

Functionalization of Cellulose through Polyurethanization by the Addition of Polyethylene Glycol and Diisocyanate

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Abstract: Plastic consumption becomes a main factor of land pollution due to poor degradability. To reduce the impact of land pollution, a biodegradable material such as cellulose, which has biodegradability, high strength, and specific modulus, is combined with plastic materials. However, the combination result poor compatibility because of different properties. Through grafting technique, the compatibility can be improved. The experimental results were conducted using Fourier-Transform Infrared (FT-IR), Simultaneous Thermal Analysis (STA), Scanning Electron Microscope (SEM) and ¹H-Nuclear Magnetic Resonance (¹H-NMR). The results revealed that the structure of hybrid material consists of cellulose as a chain extender in a hard segment which connects two diisocyanate compounds and polyol as a soft segment. The addition of 2.5 g of cellulose and 5 mole of diisocyanate can increase the melting temperature (T_m) of the hard segment from 417.92 to 460.72 °C and from 417.92 to 467.04 °C respectively. However, its melting temperatures of soft segment decrease from 378.53 to 350.74 °C and from 378.53 to 350.74 °C as well as the glass transition temperature (T_g) of the soft segment from 73.7 to 57.2 °C and from 73.7 to 71.8 °C. This study also discovers that cellulose and diisocyanate can raise thermal stability and create good interfacial bonding.

Keywords: cellulose; chain extender; polyurethane; thermal stability; grafting technique

■ INTRODUCTION

Over the last century, plastics are already known as a major commodity which is widely used in various applications including military, construction, packaging, household devices, and automotive parts. The plastic products are commonly made from petro-polymer due to low cost, low density, and easiness to process. Moreover, petro-polymer has better mechanical properties compared to metals and ceramics, and the addition of fibers, usually carbon and glass fiber, offers higher strength and higher modulus elasticity [1].

Polyurethane is one of plastics which has great versatility and variety of applications and functions, relying on the precursors chosen in the formulation [2]. It commonly can be obtained from the reaction between diisocyanate compounds and polyols or diols. A number of reactions resulting in polyurethane from biomass-based monomers have been reported recently [2-6]. These

reactions involve the synthesis of biomass polyurethane comprising of several stages namely pre-polymerization followed by chain extension. In addition, direct polymerization to create a high molecular weight of polyurethane was also reported by reacting with a relatively high molecular weight monomer [3]. The structure of polyurethane itself typically is constructed by an alternating phase called soft segment (SS) and hard segment (HS). The hard segment was formed by the diisocyanate compound, while the soft segment will be formed by polyols or diols. The ratio between HS and SS primarily determines the entire properties of polyurethane that HS is responsible for the mechanical and high thermal properties, while SS is responsible for elastic and low thermal properties. So that the properties of polyurethane can be varied by manipulating the amount of HS and SS [4-7]. In addition, the addition of cellulose fibers as a chain extender on the polyurethane

will contribute to forming a hard segment to enhance the mechanical properties as well as high thermal properties [8].

Besides, usage of carbon and glass fibers in polymer products has emerged problems of land pollution and started to be an important concern. As a result, in several decades the use of natural fiber has replaced those inorganic materials in some applications due to the ability such as degradation and decomposition [9-17]. The most important content that is extracted from natural fibers is cellulose which possesses high strength and excellent specific modulus. In particular, several scientists have carried out the experiments involving grafting technique of cellulose to polyurethane to get hybrid-polyurethane materials, for instance Belgacem et al. [8] who have combined pre-formed of PCL and phenyl isocyanate with cellulose as a chain extender and followed by Samain et al. [18] who have conducted grafting technique of isocyanate to microcrystalline cellulose with PLA and PHA polymer. Both of their researches resulted that cellulose can be added to polyurethane polymer to increase degradability, mechanical properties and reduce the land pollution.

According to the aforementioned explanations, an environmentally-friendly material which enables easily to decompose can be formed with the combination of polyurethane and cellulose. The combination between cellulose and polyurethane will enhance the high thermal properties and thermal stability of material because cellulose is likely to form covalent bonds in HS on polyurethane when it reacts with diisocyanate compounds. Therefore, the objectives of this research were to investigate the effect of the addition of cellulose and 4,4'-methylene bis (cyclohexyl isocyanate) (HMDI) on the hybrid polyurethane-cellulose material in order to raise the thermal stability and melting temperature and to study the structure of the hybrid polyurethane-cellulose material. The experimental results were evaluated by ¹H-NMR to analyze the structure, FTIR was used to confirm the functional groups, STA was carried out to analyze physical changes such as the glass transition temperature (T_g), melting temperature (T_m) and thermal stability and SEM analysis was done to observe the morphological surface within hybrid polyurethane-cellulose material.

■ EXPERIMENTAL SECTION

Materials

The polyurethane firstly was synthesized by a pre-polymerization mechanism involving a reaction between 15 g of polyethylene glycol (PEG) Mw: 6000 g/mole as the SS and 2 and 5 mole of 4,4'-methylene bis (cyclohexyl isocyanate) (HMDI) as the HS. The reaction was accelerated by adding two drops of dibutyltin dilaurate (DD) as a catalyst, and the addition of cellulose with the composition ranging from 0.5 g to 2.5 g. All materials were obtained from Sigma-Aldrich.

Instrumentation

¹H-Nuclear Magnetic Resonance (¹H-NMR)

The ¹H-NMR measurement was carried out to analyze the structure of the hybrid polyurethane-cellulose material. Characterization procedure was conducted by using Solution NMR Jeol 500MHz with DMSO-d as a solvent. Measurement conditions are 23 °C for the temperature and 6 Pa for the pressure (vacuum).

Fourier Transmission Infra-Red (FT-IR)

FT-IR spectra were recorded by using a Perkin-Elmer FTIR spectrometer. It is utilized to further analyze the structure of the material. Each sample recording consists of 30 scans and was recorded from 400 to 4000 cm⁻¹.

Simultaneous Thermal Analysis (STA)

STA measurements were recorded by using a Perkin-Elmer 6000. It has a range of temperature from 15 to 1000 °C and was carried out to analyze physical changes such as glass transition temperature (T_g) and melting temperature (T_m) and thermal stability. This technique conducts the experiment on which the material and reference are heated and chilled on certain condition.

Scanning Electron Microscope (SEM)

Surface morphology of hybrid cellulose-polyurethane material was observed by using Field Emission Scanning Electron Microscope FEI Inspect F50 to image the morphology with accelerating voltage

of 30 kV, resolution and magnification are 1 nm and 500.000 times respectively.

Procedure

Preparation of hybrid polyurethane-cellulose material consists of two steps namely pre-polymerization mechanism and grafting mechanism. Firstly, the pre-polymerization process began with filling Dimethyl formamide (DMF) as a solvent and 15 g of polyethylene glycol 6000 into a Schlenk tube. Then, the Schlenk tube was heated to 80 °C and stirred up for one hour. During stirring, it was fluxed with nitrogen gas to ensure that there is no moisture trapped in the Schlenk tube. After one hour, two moles of HMDI was injected into the Schlenk tube and followed by two drops of DD to speed up the pre-polymerization reaction. Then, the pre-polyurethane was obtained after mixing all of the components stirred for one hour and heated to 80 °C.

Secondly, after the pre-polyurethane was formed, the grafting mechanism was carried out to get the hybrid polyurethane-cellulose material. The pre-polyurethane material formed was indicated as a white viscous liquid. Then, in the same Schlenk tube, grafting mechanism was carried out by starting filling a Schlenk tube with 2.5 of cellulose. Afterward, the temperature of the Schlenk tube was raised to 80 °C and stirred up to one hour. Finally, the reaction was terminated by using 20 mL of water and waited for up to one day until a phase separation emerged. The hybrid polyurethane-cellulose precipitated in the bottom of the glass vessel and water, DMF and DD were floated on the surface. The other experiments were

conducted similarly but with the addition of the different composition of HMDI in the pre-polymerization process and cellulose in the grafting mechanism after the pre-polyurethane was formed. The samples are depicted in Table 1.

RESULTS AND DISCUSSION

The Structure of the Hybrid Polyurethane-Cellulose Material

The pre-polymerization reaction was shown in Fig. 1. It occurred when diisocyanate compound which has cyanate groups (N=C=O) was attacked by hydroxyl group as a nucleophile in the polyols or diols compounds to form urethane group which typically hints a polyurethane polymer [18].

After the pre-polymerization process, the remaining diisocyanate compound (-N=C=O) reacted with the hydroxyl group of cellulose through grafting mechanism in which diisocyanate has a role as a coupling agent which forms chemical or physical bonding between the interface of cellulose and polyurethane. It also can increase the compatibility of hybrid polyurethane-cellulose material [19]. The result of

Table 1. The material sample codes and compositions

Material Code	Composition	
	Cellulose (g)	HMDI (mol)
MP2H2.5S	2.5	2
MP5H0.5S	0.5	5
MP2H0.5S	0.5	2

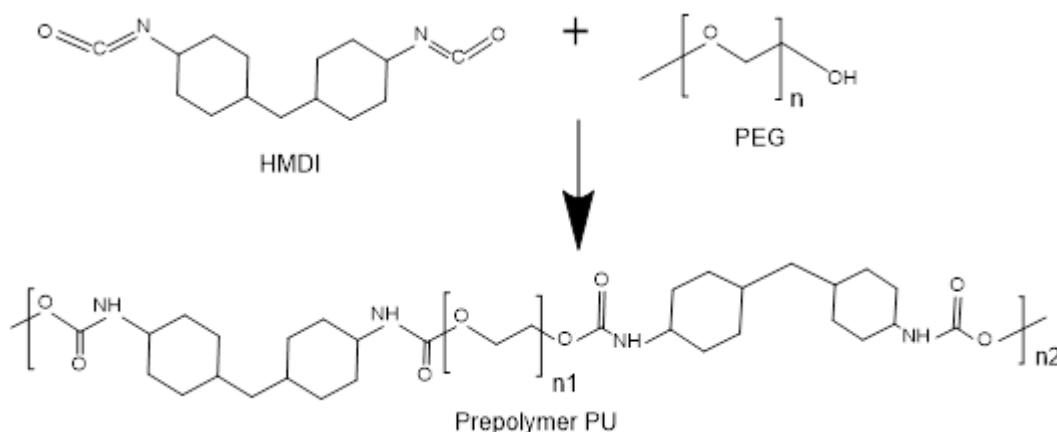


Fig 1. The pre-polymerization reaction

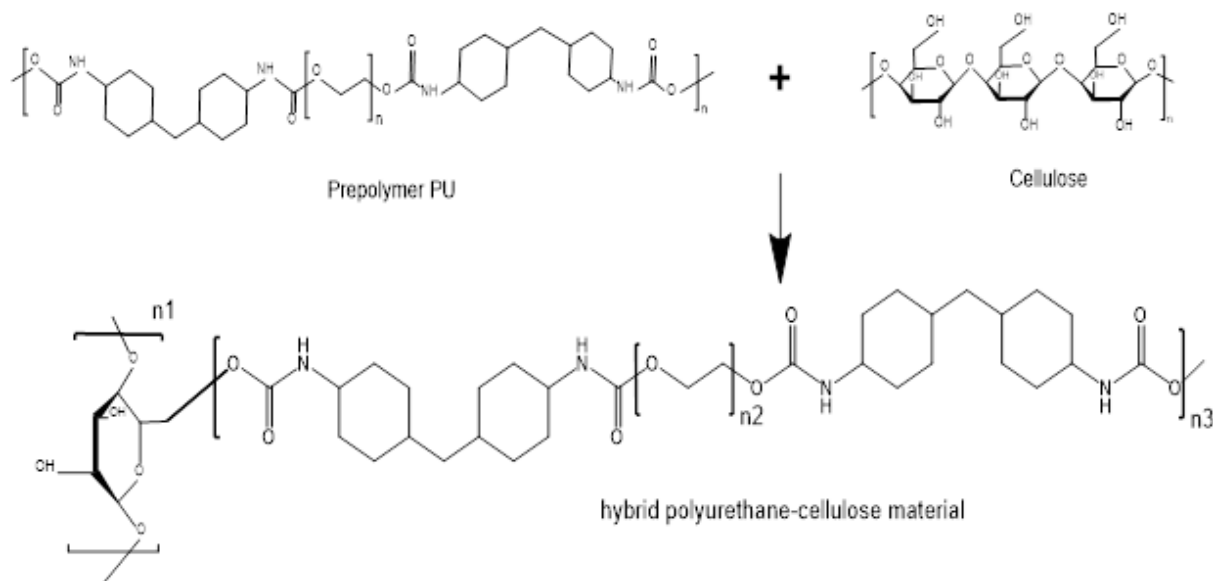


Fig 2. The grafting reaction

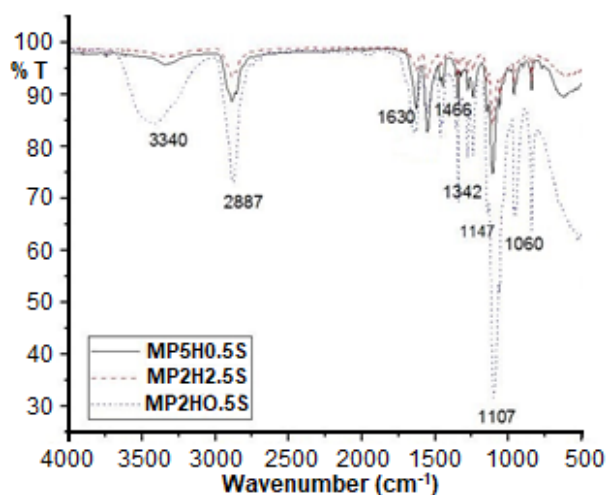


Fig 3. FTIR Spectra of the hybrid polyurethane-cellulose material

the entire polymerization process is a hybrid material between cellulose and polyurethane in which cellulose (n_1) and 4,4'-methylene bis (n_3) form hard segment, while polyethylene glycol (n_2) forms soft segment as shown in Fig. 2.

In order to depict the structure of the hybrid material, FTIR spectra, and $^1\text{H-NMR}$ spectroscopy are required to clearly show the spectra emerged and structure formed in the hybrid polyurethane-cellulose material.

According to the FTIR spectra in Fig. 3, a number of spectra emerge from the graph including O-H stretch at 3340 cm^{-1} , secondary amine (N-H stretch) at 2887 cm^{-1} , C-O acyl bond at 1242 cm^{-1} , urethane (C=O) at 1630 cm^{-1} , C-H bending/H-C-H stretch at 1466 , 1147 and 1449 cm^{-1} , C-O-C ether at 1279 , 1242 , 1107 and 966 cm^{-1} , and C-N stretch at 1342 cm^{-1} . Secondary amine itself indicates that the diisocyanate compound has reacted and created a urethane group with hydrogen atoms. In addition, the addition of cellulose fibers showed on the depth of peaks of a C-O stretch at 1107 cm^{-1} and O-H stretch at 3650 cm^{-1} [20].

Whilst Fig. 4 shows the $^1\text{H-NMR}$ spectra of MP5H0.5S, MP2H2.5S, and MP2H0.5S. All spectra almost reveal the similar results. They show that $-\text{CH}_2-$ and $-\text{CH}-$ a group from diisocyanate compound appear at chemical shift ranging from 1.2-2.4 ppm marking the characteristic of cyclohexane in HMDI. On the other hand, the typical characteristic of HMDI compound was displayed more specifically to a secondary amine which was emerged at chemical shift 8 ppm as well as urethane at chemical shift 8.2 ppm. Cellulose itself which has anhydroglucose units appears at chemical shift ranging from 2.9 to 3.5 ppm and from 4.3 to 5.3 ppm. More specifically the spectra which show the characteristics

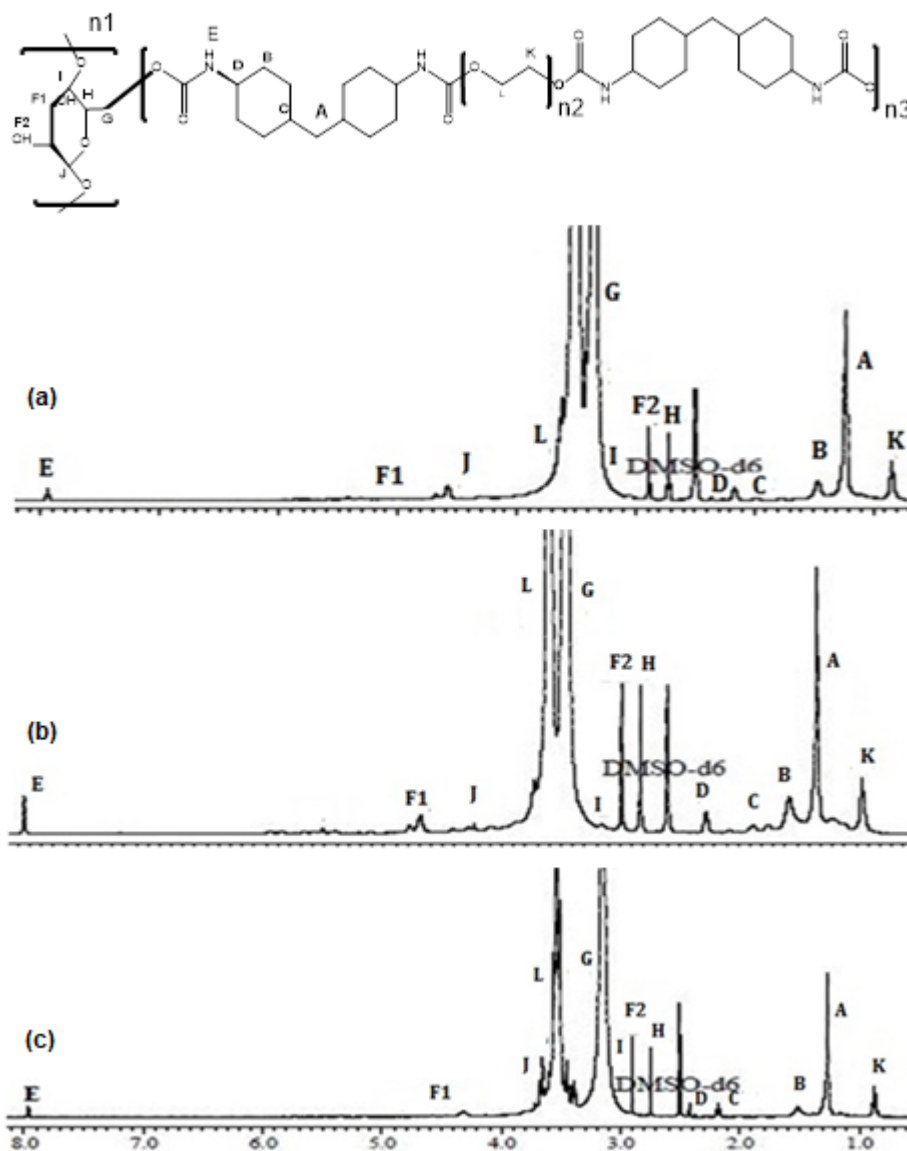


Fig 4. The H-NMR results of hybrid polyurethane-cellulose material.(a) MP5H0.5S and (b) MP2H2.5S, and (c) MP2H0.5S

of reaction between diisocyanate compound and cellulose appear at chemical shift 3.4 ppm. In addition, the OH bond in cellulose on MP5H0.5S appears at chemical shift 5.3 ppm, while on MP2H2.5S and MP2H0.5S it appears at 4.6 and 4.4 ppm respectively. Meanwhile, the chemical shift of the PEG compound appears from 3.4-3.6 ppm which connects between HMDI and PEG chain. The spectra of PEG both MP5H0.5S and MP2H0.5S appear at chemical shift around 3.5 ppm, while on MP2H2.5S they emerge at a chemical shift around 3.6 ppm. The difference of chemical shift ranges from 2.9 to 3.5 ppm in the

cellulose spectra and from 1.2 to 2.4 ppm in the HMDI spectra between MP2H2.5S, MP5H0.5S, and MP2H0.5S. It can be caused because MP2H2.5S contains more amount of cellulose so that the cellulose, which possesses anhydroglucose units, reacts excessively through OH bond with cyanate groups ($N=C=O$) of HMDI to form urethane linkage rather than reacting with polyol compound as well as MP5H0.5S has more amount of HMDI compound to react enormously with cellulose [20].

The Thermal Stability of the Hybrid Polyurethane-Cellulose Material

The hybrid polyurethane-cellulose material shows thermal characteristics related to the amount of SS and HS. Furthermore, melting and glass transition temperature rely on the addition of cellulose and HMDI as the addition of cellulose and HMDI affect the amount of HS contributing as a chain extender in the hybrid polyurethane-cellulose material. Cellulose which has internal and inter-hydrogen bondings then interacted with hydrogen bonding of diisocyanate group in the HS to form cross linking [21-22] subsequently raise the melting temperature of a hard segment of hybrid polyurethane-cellulose material. The greater amount of cellulose added to the hybrid material has definitely increased the melting temperatures of the hard segment caused by an increase in the interaction of hydrogen bonding. Alike the addition of cellulose, HMDI will contribute to increasing the melting temperature of the hard segment. HMDI will react with the other components of hybrid polyurethane forming several types of bonding such as N-H stretch, C-O acyl bond, C=O carbonyl and C-N bond. These bonds will significantly increase the melting temperature of the hybrid polyurethane-cellulose [23]. Otherwise, the decrease of glass transition and melting temperature of the soft segment caused by both cellulose and HMDI will hamper the mobility of soft segment chain [24]. The increase and decrease of the melting temperature of the hard and soft segment can be seen in Table 2.

The decomposition temperature (T_d) of MP5H0.5S and MP2H2.5S is 312.5 and 306.5 °C larger compared with 295.8 °C of MP2H0.5S as shown in Fig. 5. The addition of cellulose and HMDI is able to raise the thermal stability of hybrid polyurethane-cellulose material since it has a role to form cross-linking in the HS through hydrogen bonding mechanism and as a result, the proportion of hard segment increased the thermal stability of the material [25].

Morphological Surface of the Hybrid Polyurethane-Cellulose Material

The morphological surface has a relationship with the thermal properties. The good dispersion and distribution of cellulose are responsible to form the hydrogen bonding between urethane groups and the hydroxyl group of cellulose [24]. Furthermore, they affect the formation of the cross-linking region which contributes to stabilize the hybrid material thermally as well.

According to Fig. 6, MP2H2.5S shows that the cellulose (white dots) disperses and distributes on the whole surface of the hybrid material, while MP2H0.5S has the little white dots on its surface. It indicates that the greater amount of cellulose in the hybrid material affects the percentage of formation of cross-linking which formed by hydrogen bonding between urethane

Table 2. The temperature of the hybrid polyurethane-cellulose material

Material Code	T_g Soft (°C)	T_m Soft (°C)	T_m Hard (°C)
MP2H2.5S	57.2	350.74	460.72
MP5H0.5S	71.8	335.74	467.04
MP2H0.5S	73.7	378.53	417.92

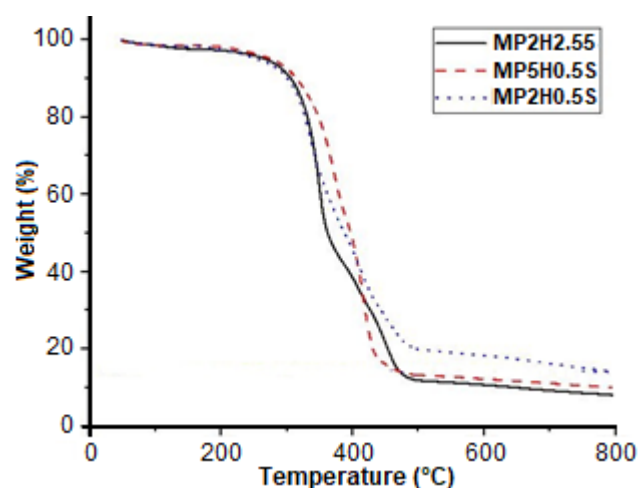


Fig 5. Thermal stability of the hybrid polyurethane-cellulose material

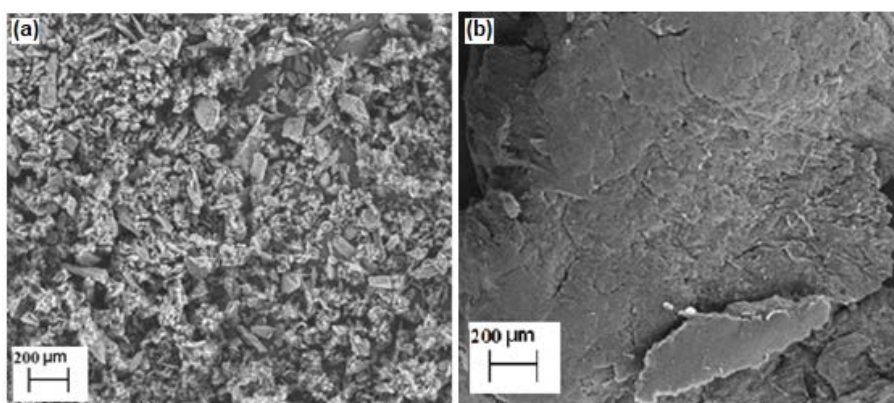


Fig 6. The morphological surface of the hybrid polyurethane-cellulose material (a) (MP2H2.5S) and (b) (MP2H0.5S)

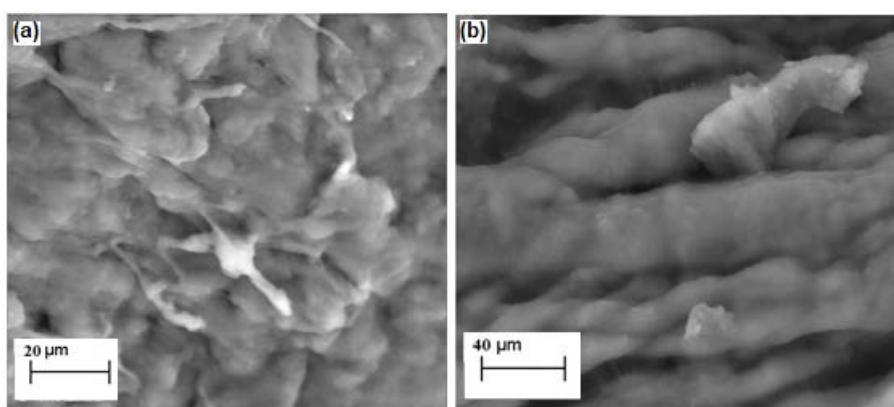


Fig 7. The morphological surface of the hybrid polyurethane-cellulose material (a) (MP5H0.5S) and (b) (MP2H0.5S)

groups and the hydroxyl group of cellulose. In other words, the greater amount of cellulose has produced a good distribution and dispersion on the surface of the material. As a result, it is thermally stable and has increased the thermal characteristics of the hybrid polyurethane-cellulose material.

In addition, the larger amount of HMDI will create the good interfacial bonding between cellulose and polyurethane since HMDI has a role as a coupling agent compared to the small amount of HMDI. The good interface between cellulose and polyurethane on MP5H0.5S marked by rough interfacial bonding, while on MP2H0.5S the interface looks less rough compared with MP5H0.5S as shown in Fig. 7.

■ CONCLUSION

The addition of cellulose and diisocyanate compound can increase the melting temperature of a hard

segment and enhances the thermal stability, but decreasing transition glass temperature of the soft segment. Morphological surface shows that the addition of cellulose also affects the thermal properties of the hybrid material due to good distribution and dispersion on the surface of the material. The structure of the hybrid polyurethane-cellulose material formed consists of cellulose as a chain extender and diisocyanate compound in the HS region and polyethylene glycol 6000 as an SS region. The use of diisocyanate compound and cellulose provide a better melting temperature of a hard segment and stabilize thermally. In addition, this material also will reduce the land pollution due to the use of cellulose as an environmentally-friendly material.

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