

Functionalization of cellulose through polyurethanization by the addition of polyethylene glycol and diisocyanate

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ABSTRACT

Plastic consumption is becoming one of environmental problems, causing land pollutions due to plastics' lack of degradability. This condition leads studies to develop environmental-friendly materials, one of them innovation on cellulose addition to plastic products. Cellulose, the largest main component of natural fibers, is known for its biodegradability and availability on earth, which also performs high strength and specific modulus to enhance polymeric materials properties. On the other side, different nature of cellulose which is non-polar and polyurethane which is polar causing poor compatibility between them. This research was focused to enhance the compatibility through interface reaction, also known as grafting technique, between isocyanate and cellulose, and investigate the effects of diisocyanate and cellulose ratio on the properties of hybrid polyurethane-cellulose material. Investigation of the experiment results was conducted by using Fourier-Transform Infrared (FT-IR) to confirm the functional groups, Simultaneous Thermal Analysis (STA) to investigate thermal stability, Scanning Electron Microscope (SEM) to examine the surface morphology and ¹H-Nuclear Magnetic Resonance (¹H-NMR) to probe the structure of hybrid material. The results has revealed that the structure of hybrid material consists of cellulose as chain extender in hard segment which connect two diisocyanate compounds and polyol as soft segment. Furthermore, the addition of cellulose could enhance thermal stability, whereas the addition of diisocyanate could decrease it.

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

1. INTRODUCTION

Over the last century, plastics are already known as a major commodity which are 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 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 synthesis of biomass polyurethane comprising of several stages namely pre-polymerization followed by chain extension. In addition, direct polymerization to create high molecular weight of polyurethane was also reported by reacting with a relatively high molecular weight monomers [3]. The structure of polyurethane itself typically is constructed by an alternating phase called soft segment (SS) and hard segment (HS). 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].

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 [8-16]. The most important content that are extracted from natural fibers is cellulose which possess 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* [17] 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.

According to the aforementioned explanations, this research was performed to study the structure of hybrid polyurethane-cellulose material and to investigate the effect of cellulose to the thermal stability. The experimental results were evaluated by ¹H-NMR to analyse the structure, FTIR to characterize chemical content, STA is to analyze physical changes such as the glass transition temperature (T_g) and melting temperature (T_m) and thermal stability and SEM to observe the morphological surface within hybrid polyurethane-cellulose material.

2. EXPERIMENTAL SECTION

2.1 Materials

The polyurethane firstly was synthesized by pre-polymerization mechanism involving reaction between 15 grams of polyethylene glycol (PEG) Mw: 6000 g/mole as the SS and two moles of 4,4'-methylenebis (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 gram to 2.5 grams. All materials were obtained from Sigma-Aldrich, inc.

2.2 Instrumentation

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

¹H-NMR measurement was carried out to analyse the structure of hybrid polyurethane-cellulose material. Characterization procedure was conducted at DTMM FTUI using NMR Jeol 500MHz. Measurement conditions are 23°C for the temperature and 6 Pa for the pressure (vacuum).

2.2.2 Fourier Transmission Infra-Red (FT-IR)

FT-IR spectra were recorded by using a Perkin-Elmer FTIR spectrometer. It was carried out to obtain an infrared spectrum of absorption of a solid, liquid or gas and to collect the resolution of high spectra on a widely range spectra data. It is utilized to further analyze the structure of material. Each sample recording comprising 30 scans recorded from 400 to 4000 cm⁻¹.

2.2.3 Simultaneous Thermal Analysis (STA)

STA measurements were recorded by using a Perkin-Elmer 6000. It has 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.

2.2.4 Scanning Electron Microscope (SEM)

Surface morphology of polypropylene composite 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. More specifically it was used to clearly investigate the compatibility between cellulose and polyurethane.

2.3. Procedure

Preparations of hybrid polyurethane-cellulose material consist of two steps namely pre-polymerization mechanism and grafting mechanism. Firstly, the pre-polymerization process began with filling Dimethylformamide (DMF) as a solvent and 15 grams of Polyethylene glycol 6000 into a schlenk tube. Then, the schlenk tube was heated to 80°C and stirred up for one hour. Before that 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 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 white viscous liquid. Then, grafting mechanism was started filling a schlenk tube with cellulose as a chain extender with the temperature 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 occurred a phase separation in which the hybrid polyurethane-cellulose precipitated in the bottom of glass vessel and water, DMF and DD were floated on the surface.

3. RESULTS AND DISCUSSION

3.1 The structure of hybrid polyurethane-cellulose material

The pre-polymerization reaction occurred when diisocyanate attack hydroxyl group 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 coupling agent which forms chemical or physical bonding between interface of cellulose and polyurethane. It also can increase the compatibility of hybrid polyurethane-cellulose material [19]. The result of the entire polymerization process is a hybrid material between cellulose and polyurethane.

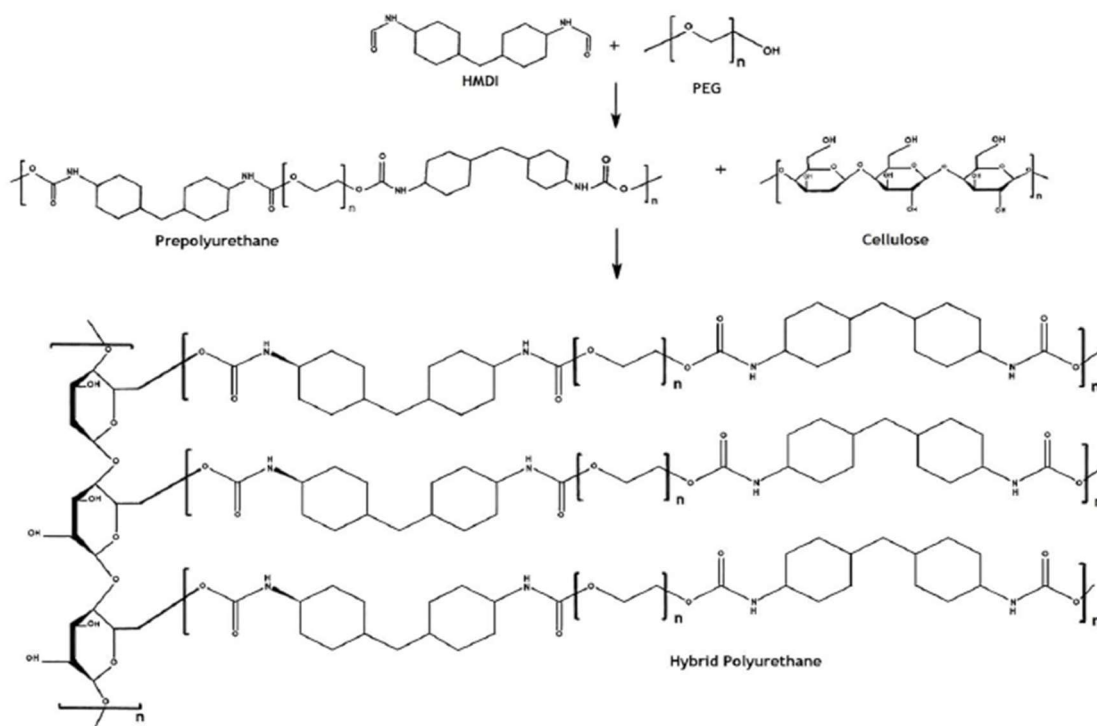


Figure 1. The scheme of formation of hybrid polyurethane-cellulose material.

According to the NMR result, the urethane C=O group and amide group formed in the hybrid structure. The formers depicted at from 0.86 to 1.07 ppm, while the spectrum at 8.22 ppm is for the NH with C=O group and at 3.75 ppm is for the NH and C group.

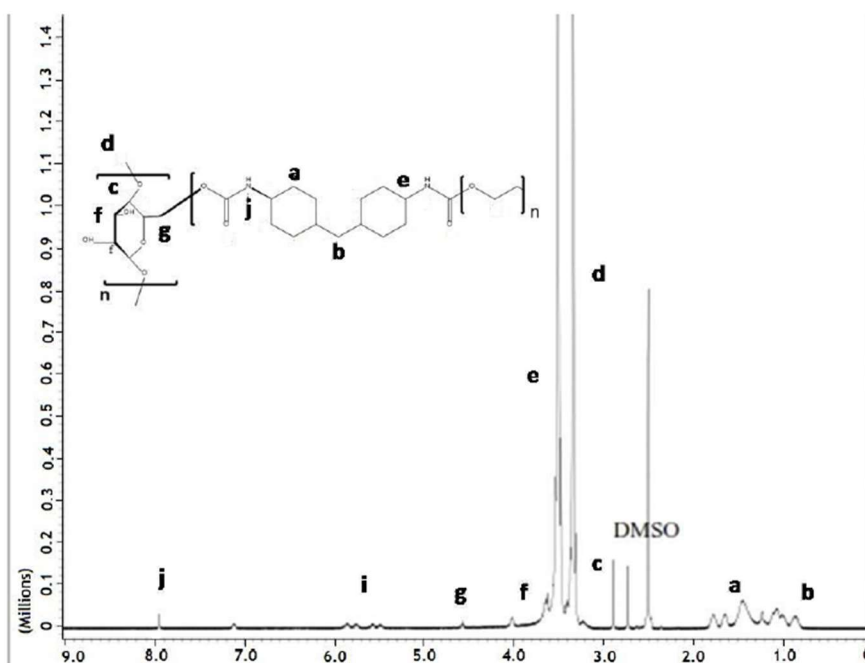


Figure 2. The H-NMR result of hybrid polyurethane-cellulose material.

In order to further depict the structure of hybrid material, FTIR spectra is needed to clearly show the spectra emerged in the hybrid material's structure.

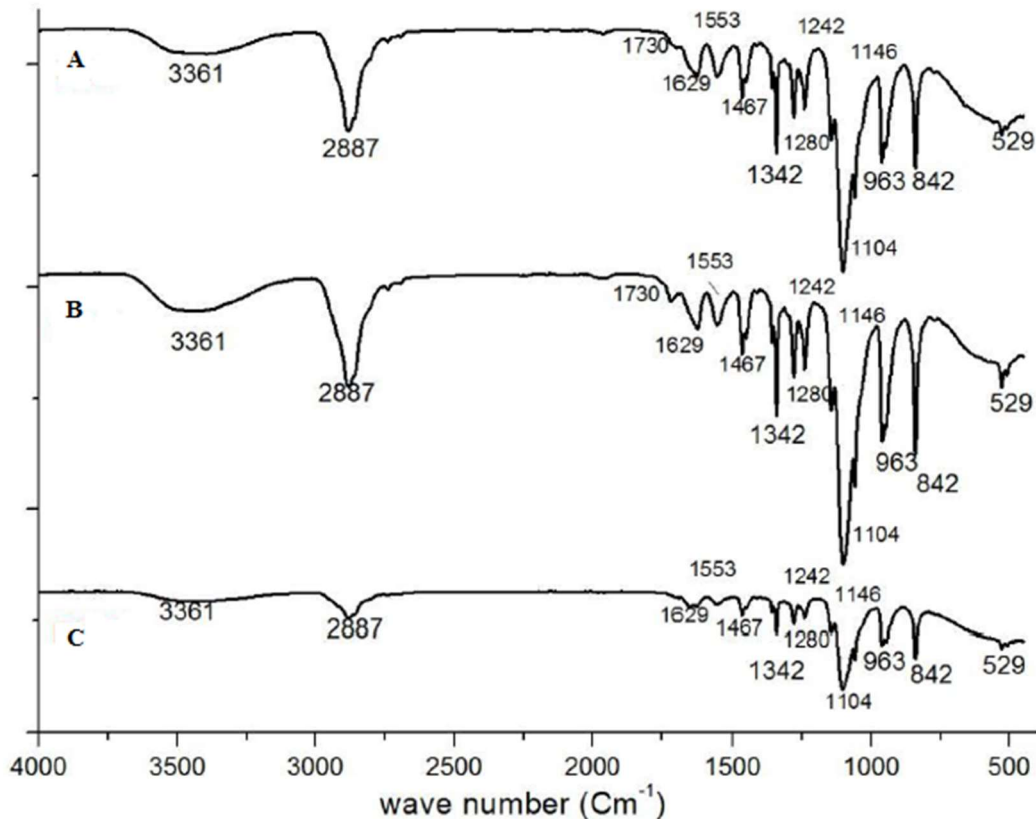


Figure 3. FTIR Spectra of hybrid polyurethane-cellulose material. A) 2.5 grams, B) 1.5 grams, and C) 0.5 gram of cellulose

According to the FTIR spectra, a number of spectra emerge from the graph including amine bonds from 1280 – 1342 cm^{-1} , secondary amine at 2887 cm^{-1} , C-O acyl bond at 1242 cm^{-1} , urethane at 1703 cm^{-1} and amide group at 1553 cm^{-1} . Secondary amine itself indicate that the diisocyanate compound has reacted and created the urethane group with hydrogen atoms. In addition, the addition of cellulose fibers showed on the depth of peaks at 1104 cm^{-1} and 3361 cm^{-1} .

3.2 The thermal stability of 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 as the addition of cellulose itself affects the amount of HS contributing as a chain extender in the hybrid polyurethane-cellulose material. Cellulose which has intra and inter hydrogen bondings then interacted with hydrogen bonding of diisocyanate group in the HS to form cross linking [20,21]

subsequently increasing the temperature of hybrid polyurethane-cellulose material. The greater amount of cellulose added to the hybrid material has definitely increased the temperatures caused by an increase of the interaction of hydrogen bonding.

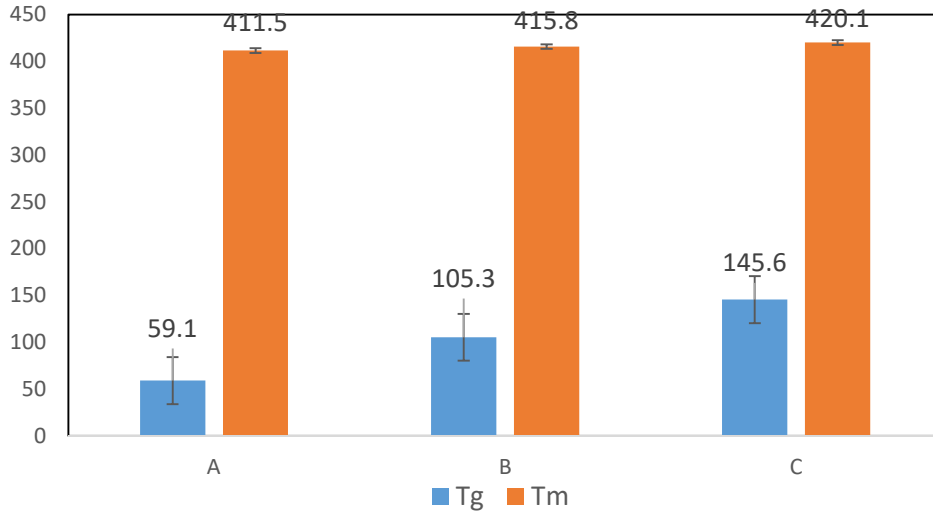


Figure 4. Thermal characteristics of hybrid polyurethane-cellulose material: A) 2.5 grams, B) 1.5 grams, and C) 0.5 gram of cellulose

The addition of cellulose has raised the thermal stability of hybrid polyurethane-cellulose material since it has 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 [22].

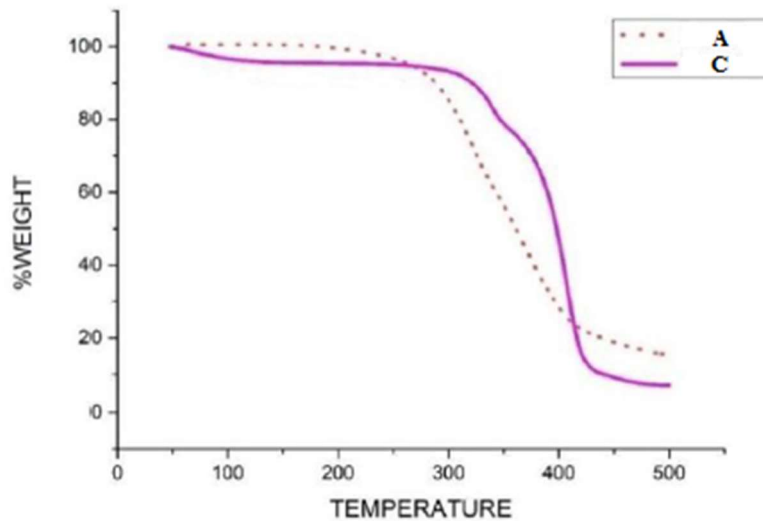


Figure 5. Thermal stability of hybrid polyurethane-cellulose material: A) 2.5 grams and C) 0.5 gram of cellulose

3.3 Morphological surface of 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 hydroxyl group of cellulose [23]. Furthermore, they affect the formation of cross linking region which contributes to stabilize the hybrid material thermally as well.

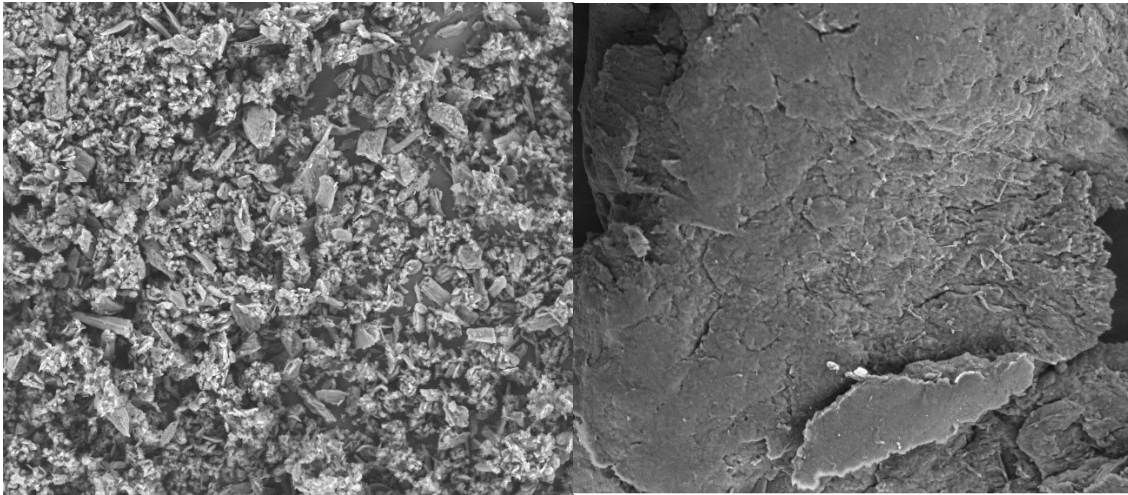


Figure 6. Morphological surface of hybrid polyurethane-cellulose material left (C) and right (A)

According to the graph, the left image (C) shows that the cellulose (white dots) disperses and distributes on the whole surface of hybrid material, while the right image (A) 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 groups and hydroxyl group of cellulose. In other words, the greater amount of cellulose has produced a good distribution and dispersion on the surface of material. As a result, it is thermally stable and has increased the thermal characteristics of hybrid polyurethane-cellulose material.

4. CONCLUSIONS

The structure of hybrid polyurethane-cellulose material consists of cellulose as a chain extender and diisocyanate compound in the HS region and Polyethylene glycol 6000 as a SS region. The addition of cellulose increases both glass transition and melting temperature, thus enhances the thermal stability. Morphological surface shows that the addition of cellulose also affects the thermal properties of hybrid material due to good distribution and dispersion on the surface of material.

5. REFERENCES

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