Journal of Metals, Materials and Minerals. Vol.17 No.1 pp.17-23, 2007

Processing and Properties of Palm Oil-Based Rigid Polyurethane Foam

Saowaroj CHUAYJULJIT, Tarasai SANGPAKDEE
and Onusa SARAVARI*

Department of Materials Science, Faculty of Science, Chulalongkorn University,
Bangkok 10330, Thailand

Received Feb. 19, 2007
Accepted May 8, 2007

Abstract

Rigid polyurethane (PU) foam has been prepared from palm oil-derived polyol. The polyol was synthesized by transesterification reaction of palm oil and pentaerythritol using calcium oxide as a catalyst. The obtained palm oil-based polyol was reacted with commercial polymeric diphenylmethane diisocyanate in the presence of water (blowing agent), *N,N*-dimethylcyclohexylamine (catalyst) and polydimethylsiloxane (surfactant) to produce rigid PU foam. The effects of the amount of the catalyst and surfactant on foam properties (i.e. density, compressive strength and thermal behaviors) were studied. It was found that the density of the foams decreased whereas the compressive strength increased with the increasing amount of catalyst and that they were in the range of 38.7-59.0 kg/m^3 and 193.6-268.4 kPa, respectively, while an increased amount of surfactant showed negligible effect on these two properties. Furthermore, TGA revealed that the degradation temperature of the prepared foams was about 377°C. Moreover, scanning electron micrographs showed that the cells of the obtained PU foams were closed cells. In addition, the foams were found to have higher number of cells as the concentration of catalyst increased, while the uniformity of cells increased with increasing amount of surfactant.

Keywords : palm oil**,** polyol, polyurethane foam

Introduction

Rigid polyurethane (PU) foam is an available material with the lowest thermal conductivity among foamed polymers used commercially.(4) It has been widely utilized in the appliance and construction industry because of its excellent and unique combination of thermal insulation and mechanical properties. In addition, it is light in weight and versatile, and is employed increasingly in a variety of applications that include thermal and acoustic insulation, core materials for sandwich panels, fabrication of furniture, and flotation materials. PU foams perform well in most areas of low-temperature insulations. Products with density ranging from approximately 30 to 200 kg/m3 withstand temperatures down to -196°C.(2) PU foam is usually synthesized by the reaction of diisocyanates with polyols. In general, blowing agent, catalyst and surfactant are also employed to regulate the properties and morphology of the cell structures. Most commercial diisocyanates and polyols are derived from petroleum which are rapidly diminishing natural resources.(1) Between the two raw materials, to date only polyols can be synthesized from renewable resources such as oils, fats and starch. Several researchers have described the use of renewable raw materials for PU preparation. Some of them have investigated the possibilities of converting vegetable oils into polyols for producing PU foams. The Malaysian Palm Oil Board (MPOB) started producing polyol from epoxidized palm oil in the late 1980 s.(5, 6) Chian, *et al.* (1998) used polyol derived from refined-bleached-deodorized (RBD) palm oil to produce rigid PU foam. The obtained PU foams provided a density of approximately 200 kg/m3 with compressive strength greater than 1 MPa. Salmiah, *et al.* (2001) indicated that palm oil-based polyols can be used for producing semi-rigid and rigid foams to be employed as insulators and wall- and ceiling-panels.

Each year, Thailand produces a large amount of palm oil not only for domestic consumption, but also for exportation. Due to the cheap and abundant supply of palm oil, the

---

Tel : (662) 2185062; fax : (662) 2185561; E-mail address : sonusa@chula.ac.th

potential use of polyol derived from palm oil as an alternative raw material for preparing rigid PU foam is possible. However, palm oil- which is a triacylglycerol produced by the palm trees- has no functional groups suitable to react with isocyanate to form urethane bonds.(1) In this work, treatment of palm oil with pentaerythritol produced a highly (OH) functionalized product. The chemical structure of the obtained polyol was characterized by FTIR technique. The rigid PU foam was prepared from the reaction of palm oil-based polyol and commercial polymeric diphenylmethane diisocyanate (PMDI) in the presence of water, N,N-dimethyl-cyclohexylamine (DMCHA) and polydimethylsiloxane (PDMS) as the blowing agent, catalyst and surfactant, respectively. In this study, the effects of catalyst content and surfactant concentration on the properties and morphology of the foams were investigated.

Experimental

Materials

Palm oil with acid value of 2, iodine value of 52 and specific gravity of 0.907 was obtained from Olene Co., Ltd. Pentaerythritol and PMDI (with isocyanate content of 31.4 wt%) were supplied by Siam Chemical Industry Co., Ltd. DMCHA was provided by South City Co., Ltd. and PDMS was donated by Thai Petrochemical Industry Co., Ltd. All materials were used as received without further purification. Preparation and characterization of palm oil-based polyol

Palm oil (200 g) in a 500 ml four-necked round-bottom flask, equipped with a stirrer, a thermometer, a condenser, a water separator, and N2 gas inlet, was heated up to 150°C with stirring at the speed of 500 rpm under nitrogen atmosphere. Pentaerythtritol (89 g) was added and the mixture was stirred and heated to 200°C followed by the addition of calcium oxide (0.15 g). The temperature was then raised to 245°C and the mixture was maintained at this temperature until a sample (1 part) was soluble in ethanol (3 parts). The obtained product was allowed to cool to room temperature under nitrogen atmosphere and its chemical structure was analyzed using an FTIR spectrophotometer (Perkin-Elmer FTIR System 200). The hydroxyl value was determined based on ASTM D 4274-94 Method C and the viscosity was determined using a Brookfield viscometer (Model RVT).

Preparation of Rigid PU Foam

The PU foams were prepared by adding PMDI to the polyol mixture, which consisted of a palm oil-based polyol, distilled water, DMCHA and PDMS with stirring at 1000 rpm using a high-speed mixer for 1 min. At the creamy stage (the mixture turning creamy), the mixture was poured into an open mold and allowed to rise freely. The cream time (the time from mixing to initiation of foaming) and rise time (the time from mixing to full expansion of foaming) were recorded. After that, the foam was removed from the mold and allowed to postcure for 2 days at room temperature before cutting into the test specimens.

Table 1 shows the chemical compositions of the PU foam samples. To investigate the effect of the catalyst and the surfactant contents on the properties of the PU foam, the amount of DMCHA and PDMS were varied from 0.25-1 php (parts per hundred polyol) and 2.5-10 php, respectively. The amount of polyol, PMDI, and distilled water were fixed at 100, 150, and 3 php, respectively.

Table 1. Chemical Compositions of Rigid Polyurethane Foam.

Sample	PMDI (g)	Polyol (g)	Distilled water[a] (g)	DMCHA[b] (g)	PDMS[c] (g)
1	60	40	1.2	0.1	1
2	60	40	1.2	0.2	1
3	60	40	1.2	0.3	1
4	60	40	1.2	0.4	1
5	60	40	1.2	0.1	2
6	60	40	1.2	0.2	2
7	60	40	1.2	0.3	2
8	60	40	1.2	0.4	2
9	60	40	1.2	0.1	3
10	60	40	1.2	0.2	3
11	60	40	1.2	0.3	3
12	60	40	1.2	0.4	3
13	60	40	1.2	0.1	4
14	60	40	1.2	0.2	4
15	60	40	1.2	0.3	4
16	60	40	1.2	0.4	4

[a] 3 parts by weight based on 100 parts of the polyol.
[b] 0.25-1 parts by weight based on 100 parts of the polyol.
[c] 2.5-10 parts by weight based on 100 parts of the polyol.

Characterization and Property Measurements of PU Foam

The chemical structures of the obtained PU foams were characterized using an FTIR spectrophotometer (Perkin-Elmer FT-IR System 200). A scanning electron microscope (Jeol JSM-5900 LV) was used to examine the morphology of the foam. The accelerated voltage was 15 kV.

For density measurement, the PU foams were cut into specimens with dimensions of about 50 × 50 × 30 mm (width × length × thickness). The exact dimensions were measured using a vernier caliper. The specimens were accurately weighed to determine their densities using the equation, density = mass/volume. The density for each foam was ascertained using the average value from six specimens.

The compressive strength of the foams was determined using an Instron Universal Testing Machine (LLOYD L500) with a load cell of 1.5 kN. The test was performed according to ASTM D 1621-00. The size of the specimen was 50 × 50 × 25 mm (width × length × thickness), and the crosshead speed was 12.5 mm/min. The compressive stress at 10% deformation of its original thickness was calculated. The compressive strength for each foam was obtained using the average value from six specimens.

Thermogravimetric analysis (TGA) of the foams was performed using a thermogravimetric analyzer (Mettler Toledo TGA/SDTA 851e) at the temperature range from 35 to 800°C with the heating rate of 10°C/min under nitrogen atmosphere.

Results and Discussion

Characterization of Palm Oil-Based Polyol

The obtained palm oil-based polyol was a viscous yellowish liquid with viscosity of 355 poises which was much higher than that of the regular palm oil (60 poises). This high viscosity is due to hydrogen bonding associated with the hydroxyl groups. This polyol had a hydroxyl value of 385 mg KOH/g, which is suitable for rigid PU foam preparation.(7)

The FT-IR technique was employed to analyze the functional groups of palm oil-based polyol. Figure 1 shows the spectra of palm oil and palm oil-based polyol. The presence of hydroxyl group in the palm oil-based polyol is reflected by the transmittance peaks at wavenumbers of 3374 cm^{-1}, 1100 cm^{-1} (due to -OH in secondary alcohol) and 1050 cm^{-1} (due to -OH in primary alcohol). Furthermore, the obtained product was found to completely dissolve in ethanol. The results indicate that palm oil was converted into a highly (OH) functionalized product by transesterification reaction.

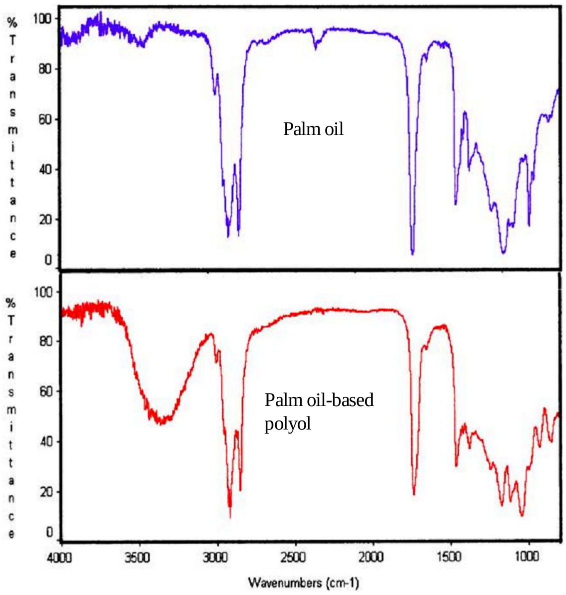


Figure 1. FTIR spectra of palm oil and palm oil-based polyol.

Preparation of Rigid PU Foam

When water is used as a blowing agent, a reaction occurs between the water and the isocyanate group to form an amine and carbon dioxide gas in the form of bubbles. After several seconds, the carbon dioxide produced in situ will diffuse into small air bubbles and enlarge them giving the mixture a creaming appearance. The time taken for the appearance to change, as measured from the initial mixing, is known as the cream time. As more carbon dioxide is generated, the bubbles expand and the foam begins to rise. While the bubbles are expanding, a polymerization reaction takes place in the liquid phase and the viscosity starts to increase. At full rise time, the reactions generating the gas stop. In this work, the cream time and rise time varied in a range of 32-148 s and 179-529 s, respectively, as shown in Figures 2 and 3. Both the cream time and rise time of the prepared foams are longer than those of a typical rigid PU foam.(11) This phenomenon could be attributed to the secondary hydroxyl groups, which have lower reactivity existing in the palm oil-based polyol. It was previously found that an increase of the amount of catalysts in the foam formulation shortens the reaction time.(3) This is in good agreement with our observation that the cream time and rise time of the prepared foams were reduced with increasing amount of DMCHA catalyst. On the other hand, as the amount of DMCHA remained constant, the increase in PDMS would slightly increase the cream time and rise time of the foams. This may be explained by the fact that increasing the surfactant level will effectively reduce functional group concentration. Consequently, the rate of foam rise and overall reaction rate are reduced.(8) The results indicate that the catalyst plays an important role to control the foaming and curing rate of the rigid PU foam, whereas the surfactant seems to have only small effect on the foaming reaction.

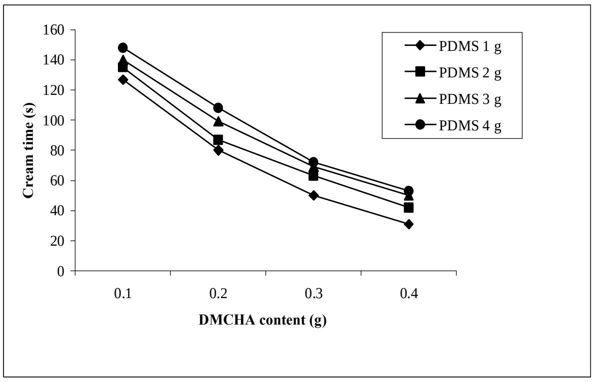


Figure 2. Cream time of rigid PU foams.

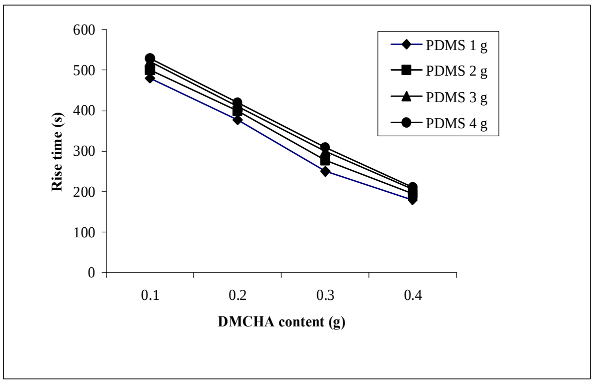


Figure 3. Rise time of rigid PU foams.

Characterization of PU Foam

The foams produced are very rigid and light weight. They are light yellow due to aromatic isocyanate content. However, we observed that the yellowness of the foams tends to be reduced with increasing amount of DMCHA.

The FTIR spectra of the PU foams prepared from palm oil-based polyol shown in Figure 4 and Figure 5 exhibit the characteristic peaks of urethane bonds at wavenumbers of 3385 cm^{-1} (-NH stretching), 1741 cm^{-1} (-CO stretching), 1514 cm^{-1} (-NH bending) and 1382 cm^{-1} (-OCONH asymmetric stretching). They also exhibit a characteristic peak of unreacted NCO groups at 2273 cm^{-1}. However, it can be seen (in Figure 4) that the intensity of these peaks decreases as the amount of DMCHA increases. This confirms the accelerated effect of the catalyst on the reaction of isocyanates with water and with polyols. On the other hand, Figure 5 shows that with various amount of PDMS, the intensity of the peaks corresponding to the NCO group is nearly the same. This suggests that the surfactant has no effect on the reaction rate.

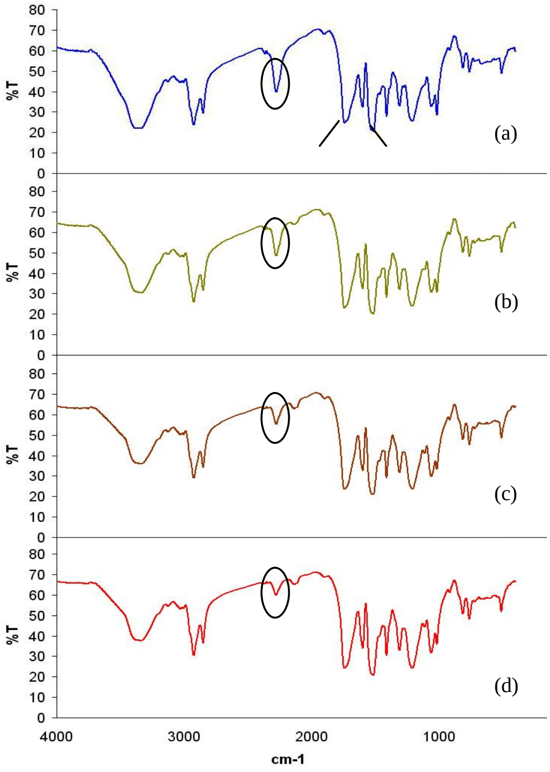


Figure 4. FTIR spectra of rigid PU foams prepared from 1 g PDMS and DMCHA (a) 0.1 g, (b) 0.2 g, (c) 0.3 g, and (d) 0.4 g.

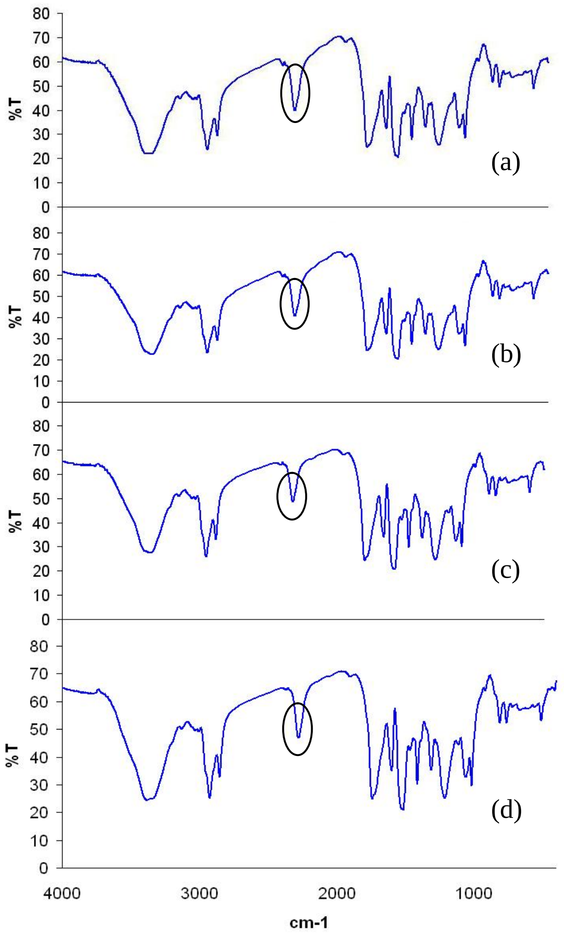
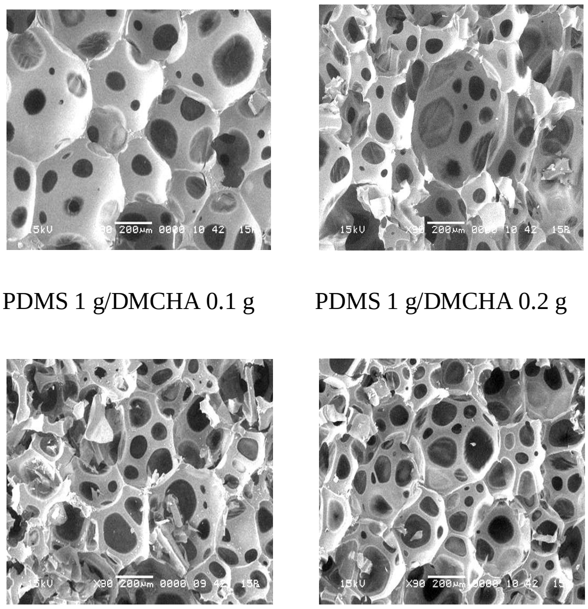


Figure 5. FTIR spectra of rigid PU foams prepared from DMCHA 0.1 g and PDMS (a) 0.1 g, (b) 2 g, (c) 3 g, and (d) 4 g.

Morphology of PU Foam

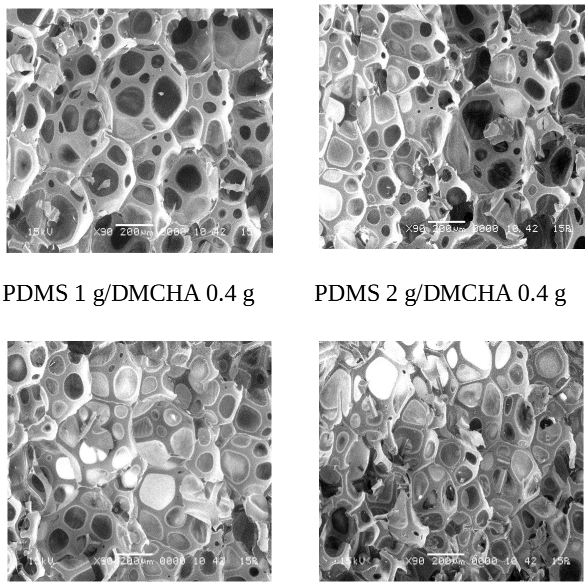
The cross-sectional surfaces of PU foam observed with scanning electron microscope (SEM) are shown in Figures 6 and 7. The shapes of the cells are spherical with many windows. The spherical shape cells are found to be closed cells. Figure 6 shows that the foams have a higher number of cells as the concentration of DMCHA increases. This indicates that more carbon dioxide gas has been generated at the higher level of catalyst and the number of closed cells will be increased. Figure 7 shows the micrographs of the PU foam samples with different PDMS contents. It is found that the cell size of PU foams decreases and the uniformity of the cells increases with increasing amount of surfactant. It is known that this silicone surfactant lowers the surface tension between cells, and it stabilizes the cell walls (Seo, et al. 2002). The silicone surfactant prevents the coalescence of the cell, so it makes the cell size smaller.



PDMS 1 g/DMCHA 0.1 g PDMS 1 g/DMCHA 0.2 g

PDMS 1 g/DMCHA 0.3 g PDMS 1 g/DMCHA 0.4 g

Figure 6. SEM micrographs of rigid PU foams with various amount of the catalyst.



PDMS 1 g/DMCHA 0.4 g PDMS 2 g/DMCHA 0.4 g

PDMS 3 g/DMCHA 0.4 g PDMS 4 g/DMCHA 0.4 g

Figure 7. SEM micrographs of rigid PU foams with various amount of the surfactant.

Properties of PU Foam

The densities of the PU foams blown by distilled water are presented in Figure 8. It is found that when the DMCHA increases, the densities of the PU foams are decreased. This suggests that at a higher amount of catalyst, the foam rises more rapidly and causes a material of reduced density. On the other hand, the densities of the foams do not change significantly with the surfactant content.

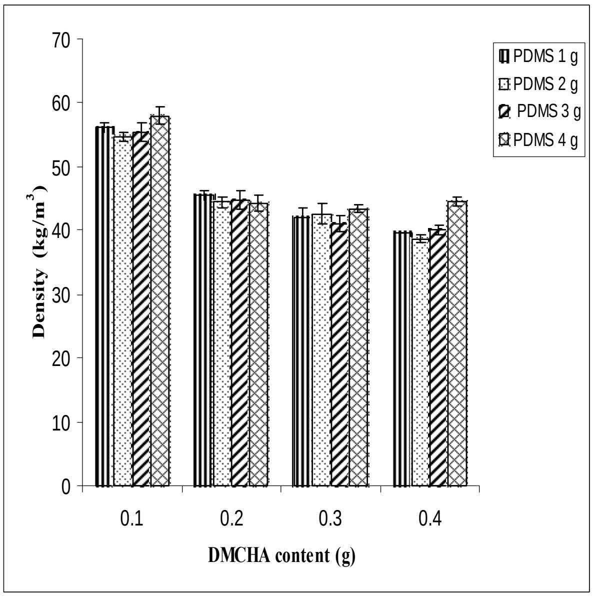


Figure 8. The effect of catalyst and surfactant on rigid PU foam density.

As shown in Figure 9, the compressive strength of the PU foams with various amount of DMCHA and PDMS is in the range of 194.6-268.4 kPa. It can be seen that the compressive strength decreases with an increase in DMCHA from 0.1 to 0.4 g at an equal content of PDMS. It is generally known that the mechanical properties of a cellular material mainly depend on its density. Therefore, when the amount of DMCHA is increased, the decrease of the compressive strength may be due to the decrease of foam density. On the other hand, if DMCHA is kept constant, the compressive strength of the PU foam is slightly different with various amount of PDMS. This indicates that the surfactant plays an insignificant role on the foam density as shown in Figure 8. Figure 10 shows the relationship between the compressive strength and the foam density. It can be clearly seen that density provides a significant effect on the compressive strength of the rigid PU foam.

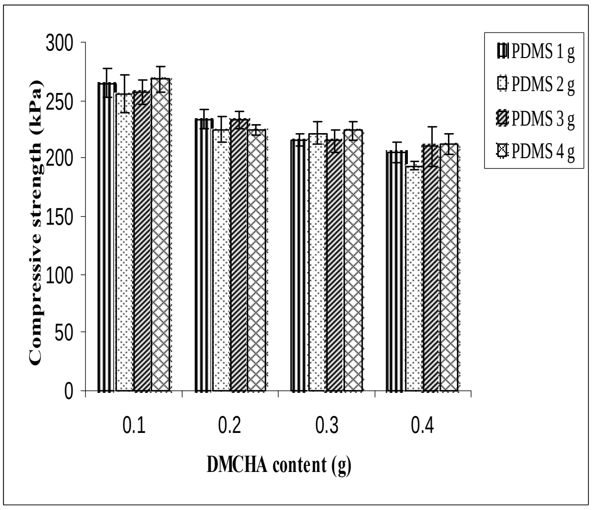


Figure 9. The compressive strength of rigid PU foams with various amount of the catalyst and surfactant.

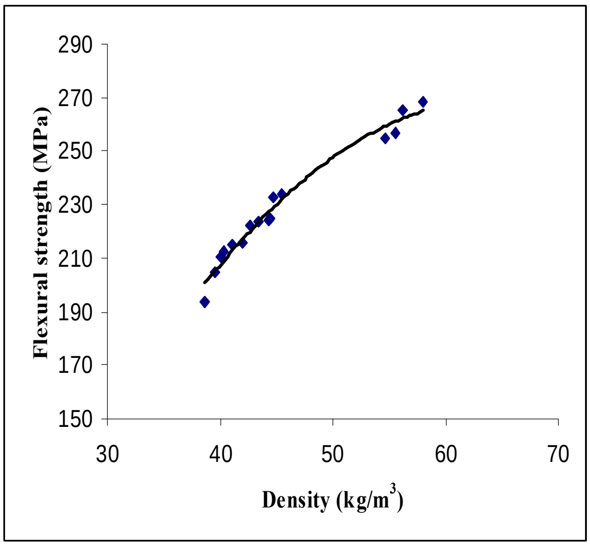


Figure 10. The compressive strength of rigid PU foams versus foam density.

It can be seen from the TGA thermogram as shown in Figure 11 that two stages of degradation occurred during heating. The first stage is at 285°C which may correspond to urethane bond break, while the second stage occurred at 377°C and may be due to polyol decomposition. All the rigid PU foams have approximately the same degradation temperature (Td).

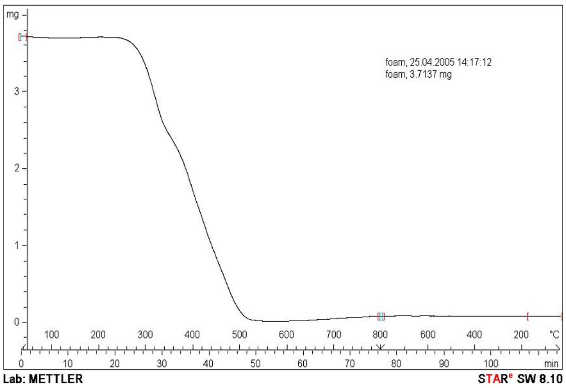


Figure 11. Example of TGA thermogram of rigid PU foam.

Conclusion

The polyol based on palm oil could be used as one of the raw materials for preparing rigid polyurethane foams after transesterification of the palm oil with pentaerythritol. The prepared polyol was reacted with commercial PMDI in the presence of DMCHA catalyst and PDMS surfactant using distilled water as a blowing agent. The PU foams obtained exhibited densities and compressive strengths in the range of 38.7-58.0 kg/m3 and 194-268 kPa, respectively. The results of the morphology by SEM revealed that the cells of these foams were closed cells. Increasing catalyst content in the foam formation shortens the reaction time and increases the number of cells and compressive strength. Meanwhile, the surfactant seems to have only small effect on the foaming reaction and properties of the foam. From TGA results, all the rigid PU foams have approximately the same degradation temperature of about 377°C.

The authors gratefully acknowledge Chulalongkorn University for financial, materials and instruments support. We also would like to thank Olene Co., Ltd., Siam Chemical Industry Co., Ltd., South City Co., Ltd., and Thai Petrochemical Industry Co., Ltd. for materials support.

References

1. Chian, K.S. and Gan, L.H. 1998. Development of a rigid Polyurethane Foam from palm oil. *J. Appl. Polym. Sci*. **68** : 509.

2. Demharter, A. 1998. Polyurethane Rigid Foam, a Proven Thermal Insulating Material for Applications between +130°C and -196°C. *Cryogenics*. **38** : 113.

3. John, J., Bhattachaiya, M. and Turner, R. B. 2002. Characterization of Polyurethane Foams from Soybean oil. *J. Appl. Polym. Sci*. **86** : 3097.

4. Kacperski, M. and Spaychaj, T. 1999. Rigid Polyurethane Foams with Poly(ethylene terephthalate)/Triethanolamine Recycling Products. *Polym. Adv. Technol*. **10** : 620.

5. Maznee, T. I., Norin, Z. K. S., Ooi, T. L., Salmiah, A. and Gan, L. H. 2001. Effects of Additives on Palm-Based Polyurethane Foams. *J. Oil Palm Res*. **13** : 7.

6. Norin, Z. K. S., Ooi, T. L. and Salmiah, A. 2004. Effect of Triethanolamine on the Properties of Palm-Based Flexible Polyurethane Foams. *J. Oil Palm Res.* **16** : 66.

7. Oertel, G. 1994. *Polyurethane Handbook*. 2nd ed. Hanser : Munich.

8. Pentrakoon, D. and Ellis, J. W. 2005. *An Introduction to Plastic Foams.* Bangkok : Chulalongkorn University Press.

9. Salmiah, A. 2001. Palm-based polyol and polyurethanes. *MPOB Technology*. **24** : 29.

10. Seo, W. J., Jung, H. C., Hyun, J. C., Kim, W. N., Lee, Y. B., Choe, K. H. and Kim, S. B. 2003. Mechanical, morphological, and thermal properties of rigid polyurethane foams blown by distilled water. *J. Appl. Polym. Sci.* **90** : 12.

11. Woods, G. 1990. *The ICI Polyurethanes Book.* 2nd ed. New York : Wiley.