THE PROPERTIES OF SILYLATED POLYVINYL ALCOHOL BASED FOAM REINFORCED BY MICROFIBRILLATED CELLULOSE (MFC)

BY

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ABSTRACT

In this study, polyvinyl alcohol (PVA) composite foam reinforced with microfibrillated cellulose (MFC) was prepared using freeze-drying process. The MFC from sugarcane bagasse (SCB) was extracted via chemical treatment assisted with ultrasonication. However, a noteworthy problem of incorporating MFC-SCB into PVA foam is that their low melting point, lacks fine interfacial adhesion and high moisture absorption. Therefore, in this study, the PVA-MFC foam was chemically silylated with Υ- methacryloxypropyltrimethoxysilane (MPS) and tetraethoxysilane (TEOS) to overcome the weakness of incorporating MFC-SCB into PVA foam. It was found that PVA-MFC foam with PVA molecular weight of 50 kDa, concentration of MFC-SCB suspension 2 w/v % and 20 w/v % concentration of PVA resulted the highest porosity (68 %) and lowest density (0.48 g cm^{-1}). This PVA-MFC foam denoted as $_{2,20}$PVA-MFC. Preferred silanization parameter of $_{2,20}$PVA-MFC foam was found at 10 wt % of silane concentration and two hours of reaction time. The wetting ability and mechanical strength of the silylated $_{2,20}$PVA-MFC foam was greatly enhanced compared with unmodified $_{2,20}$PVA-MFC foam. The silane chemicals (MPS and TEOS) had been confirmed grafted on $_{2,20}$PVA-MFC foam due to presence of Si-C and Si-O-C stretching vibration in fourier transform infrared (FTIR) spectra and cloud-like coating of porous pore was observed in scanning electron microscopy (SEM) micrographs. In addition, the silylated $_{2,20}$PVA-MFC foam (MPS and TEOS) exhibit a series of desirable properties such as lower swelling ratio and high absorption capacity of solvents and oils. The characterization of $_{2,20}$PVA-MFC foam using TEOS was further investigated by field emission scanning electron microscopy (FESEM), X-ray photoelectron spectrometer (XPS) analysis and Brunauer-Emmett-Teller (BET) specific surface area. A significant morphological difference between the unmodified and silylated $_{2,20}$PVA-MFC-TEOS foam was clearly observed through FESEM micrographs. Despite that, the XPS and BET analysis also exhibit Si 2p spectrum and low specific surface area on the silylated $_{2,20}$PVA-MFC-TEOS foam, respectively. This versatile silylated $_{2,20}$PVA-MFC foam could therefore be a promising option as a novel adsorption material for solvent and oil removal in the treatment of polluted water.

ملخَص البحث

في هذه الدراسة ، تم تحضير الرغوة المركبة من البولي فينيل كحول (PVA) المدعومة بالسيليلوز المجهري بالميكروفيلت (MFC) باستخدام عملية التجفيف بالتجميد.تم استخراج MFC من تفل قصب السكر (SCB) عن طريق العلاج الكيميائي بمساعدة الموجات مافوق الصوتية. ومع ذلك ، هناك مشكلة جديرة بالملاحظة عند دمج MFC-SCB في رغوة PVA وهي ان درجة الإنصهار ضعيفة، لأنه يفتقر إلى التصاق بيني دقيق وامتصاص عالي تجاه الرطوبة. لذلك، في هذه الدراسة ، تم ترشيح الرغوة PVA-MFC كيميائياً باستخدام Y- Methacryloxypropyltrimethoxysilane (MPS) و tetraethoxysilane (TEOS) للتغلب على ضعف دمج MFC-SCB مع رغوة PVA . وجد أن رغوة PVA-MFC مع PVA بوزن الجزيئي 50kDa ، المركب من مزيج%MFC-SCB 2w/v و 20w/v% من المركب PVA الذي انتج مسامية عالية (68 %) و كثافة قليلة ($0.48\ g\ cm^{-1}$). هذه الرغوة PVA-MFC تشير الى $_{2,20}$PVA – MFC. وقد أظهرت نتائج طريقة سيلان ان المعامل الافضل لرغوة $_{2,20}$PVA-MFC كانت10wt% من المركب السيلاني خلال ساعتين من وقت التفاعل. تم تحسين قدرة الترطيب والقوة الميكانيكية لرغوة $_{2,20}$PVA-MFC المرشحة بشكل كبير مقارنة مع الرغوة غير المرشحة $_{2,20}$PVA-MFC. كما تم تاكيد ارتباط المركب الكيميائي سيلان (MPS and TEOS) مع رغوة $_{2,20}$PVA-MFC نتيجة وجود الاهتزازات التمددية Si-C و Si-OC كما موضح في جهاز تحويل الأشعة تحت الحمراء (FTIR) وقد لوحظت الأطياف والطبقة الشبيهة بالغيوم للمسام المسامية في صور المجهر الإلكتروني (SEM). بالإضافة, رغوة $_{2,20}$PVA-MFC المرشحة عرضت سلسة من الخواص المرغوب فيها والتي تتميز بنسبة منخفضة في الانتفاخ و نسبة مرتفعة في امتصاص الزيوت و المذيبات. علاوة على ذلك ، تمت دراسة خصائص رغوة $_{2,20}$PVA-MFC باستعمال TEOS و بالقيام بالمزيد من التحري عن طريق المسح المجهري الإلكتروني للانبعاثات (FESEM) ,جهاز قياس طيف الصور بالأشعة السينية (XPS) وبرونور-إيميت-تيلر (BET) لمساحة محددة. لوحظ وجود فرق معنوي في الشكل المورفولوجي بين الرغوة غير المعدلة و رغوة $_{2,20}$PVA-MFC-TEOS المرشحة بمحلول سيلان عن طريق صور FESEM. على الرغم من ذلك ، أظهر تحليل XPS و BET أيضًا طيف Si 2p ومساحة سطح محددة منخفضة على الرغوة المرشحة $_{2,20}$PVA-MFC-TEOS بالترتيب .وبالتالي ، يمكن أن تكون هذه الرغوة المصممة متعددة الاستخدامات والتي تبلغ $_{2,20}$PVA-MFC مرشحة من احسن مواد الامتصاص و التي يمكن استعمالها في العديد من التطبيقات لازالة الزيوت ومعالجة المياه الملوثة.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Biotechnology Engineering)

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DECLARATION

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LIST OF ABBREVIATIONS

CD	Compression Deflection
CH_3COOH	Glacial Acetic Acid
C_m	Absorption Capacity
FESEM	Field Emission Scanning Electron
FTIR	Fourier Transform Infrared Spectroscopy
H_2O_2	Hydrogen Peroxide
H_2SO_4	Sulphuric Acid
MFC	Microfibrillated Cellulose
NaOH	Sodium Hydroxide
O/C	Oxygen to carbon
PVA	Polyvinyl Alcohol
SCB	Sugarcane Bagasse
$ScCO_2$	Supercritical drying carbon dioxide
SEM	Scanning Electron Microscopy
S_r	Swelling Ratio
TGA	Thermal Gravimetric Analysis
WCA	Water Contact Angle

LIST OF SYMBOLS

°C	Degree Celcius
eV	Electron Volts
KBr	Potassium Bromide
kDa	Kilo Dalton
m	Mass
MPa	MegaPascal
P%	Porosity
V	Volume
W	Watt
w/v %	Percent weight/volume
w/w %	Percent mass
ρ_c	Density of bulk cellulose
ρ_{foam}	Apparent Density of Foam

CHAPTER ONE

INTRODUCTION

1.1 INTRODUCTION

Polymer foams are extensively utilized in numerous applications, including heat and acoustic insulation, packaging, shock protection and much more (Avella et al., 2012). This is because of their specific properties like low thermal conductivity and high compressibility at a constant load (Ridha, 2007). At the end of their life cycle, waste derived from non-degradable polymer foams will eventually filling up an ever-shrinking landfill sites. In this respect, the development of 'green foams' from biodegradable polymer reinforced with fibres from renewable resources is necessity as an alternative to non-degradable polymer foams. One of the polymers is polyvinyl alcohol (PVA), which is safe, biodegradable and easy to be combined. In presence of suitable microorganisms, PVA is easily susceptible to biodegradation and water-soluble polymer which has ability to provide a porous matrix (Avella et al., 2012). Meanwhile, incorporating of cellulose fibrils in PVA foams could increase the mechanical performance of foams as well as preserving its biodegradability (Avella et al., 2012).

In this study, the cellulose fibrils were extracted from sugarcane bagasse (SCB). It is a agro-waste product which is generated after juice extraction from sugarcane mills (Sajjad et al., 2017). The dry weight basis of cellulose in SCB is approximately 43.8% (Pereira et al., 2011). It becomes attractive materials in many research studies and be used in industries such as pulp and paper production (Vena et al., 2013), xylitol production (Martinez et al., 2003), textiles (Cueva-orjuela et al., 2017) and furniture industry (Oliveira et al., 2016). Besides that, it can be utilized to build hierarchical structures because of its constitutive mechanical and chemical properties (Fatona et al., 2018 and Peponi et al., 2014).

Microfibrillated celluloses (MFCs) obtained from lignocellulosic materials are commonly rigid rod-like monocrystalline cellulose with a diameter of between 1 to 100 nm (Ruiz et al., 2014). Besides that, they have very fine capability to structure a rigid network which could be obtained through mechanical disintegration (Lavoine et al., 2012). Moreover, due to their desirable properties such as lightweight, nontoxic and biodegradable, they are used as reinforced materials in composites (Kalia et al., 2009). However, these materials are unable to disperse uniformly in most non-polar polymer media due to theirs hydrophilicity nature (Abdul Khalili et al., 2012).

Therefore, appropriate approach is required to reduce the inherent hydrophilicity of PVA-MFC foams by performing chemical functionalization with hydrophobic molecules. Alkoxysilane is one example of organosilicon compounds which particularly effective in hydrophobizing hydroxylated substrates (Zhang et al., 2014). The coupling agents used in this study are Y-methacryloxypropyltrimethoxysilane (MPS) and tetraethoxysilane (TEOS).

This study aims to develop PVA-MFC composite foams by investigating the optimum composition of MFC to be incorporated into PVA based composite foam. Furthermore, the PVA based composite foams reinforced with MFC were silylated with MPS and TEOS at different silane concentration and reaction time. The physicochemical characteristics and its absorption capacity to different solvents and oils of unmodified and silylated foams were compared.

1.2 PROBLEM STATEMENT

Every year, increasing usage of foams in various industry sectors had causing serious disposal problems once it reaches the end of its life-cycle. Moreover, it inevitably caused substantial waste and serious pollution of the environment (Liu et al., 2014). Therefore, by using PVA and natural fibres such as MFC as reinforcing phase could provide as an alternative strategy to overcome their disposal problems (Avella et al., 2011). In addition, owing to sugar production industry expands, abundant of SCB is produced. In most instances, this bagasse causes environmental problems owing to direct disposal on the open ground and forms trash heaps in the region (Sajjad et al., 2017 and Abdul kadir et al., 2014).

According to Liu et al., (2014), PVA foam has a poor dimensional stability and mechanical properties. Meanwhile, pure fibres cellulose foam has a loose and fragmentary characteristic. Hence, it could be overcome by using PVA reinforced with natural fibres cellulose to prepare porous composites by decreasing the MFC composition in this study. However, the incorporation of MFC into PVA foam can be less attractive because it has low melting point and poor resistance towards moisture. Thus, poor compatibility between water-soluble synthetic polymer (PVA) and natural fibers (MFC of SCB) may lead to agglomeration of fibers, poor mechanical characteristics and elevated absorption of composites by moisture (Orhan, 2010). In addition, these materials tend to be affected by fungal attacks in humid circumstances and absorbing moisture may swell up the fibers and cause composite swelling. This is due to the hydrophilic nature of the MFC which has low thermal stability that can restrict the option of polymer matrices and handling techniques for foam composites manufacturing (Oksman et al., 2016). PVA is also known as hydrophilic polymer which is loaded in pendant hydroxyl groups that function as biomolecular attachment locations (Tummala, 2018). It is therefore necessary to increase the hydrophobicity of PVA-MFC composite foams in order to develop composites with better mechanical properties and performance.

Thus, by using coupling agents such as alkoxysilane, hydrophobic PVA-MFC foam bonds can be formed. This because, the amount of cellulose hydroxyl groups in the fiber matrix interphase could be reduced by silane coupling agents. Therefore, hydrolysable alkoxy group contributes to the creation of silanols in the presence of moisture (Ochsner, 2018). Hence, following the reaction of silanols with SCB and PVA hydroxyl groups MFC, they may form stable covalent bonds to the cell wall during chemisorbation on the MFC fiber surface. According to Kalia et al., (2011), silane coupling agents could enhance the degree of cross-linking between PVA and MFC in the interface area. In addition, the swelling proportion of PVA-MFC composite foams (i.e. creation of a crosslinked network) owing to covalent matrix bonding may be restricted by silane alteration.

1.3 RESEARCH SIGNIFICANCE

The results of this study will contribute to the benefit of producers and society. In this respect, the productions of silylated bio-based PVA foams reinforced with MFC could serve as alternative polymer foams to the existing non-degradable polymers. The positive impact on environment by employed MFC to be supported in PVA foam is worth noting. In addition, the use of cellulose-based products from crop by-products has received considerable attention as it is one of the most promising waste management strategies. Besides, by making PVA-MFC composite foams hydrophobic, improvement in its moisture resistance and stability could be attained. It can also be very promising for practical applications in water treatment, heat insulation and fire-retardant materials as well as for use in electrical equipment and energy storage systems.

1.4 RESEARCH OBJECTIVES

This study aimed to achieve the following objectives:

1) To determine the optimum PVA and MFC-SCB composition in preparing PVA-MFC composite foam based on its density and porosity characteristics.

2) To investigate the optimum silane concentration and reaction time in silylation of PVA-MFC composite foam.

3) To evaluate the physicochemical characteristics of PVA-MFC composite foam and its absorption capacity to different solvents and oils.

1.5 RESEARCH SCOPE

This study's primary focus is on developing silanized bio-based PVA-based composite foam reinforced with MFC from SCB (MFC-SCB). The silane treatment was aimed to confer hydrophobic character of PVA-MFC composite foam. By varying the silane concentration (MPS and TEOS) and reaction time, different degree of hydrophobicity can be imparted toward the foam. The PVA-MFC foams were prepared with different molecular weight, different composition of PVA and MFC-SCB by using freeze-drying technique. In this research, two-level factorial design was used to investigate the relationship between distinct PVA structure and MFC-SCB suspension structure towards PVA-MFC composite foam density.

The physicochemical characteristics of unmodified and silylated PVA-MFC composite foam were assesed using scanning electron microscopy (SEM), Fourier transform infrared (FTIR), contact angle, thermogravimetric analysis (TGA) and compression test analysis. The absorption capacity to different solvents and oils were also determined in this study. In respect to the physicochemical characteristics analysis and absorption capacity test results, the best silylated PVA-MFC foams between MPS and TEOS were selected and evaluated by using X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscope (FESEM) and Brunauer-Emmett-Teller (BET).

1.6 THESIS ORGANIZATION

This thesis consists of five chapters. The first part of this chapter is general background of this study which includes introduction of polymer foam, PVA, MFC which extracted from SCB and modification of PVA-MFC foam using silane chemicals. Also includes in this section are problem statement, research significance, research objectives and scope of studies.

Chapter two provides an overview of polymer foams reinforced by MFC of SCB which includes the study of foam modifications based on the previous studies. This chapter also covers an overview of different types of polymer matrices that currently used to prepare foam. Besides that, the fabrication and modification methods of foams were reviewed in this chapter.

Chapter three explains the materials and methods used in this research in a more particular way. Method of extraction of MFC from SCB, fabrication, modification and characterizations of PVA-MFC composite foams were described in this chapter as well.

Meanwhile, chapter four covers the findings obtained in this study. The density and porosity of PVA-MFC foams with different molecular weight of PVA, composition of PVA and MFC-SCB were reported in this chapter. After modified with different silane composition and reaction time, the physicochemical characteristics and absorption capacity of PVA-MFC foams were evaluated.

The final part in the chapter five presents the conclusions and recommendations for future studies.