CHAPTER 22

Biodegradation of Palm-Based Polyurethane Filled with Cellulose by Using *Bacillus Subtilis*

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Abstract

The degradation ability of *Bacillus subtilis* to degrade Palm-based polyurethane foam filled with cellulose (PU-CEL) was evaluated by reacting monoester-OH from palm-kernel oil and isocyanate with ratio 1:1. Addition of microcrystalline cellulose in PU systems was at 20% and 40% by weight, mixed using the mechanical stirrer. Rate of biodegradation of PU-CEL foam was measured by calculation weight loss and FTIR analysis. The weight loss of PU-CEL of 0%, 20% and 40% of PU-Cel foam was taken after 30 days and showed difference 0.62%, 1.49% and 1.91% from its initial weight. The IR spectra analysis shown the loss of peaks from ester functional group (-N-CO-O-). The morphological surface of PU-Cel foam were analyzed at 20x and 50x magnification using digital microscope. Lime water test was used to determine the presence of carbon dioxide when the PU-CEL foam was digested by the *Bacillus subtilis.*. The clear lime water turned cloudy indicating the presence of carbon dioxide. This study provides the evidence on how the susceptibility of cross-linked polymer over degradation can be tailored by substituting the petroleum-based polyol to palm-based polyol and the addition of suitable biodegradable filler such as cellulose.

Introduction

Polyurethane is one of very versatile man-made polymer in its group. It has a very wide range of applications based on its physical and chemical properties. Dr. Otto Bayer was the first person to discover and researched about polyurethane in 1937 (Howard, 2002). Polyurethane is made of reactions between polyisocyanates and polyols, derived from the crude oil petroleum (Zhang and Luo, 2015). The reactions of both groups are synthesized by polycondensation process.

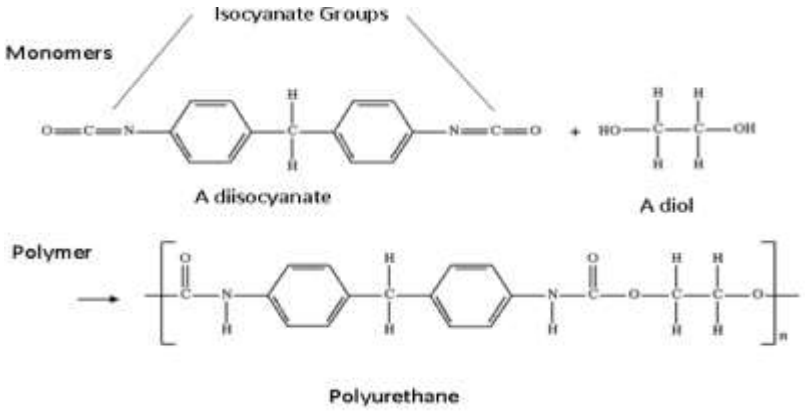

Fig. 1: Structure of monomers and polymers of polyurethane
(Source: Badri et.al., 2010)

The commercial polyurethane is derived from the petroleum-based polyol with isocyanates, which the resources are non-renewable and depleting as continually being used in vast amount. Thus, as the technologies are developing fast nowadays, the polyurethane is reinforced with biodegradable properties from bio-based polyols and natural resources which will enhance its productivity and properties (Hadjadj *et al*., 2015). Bio-based polyurethane is derived from the naturally occurring resources such as from starch, sugar, and natural oil polyols. According to Sang *et.al*., (2013) the natural oil polyols comes from soybeans polyols, rapeseed oil polyols, castor oil polyols and palm oil polyols. These three types of natural oil polyols are the most preferable in industry as they are of abundant and renewable resources that can be obtained at a cheaper cost.

As for the natural oil polyurethane, the properties may be slightly different from the petroleum-based polyurethane. The physical properties can show a lacking in terms of physical strength and modulus. Thus, addition of additives will probably be a help to reinforce the optimal properties of the produced polyurethane to meet the need of specific applications (Xiaojian *et.al*., 2015). The natural additives commonly used in the production of polyurethane are the cellulose, starch and chitosan. These are the types of naturally occurring polymers. Cellulose is known for its abundant naturally occurring

polymer resources which can be renewable and undergoes biodegradation (Li *et al.*, 2013; Saralegi *et.al*., 2013). The addition of cellulose to the polyurethane will enhance its mechanical properties and also help with the natural degradation of polyurethane (Floros *et al.*, 2012).

Methodology

Synthesis of PU-CEL

A polyhydric compound was formed by mixing homogeneously diethanolamine (DEA), diethylene glycol (DEG) and potassium acetate (KA) with a ratio of 90:7:3. Palm kernel oil (PKO) was added to the polyhydric mixture at a stochiometric ratio with continuously stirring in a glass reactor until reach temperature at 195 ˚C forming polyol. During esterification and condensation process of polyol, nitrogen gas (N_2) was flushed throughout the process in order to prevent the oxidation reaction occur (Badri, 2012). The microcrystalline cellulose (MCC) was added into polyol with 20% and 40% by weight ratio. 140 g of crude 2,4-diphenylmethane diisocyanates (MDI) was added to 100 g mixture of resin with ratio of 140:100 parts by weight, pbw. The blowing agent (water) added to the mixture and foaming occurred after a short time. Neat polyurethane prepared in similar steps with the absence of MCC. The produced PU-CEL were cut into small cubes to be ready for biodegradation process.

Biodegradation of PU-CEL

The degradation was conducted using *Bacillus subtilis* bacteria. The bacteria was cultured and incubated in first, nutrient agar and transferred into nutrient broth. The bacterial broth then poured into each container sample containing PU-CEL.

Results and Discussion

FTIR (Fourier Transform Infrared Spectroscopy)

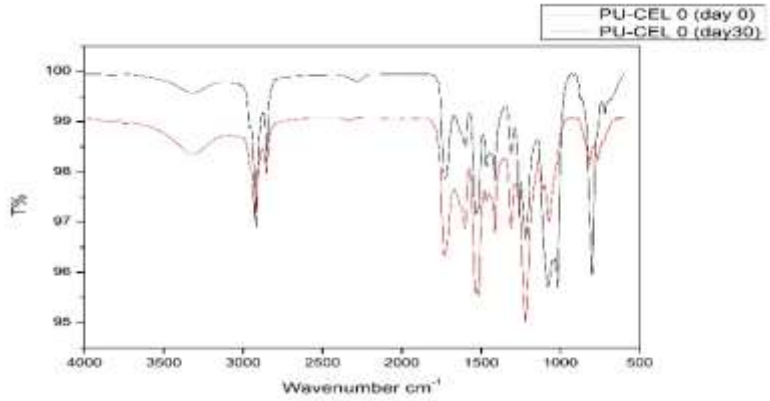

Fig. 2: FTIR result for PU-CEL 0 at day 0 and day 30.

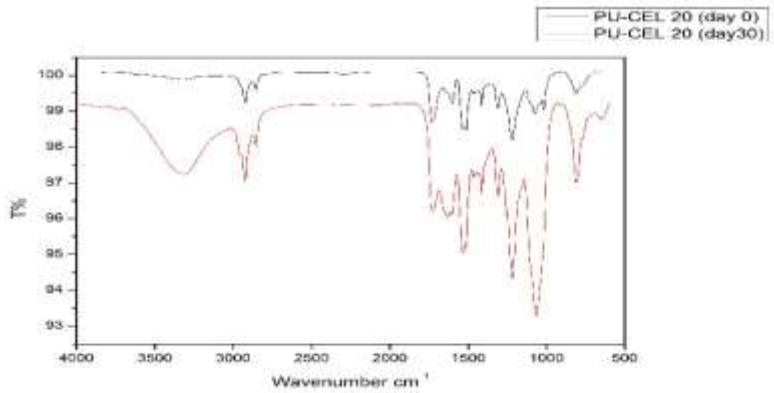

Fig. 3: FTIR result for PU-CEL 20 at day 0 and day 30.

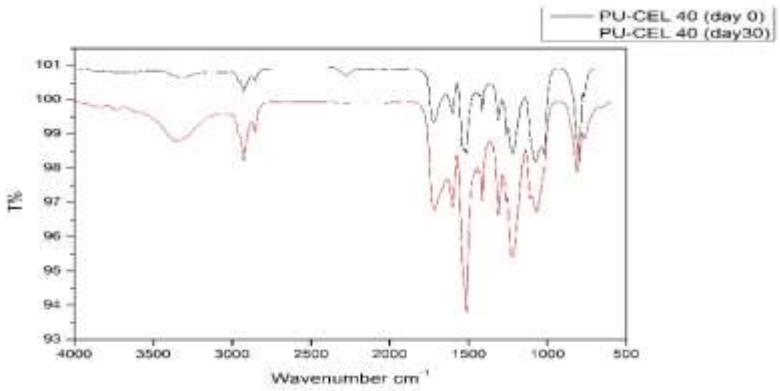

Fig. 4: FTIR result for PU-CEL 40 at day 0 and day 30.

Table 1:
Functional groups assignment of PU-CEL 0, PU-CEL 20 and PU-CEL 40 before and after bacterial degradation.

Functional group	**Wavenumber cm-1**					
	PU-CEL 0		**PU-CEL 20**		**PU-CEL 40**	
	Day 0	**Day 30**	**Day 0**	**Day 30**	**Day 0**	**Day 30**
C-H (aromatic) bending	798.26	761.84	798.67	763.87	814.53	808.38
C-O (ester)	1018.78	-	1016.74	-	1018.72	-
N-(C=O)-O (amine)	1075.43	1073.41	1074.22	1063.29	1074.22	1067.34
-(C=O)-O- (ester)	1728.90	1730.92	1728.41	1724.85	1718.50	1714.73

Due to the degradation process by *Bacillus subtilis* bacteria, some functional group showed changes either shifting of wavenumber or disappearance of peaks. For ester functional group (C-O), the peaks disappeared after 30 days of incubation with the bacteria. Some other peaks shown shifting to lower wavenumber. These results indicated that the bacteria has degraded the solid PU-CEL samples within 30 days on incubation.

Weight Loss (percentage, %)

Table 2
Tabulation of average percentage weight loss of PU-CEL 0, PU-CEL 20 and PU-CEL 40

Type	Control, %	Weight loss, %		Average, %
		1	2	
PU-CEL 0	0.01	0.17	1.06	0.62
PU-CEL 20	0.02	1.37	1.60	1.49
PU-CEL 40	0.02	2.01	1.80	1.91

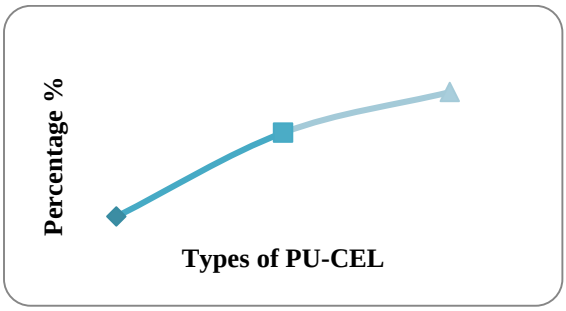

Fig. 5: Graph showing the increasing trend of weight loss in percentage value for PU-CEL 0, PU-CEL 20 and PU-CEL 40 after 30 days.

Morphology Analysis

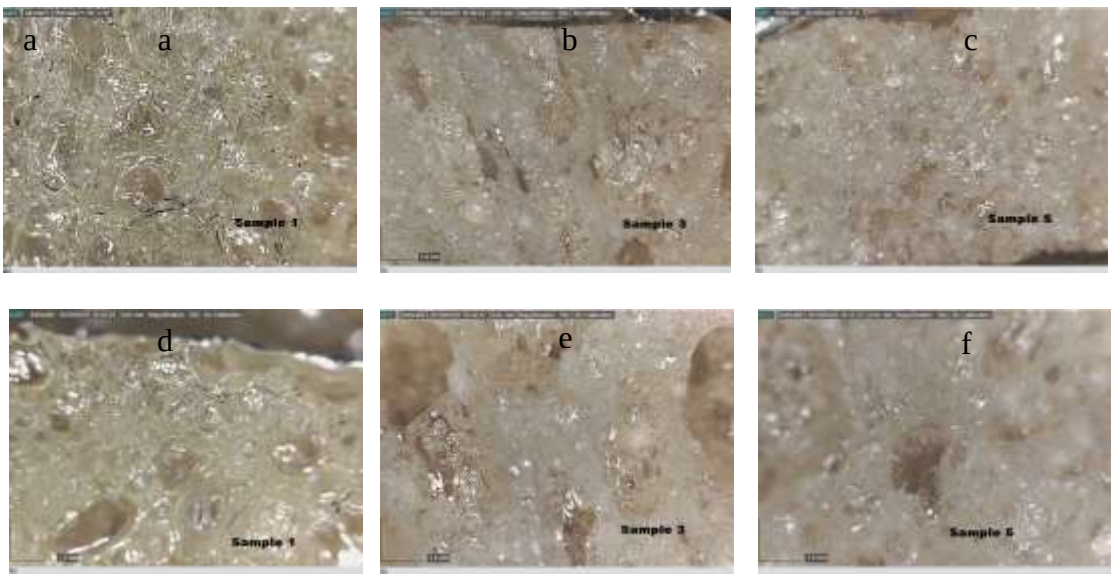

Fig. 6 Magnification of PU-CEL at 20x (a: PU-CEL 0, b: PU-CEL 20 , c: PU-CEL 40); Magnification of PU-CEl at 50x (d: PU-CEL 0, e: PU-CEL 20, f: PU-CEL 40)

Conclusion

A polyurethane made of palm kernel oil polyol with microcrystalline cellulose as a filler has been successfully developed. The morphology analysis exposed that MCC has dispersed uniformly in the polyurethane system. Results from FTIR analysis and weight loss analysis indicate *Bacillus subtilis* able to degrade PU-CEL 0, 20 and 40 and proved that the addition of cellulose as a filler increased the degradation rate.

References

Badri, K. H. (2012). Biobased polyurethane from palm kernel oil-based polyol (page 447-470). Intech.

Badri, K. H., Wong, C. S., Shahrom, M. S. R., Liow, C. H., Baderuliksan, N. Y., & Norzali, N. R. A. (2010). FTIR spectroscopy analysis of the prepolymerization of palm-based polyurethane. *Journal of Solid State Science and Technology, 18*(2), 1-8.

Floros, M., Hojabri, L., Abraham, E., Jose, J., Thomas, S., Pothan, L., Leao, A. L., & Narine, S. (2012). Enhancement of thermal stability strength and extensibility of lipid-based polyurethane with cellulose-based nanofibres. *Journal of Polymer Degradation and Stability, 97*, 1970-1978.

Hadjadj, A., Jbara, O., Tara, A., Gilliot, M., Malek, F., Maafi, E. M., & Tighzert, L. (2016). Effect of cellulose fibre content on physical properties of polyurethane based composites. *Journal of Composite Structres, 135*, 217-223.

Li, S., Li, C. Chunjie, Li, C. Changyu, Yan, M., Wu, Y., Cao, J., & He, S. (2013). Fabrication of nano-crystalline cellulose with phosphoric acid and its full application in a modified polyurethane foam. *Journal of Polymer Degradation and Stability, 98*, 1940-1944.

Sang, H. P., Kyung, W. O., & Seong, H. K. (2013). Reinforcement effect of cellulose nanowhisker on bio-based polyurethane. *Journal of Composites Science and Technology, 86*, 82-88.

Saralegi, A., Rueda, L., Martin, L., Arbelaiz, A., Eceiza, A., & Corcuera, M. A. (2013). From elastomeric to rigid polyurethane/cellulose nanocrystal bionanocomposites. *Journal of Composites Science and Technology, 88*, 39-47.

Xioajian, Z., Sain, M. M., & Oksman, K. (2015). Semi rigid biopolyurethane foams based on palm-oil polyol and reinforced with cellulose nanocrystals. *Journal of Composites: Part A.*