 phr) ke atas sifat - sifat mekanikal, morfologikal, termal, proses pecutan penuaan, dan biodegradsi filem lateks ANS/XNBR telah dijalankan. Keputusan kajian menunjukkan DS ANS bergantung kepada kepekatan akrilonitril akan tetapi kestabilan ANS bergantung kepada saiz partikel dan 'zeta potential'. Sifat akhir filem bergantung kepada kepekatan ANS. Penambahan ANS tidak meningkatkan sifat mekanikal filem lateks ANS/XNBR tetapi memberikan kesan ketara keatas sifat biodegradasi filem. Kajian morfologi menunjukkan penggunaan ANS di dalam sebatian lateks XNBR menjadikan permukaan filem lateks kasar dengan filem yang mempunyai jumlah ANS tertinggi menunjukkan pembentukan beberapa rongga dan gumpalan pengisi. Analisa TGA-DTG menunjukkan bahawa penambahan ANS

meningkatkan rintangan filem lateks terhadap degradasi terma. Walaubagaimanapun, ujian pecutan penuaan (isoterma) pada 100 °C menunjukkan bahawa penambahan ANS meningkatkan kadar penuaan lateks filem. Pembentukan rongga ini mempercepatkan serangan mikroorganisma ketika proses biodegradasi sekaligus meningkatan kadar biodegradasi filem. Akan tetapi, jumlah pembebanan optimum untuk filem lateks ANS/XNBR dicapai pada 10 phr dengan merujuk kepada ketinggian sifat - sifat mekanikal filem yang dipamerkan berbanding filem ANS/XNBR pada pembebanan yang lain.

THE EFFECT OF AMINO FUNCTIONAL STARCH ON THE MECHANICAL AND DEGRADATION PROPERTIES OF CARBOXYLATED NITRILE BUTADIENE RUBBER LATEX FILMS

ABSTRACT

Carboxylated nitrile butadiene rubber (XNBR) latex was compounded with amino functional starch (ANS) and latex thin films were prepared by coagulant dipping technique. Prior to the process, ANS was synthesized with different acrylonitrile concentration to study the effect of acrylonitrile concentration on the degree of substitution (DS) and the stability of the ANS particle in XNBR latex. The ANS produced was characterized by proton nuclear magnetic resonance (^{1}H-NMR), elemental analysis (EA), Fourier transform infrared (FTIR) analyses. The product viscosity and viscosity average molecular weight were determined by ubbelohde viscometer and the stability of the particle was obtained via zeta potential analysis. A study was conducted to determine the effect of ANS loadings (0, 5,10,15,20 phr) on the films mechanical, morphological, thermal, accelerated aging process, and biodegradation properties of ANS/XNBR latex films. Results show that, the DS of ANS depends on the acrylonitrile content, but the stability of ANS depends on the particle size and its zeta potential. The final properties of the films depend on the ANS concentration. The addition of ANS did not improve the mechanical properties of ANS/XNBR latex films, but give a significant contribution towards films biodegradability. Morphological study shown the incorporation of ANS in XNBR latex compound results in surface roughness with higher loading films shown a number of void and agglomeration of filler. TGA-DTG analysis shows that the addition of ANS increased the latex film resistance towards thermal degradation.

However, accelerated ageing test (isothermal) at 100 °C indicates that introduction of ANS increased the ability of the film aged. The formation of void in higher loading films accelerates the microbial attack during biodegradation test and contribute significantly towards films biodegradability. However, optimum filler loading for ANS/XNBR latex obtained was 10 phr due to higher mechanical properties showed by the films compared to other loading of ANS/XNBR latex films.

CHAPTER ONE

INTRODUCTION

1.1. Overview

Elastomeric materials are one of the highest utilized products in the world. The materials offer several advantages such as; the ability to be stretched with low hysteresis and high tensile strength with low modulus. Out of total elastomer based products produced, 82 % of the products are latex based products. **Table 1.1** shown the total consumption of rubber products in Malaysia for 16 consecutive years (MRB 2016). Based on **Table 1.2,** in year 2014, latex thin film product (gloves and condoms) made up to almost 43 billion pieces or 73 % of the total rubber products consumed.

Latex thin film products usually are made by a coagulant dipping process. One of the most manufactured products via this method are rubber glove. Latex gloves vary from the medical to industrial type and the products was made distinctively in their physical properties, appearance, patterns, as well as the materials to meet the needs of the end-user.

However, latex gloves usually being distinguished either as natural or synthetic based gloves. Synthetic rubber glove industries started to flourish at the end of the 19th century, when rubber industries started to produce synthetic latexes due to the shortage of natural rubber supply and increased in demand for non-allergy latex gloves. Since then, the industry continue to expand in the 20th century with an