

Mechanical Properties and Fire Retardant Behavior of Polyurethane Foam Reinforced with Oil Palm Empty Fruit Bunch

G. S. Tay, L. N. Ong, H. D. Rozman

School of Industrial Technology, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Received 12 April 2010; accepted 23 July 2011

DOI 10.1002/app.35568

Published online 17 December 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The objective of this study was to investigate the effects of isocyanate/hydroxyl ratio and ammonium polyphosphate (APP) content on the properties of polyurethane foam. Polyurethane (PU) foam was prepared from polymeric diphenylmethane diisocyanate and polyethylene glycol with molecular weight of 200, reinforced with oil palm empty fruit bunch (EFB) using one shot process. The effect of EFB content on the properties of PU foam was also studied. It was noticed that EFB enhanced the properties of the PU foam. This was due to EFB acting

as hard segment in PU foam system. The NCO/OH ratio played an important role in determining the properties of the PU foam produced. However, since EFB is a highly flammable material, APP was introduced to the PU foam system. From the results, APP improved the fire retardant behavior of the PU foam. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 158–164, 2012

Key words: polyurethane; limited oxygen index; fire retardancy; oil palm empty fruit bunch

INTRODUCTION

The use of natural fiber has been the interest of many scientific studies due to vast advantages offered, such as lower production cost and less abrasive to equipment. Natural fiber or lignocellulosic materials based plastic composite is among the most rapidly growing markets in this decade. According to Rossi (2002),¹ the demand for these products in North America and Western Europe amounted to about 1.3 billion pounds valued at roughly US\$ 900 million, which represents almost 20% growth from the year 2001 level. In North America, building products made from lignocellulosic materials, especially decking, account for two-thirds of the market due to its cost effectiveness as compared to natural wood. In the western countries, automotive products such as interior door panels, exterior skirting, and underbody panels were produced from long natural fiber, such as flax, hemp, jute, or kenaf, reinforcing a variety of thermosets and thermoplastics. These applications of lignocellulosic materials are principally replacing glass fiber in reinforced plastic.

However, in producing a good lignocellulose-based composite, the mechanism and efficiency of

stress transfer between the components often determine the performance of the composite, and this transition region is called the interface. With possible chemical reactions between the components at the interface, the performance of the composites will be improved. One of the examples of these composites is lignocellulosic fiber based-polyurethanes (PU). Lignocellulosic fibers are classified as hydroxyl-rich materials that may react with the isocyanate groups to form an interfacial region, which is a urethane linkage.²

Polyurethane (PU) is one of the environmental compatible polymers which has been extensively prepared using different types of natural resources. This is due to the fact that natural resources (e.g., lignocellulosic materials) possess hydroxyl groups that can interact chemically with isocyanate compound to form urethane linkage. According to Hatakeyama et al. (1993), lignocellulosic material consists of two or more hydroxy (OH) groups per molecule, and it can be used as polyol in the preparation of PU.³ Recently, various studies have been carried out to utilize lignocellulosic materials to produce PU. Desai et al. (2003) prepared polyurethane adhesive from potato starch and natural oils. They found that the adhesive produced was superior as compared to the commercially available adhesives.⁴ Wang and Chen (2007) prepared PU foam using liquefied wheat straw. Based on the results, PU foam prepared from liquefied wheat straw showed good mechanical properties and is comparable with commercial PU foam.⁵ On the other hand, Wang et al.

Correspondence to: G. S. Tay (taygs@usm.my).

Contract grant sponsor: Universiti Sains Malaysia; contract grant number: 304/PTEKIND/639002.

(2008) prepared PU foam from liquefied corn stover and the results demonstrated that the properties of the PU foam could be adjusted by varying the NCO/OH ratio.⁶ Ferrer et al. (2008) compared PU produced from vegetable derived polyol and synthetic polyol. They found that vegetable derived polyol produced PU with compact network as compared to the one prepared from synthetic polyol.⁷ Rozman et al. prepared PU composite using oil palm empty fruit bunch (EFB) and they found that EFB could act as a reactive component in the preparation of PU composite.^{8–10}

Many attempts have been carried out using natural resources in the preparation of PU foam. Yao et al. (1996) had prepared PU foam from liquefied starch as a polyol. From the results, they found that liquefied starch prepared has feasible viscosity and hydroxyl number for the preparation of PU foam.¹¹ Kwon et al. (2007) had also prepared PU foam from starch with different NCO/OH ratio. It was found that the cell size and compression strength of the PU foam increased as the NCO/OH ratio was increased.¹² Yan et al (2008) had prepared PU foam from liquefied cornstalk. They found that PU foam prepared from liquefied cornstalk showed excellent mechanical properties and thermal properties.¹³ Chen and Lu (2009) had prepared PU foam from liquefied wheat straw and the result showed that thermal stability of the PU foam prepared was improved with the presence of liquefied wheat straw.¹⁴

Malaysia has a lot of lignocellulosic materials available and most of them are industrial waste and agricultural by-products which are under utilized. Among others, saw dust from wood industry, risk husk from rice mill, coir from coconut industry, and empty fruit bunches, fronds, and trunks from oil palm industry are promising resources of lignocellulosic materials for preparation of value-added products. Currently, there is no specific application of lignocellulosic materials produced in Malaysia due to various reasons and flammability of the product could be one of the reasons. In this study, PU foam incorporated with oil palm empty fruit bunch (EFB) was prepared and the effects of NCO/OH, EFB content, and the amount of fire retardant additive added on the compression properties and fire retardancy of PU foam were investigated.

EXPERIMENTAL

Materials

Oil palm empty fruit bunch in fiber form was supplied by Ecofuture Bhd., Malaysia, and polyethylene glycol with molecular of 200 (PEG 200) was supplied by Fluka Chemika. Polymeric diphenylmethane

diisocyanate (MDI) was obtained from Maskimi Polyol (M) Sdn. Bhd. Malaysia, whereas ammonium polyphosphate (APP) was purchased from Clariant (M) Sdn. Bhd.

Preparation of EFB powder

The EFB fiber was washed with commercial detergent in order to remove the impurities such as oil residue on fiber surface before it was ground. Then, the EFB powder was sieved using Retch sieve to separate the powder into different particle size. In this study, EFB particle with the size of 53–180 μm was used.

Preparation of PU foam

The PU foams were prepared by a one-shot process, where all the ingredients were mixed simultaneously and allowed to cure at room temperature. First, a small amount of silicone oil (surfactant), dibutyltin dilaurate (catalyst), triethylamine (TEA), and water were mixed with PEG 200 and stirred with a propeller stirrer for 5 minutes at approximately 500 rpm to ensure a homogeneous mix, followed by addition of MDI to the mixture. The mixture was stirred for 30 s, before it was poured into a larger container and allowed to rise at room temperature. The obtained PU foams were left for complete cure for 24 hours at room temperature before cutting into specific dimensions for different types of testing. Preparation of foam was repeated for different NCO/OH ratio (0.7, 0.9, 1.1, and 1.3, respectively), filler contents (5%, 10%, 15%, and 20%) and different fire retardant content (1%, 3%, and 5%).

PU foam measurements

Compression test

Compressive strength and modulus of foams was determined by Universal Testing Machine, GOTECH GT-TGS-2000 with a load cell of 20 kN. The test was performed according to ASTM D1621 with a cross-head speed of 5 mm/min. Size of the specimens were 60 \times 60 \times 50 mm (width \times length \times thickness). The compressive stress at 10% deformation of its original thickness was calculated. Compression modulus was then calculated according to formula as follows:

$$E_c = WH/AD$$

where E_c , compression modulus (Pa or Psi); W , load (N or lbf); H , initial specimen height (m or in); A , initial horizontal cross-sectional area (m^2 or in^2); D , deformation (m or in).

Impact testing

Impact tests were conducted using Ray-Ran Pendulum Impact Tester. The Charpy method was carried out using samples with dimensions of $65 \times 12 \times 10$ mm (length \times width \times thickness).

Scanning electron microscopy (SEM) study

PU foams were investigated with a field-emission scanning electron microscope (FE-SEM) Leo Supra 50VP. The specimens were mounted on an aluminum stub and sputter coated with a thin layer of gold to avoid electrostatic charging during examination.

Fire retardancy test

Limiting oxygen index (LOI) test was carried out according to the British Standard BS2782 to determine the relative flammability of foam. LOI is defined as the minimum concentration of oxygen in an oxygen–nitrogen mixture, required to just support downward burning of a vertically mounted test specimen. Hence, higher LOI values represent better flame retardancy. Test specimen dimensions used were $100 \times 10 \times 4$ mm (length \times width \times thickness).

Thermogravimetry

Thermogravimetry analysis was carried out using Perkin Elmer Pyris 6. Small amount of sample (approximately 7 mg) was placed in the platinum pan before it was put in the furnace. Then, the sample was heated from 30 to 800°C with a heating rate of 10°C/min.

Fourier transform infrared (FTIR) spectroscopy

The FTIR analysis was done using a Nicolet Avatar FTIR Spectrophotometer. Approximately 1 mg of EFBPU foam was mixed with dried potassium bromide (KBr). Then, the mixture was grinded into fine powder using a mortar and pressed into a disc-like shape and finally used for the FTIR test in the range 4000–400 cm^{-1} , with 64 scans.

RESULTS AND DISCUSSION

Effect of EFB content on cell size

Figure 1(a) depicts the SEM micrograph for PU foam prepared from MDI and PEG 200 without EFB, while Figure 1(b,c) shows the SEM micrograph for PU foam filled with 5% and 20% EFB, respectively. By comparing the SEM micrograph, it can be seen that the size of the PU foam cell decreases when

EFB is incorporated. This could be attributed to the presence of EFB which is believed to fill up the space in PU foam. In addition, the formation of PU cell could be interrupted by the presence of EFB, thus resulting in the irregular size of the cell. This is evident in Figure 1(d,e), in which EFB is seen embedded between two cells. This phenomenon could have reduced the size of PU foam cell.

Effect of EFB content on mechanical properties

In the preparation of PU foam reinforced with EFB, a preliminary study was carried out in order to determine the appropriate EFB content for obtaining the optimum strength of PU foam. Table I depicts the effect of EFB loading on compression strength and compression modulus of PU foam prepared with NCO/OH of 1.1. As can be observed, the compression strength increases as the EFB fiber content is increased. This is similar to a previous study carried out by Hatakeyama et al.³ and Chang et al.¹⁵ According to Chang et al.,¹⁵ the compression strength, glass transition temperature (T_g), and thermal conductivity of PU foam could be enhanced by increasing the soy flour content. Meanwhile, Hatakeyama et al.³ observed a similar trend and they attributed this phenomenon to the lignocellulosic material which acts as a hard segment in the PU foam. According to a previous study by Rozman et al.,¹⁰ EFB was found to interact with the PU matrix and enhance the interfacial properties between PU matrix and EFB. This is evident in SEM micrographs [Fig. 1(d,e)] where EFB was well embedded within the PU matrix. Consequently, the efficiency of the stress transfer from the PU matrix to EFB is enhanced. This explanation also applied to the observation on compression modulus (Table I); as the EFB content increases, the compression modulus is increased. Hence, it can be said that EFB could act as a hard segment in the PU foam system and its inherent stiffness has produced PU foam with higher modulus as compared to the one without EFB.

Table II depicts the effect of EFB content on impact strength of the PU foam. It can be seen that impact strength decreases as the EFB content is increased. According to Strong,¹⁶ impact strength is strongly dependent on the ability of the material to move or deform to accommodate impact, whereas Folkes¹⁷ stated that major energy absorbing mechanism in a composite material refers to the energy required in deforming the fiber-matrix bonding and pulls it out completely. Generally, polymer with high strength and stiffness would result in low elongation to failure. Therefore, the decreasing of PU foam impact strength is believed to be due to the increment of the hard segment in PU foam and the

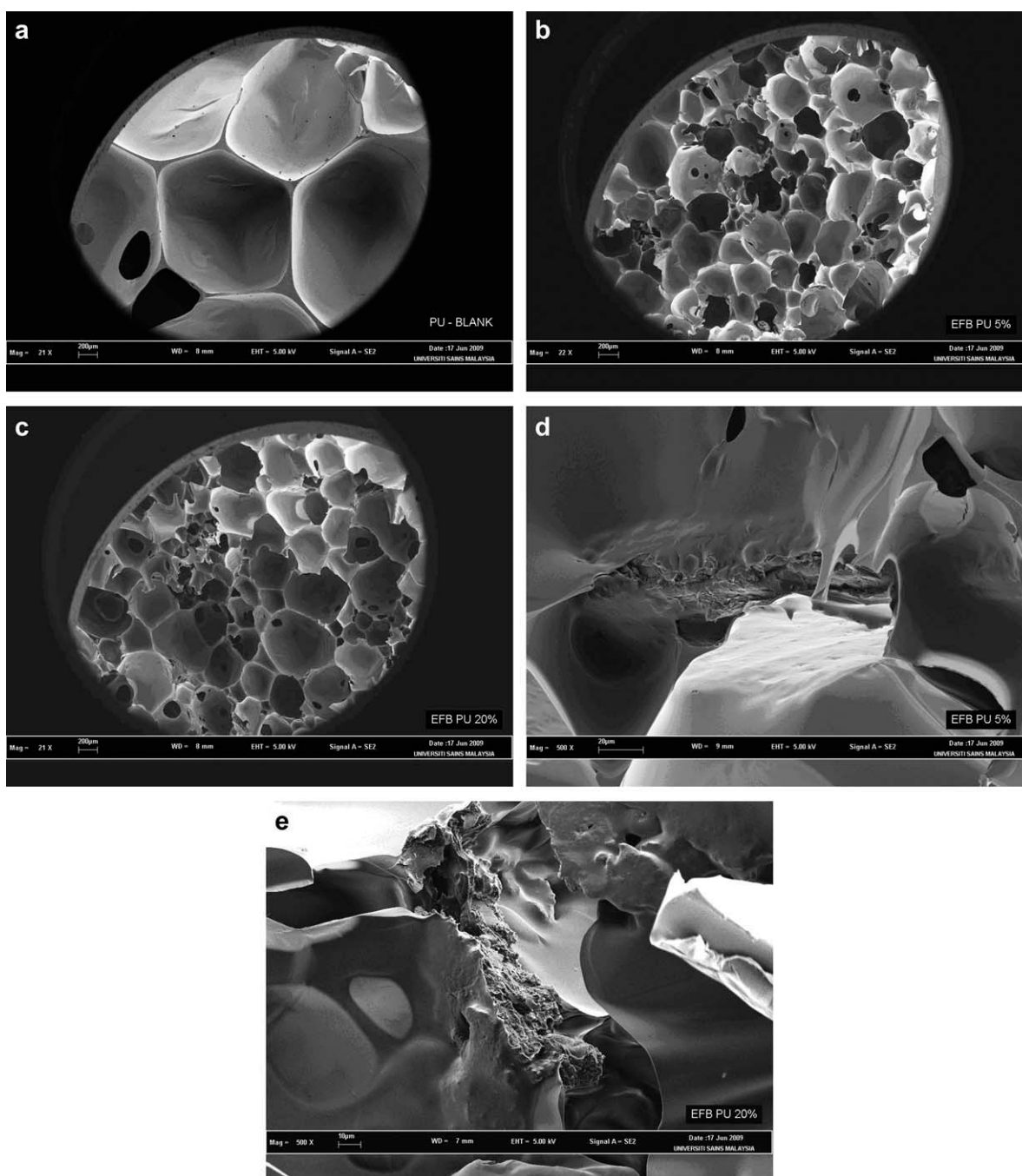


Figure 1 (a) SEM micrograph for PU foam without EFB (magnification $\times 21$). (b) SEM micrograph for PU with 5% EFB (magnification $\times 22$). (c) SEM micrograph for PU with 20% EFB (magnification $\times 21$). (d) SEM micrograph for PU with 5% EFB (magnification $\times 500$). (e) SEM micrograph for PU with 20% EFB (magnification $\times 500$).

increase of stiffness of PU foam as the EFB content is increased.

From this study, it is noticed that the optimum EFB content is about 20%. Further increase in EFB content results in difficulties in mixing due to the increase in the viscosity of polyol and the EFB mixture. Hence, in the subsequent study, the effects of NCO/OH ratio and APP content are based on PU foam prepared from 20% EFB.

TABLE I
Compression Properties of PU Foam with Different EFB Content (NCO/OH = 1.1)

EFB content (%)	Compression strength (MPa)	Compression modulus (GPa)
5	5.07 (± 0.23)	2.35 (± 0.31)
10	5.55 (± 0.16)	2.91 (± 0.27)
15	6.19 (± 0.37)	3.33 (± 0.25)
20	6.54 (± 0.24)	3.45 (± 0.15)

TABLE II
Impact Strength of PU Foam with Different EFB Content
(NCO/OH = 1.1)

EFB content (%)	Impact strength (kJ/m)
5	16.75 (± 0.14)
10	15.27 (± 0.15)
15	11.86 (± 0.21)
20	11.01 (± 0.43)

Effect of NCO/OH ratio and APP content on PU foam mechanical properties

Figure 2 shows the effect of NCO/OH ratio and APP content on compression strength at 10% strain. Generally, compression strength of PU foam increases from 0.9 to 1.1, after which no significant difference is observed, regardless of APP content. This is probably due to the interaction between MDI and hydroxyl group from EFB and PEG 200. According to Cheradame et al. (1989),¹⁸ when NCO/OH ratio was lower than unity, the PU obtained was mostly from the condensation of isocyanate and glycol. For NCO/OH value closes to 1, lignocellulosic material (lignin) would participate in the polycondensation reaction that resulted in an improvement in the mechanical properties. When NCO/OH value was greater than 1.2, PU terminated with NCO would be formed, which could further react with other urethane groups leading to a change in the morphology.⁵ From previous study,¹⁰ unreacted OH in the PU system could act as a stress concentration point, which reduced the strength of the PU system. Hence, it can be said that the hydroxyl group from EFB or polyol in the PU system has reacted with the isocyanate group from MDI when the increase in the NCO/OH ratio is up to 1.1. This is in line with a previous investigation¹⁹ where the increment of NCO/OH ratio resulted in the increase of intermolecular cross-linking.

It is observed that there is a tendency for compression strength to be decreased as the APP content is

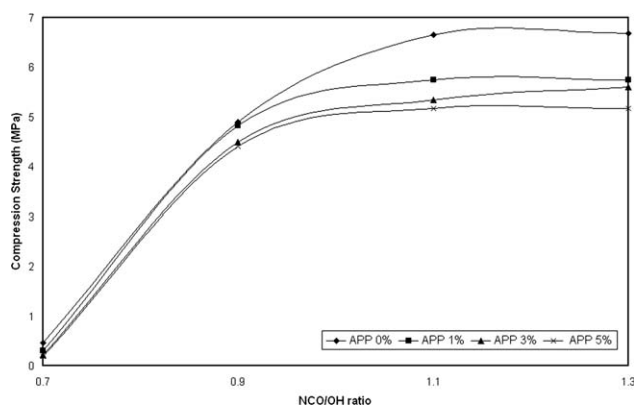


Figure 2 The effects of NCO/OH ratio and APP content on compression strength of PU foam with 20% EFB.

increased. This could be attributed by two factors: (i) the possibility that unreacted APP presented in the foam serves as stress concentration points, which reduces the strength and (ii) the brittleness of the PU foam which is due to the inherent rigidness of APP. As can be seen in Figure 3, when the APP content increases, the stiffness (compression modulus) of the PU foam is increased.

Compression modulus of the PU foam can also be affected by NCO/OH ratio as observed in Figure 3. However, no significant difference is observed between those with NCO/OH of 1.1 and 1.3. The increase in the modulus may be attributed to two benzyl rings of MDI which can restrict the molecular movement in the PU system. The increase of NCO/OH ratio increases the amount of MDI used and subsequently increases the number of benzyl rings in the PU system. Tanaka et al. (2008) stated that when pressure is applied, the sample containing more soft segments was easier to be compressed.²⁰ Thus, it can be said that a stiffer PU can be obtained when higher NCO/OH ratio is used.

The ratio of NCO/OH and APP content can also play a crucial role in determining the impact properties of PU foam reinforced by EFB. From Figure 4, the impact strength decreases as NCO/OH ratio and APP fire retardant content are increased. As mentioned earlier, increasing of NCO/OH ratio results in molecular restriction of PU foams, and, therefore, the ability of foams to absorb energy decreases. According to the study carried out by Stael et al. (2001), composites with low impact strength could be attributed to the inhibition of deformation capacity of matrix due to the presence of a stiffer material.²¹ As for APP content, it is in agreement with the result obtained in compression modulus. As mentioned earlier, PU with higher stiffness possesses lower impact properties. Hence, it is clear that APP has a positive effect on the stiffness of the PU foam.

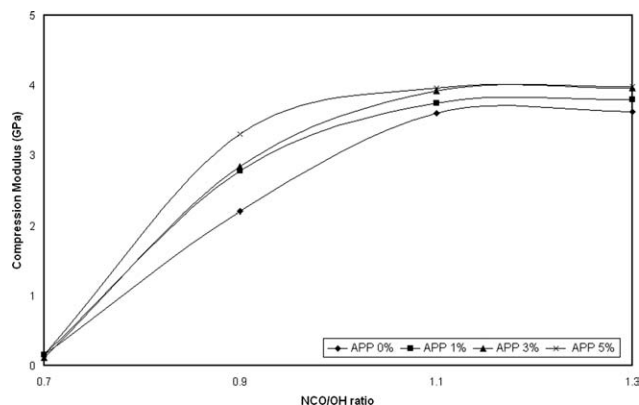


Figure 3 The effects of NCO/OH ratio and APP content on compression modulus of PU foam with 20% EFB.

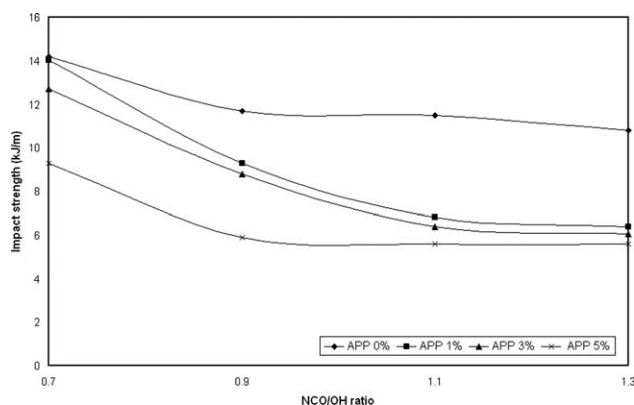


Figure 4 The effects of NCO/OH ratio and APP content on impact strength of PU foam with 20% EFB.

Limited oxygen index

Limited oxygen index (LOI) is used as a qualitative method to evaluate the fire retardancy of polymeric materials. Table III shows the relationship of oxygen index (OI) value of PU foams with different EFB content. As expected, OI value decreases as EFB content increased. This is due to EFB being a lignocellulosic filler which is a highly flammable material. However, there is no significant difference on OI value as the EFB filler loading is further increased (10%, 15%, and 20%). This indicates that the EFB content of 10% is the minimum amount of EFB where a significant change in OI is observed.

The effect of NCO/OH ratio and APP content on OI value is shown in Figure 5. OI value increases when NCO/OH ratio is increased. According to Lanrock (1995) higher NCO/OH ratio gave higher isocyanurate linkages which were found to be thermally stable and to produce less combustible gasses in the PU foam.²² According to Bhattacharjee and Engineer (1996), the presence of isocyanurate can be determined using FTIR spectroscopy, the absorbance of which is 1415 cm^{-1} , shown due to C–N vibration in the six-membered heterocycle. Meanwhile, absorbance of 1220 cm^{-1} can also be observed, which is attributed to the presence of the urethane group.²³ By looking at the FTIR spectrum depicted in Figure 6, it can be seen that the transmittance of 1415 cm^{-1} and 1220 cm^{-1} are evident. In addition, no isocyanurate transmittance is observed in the region of 2260–

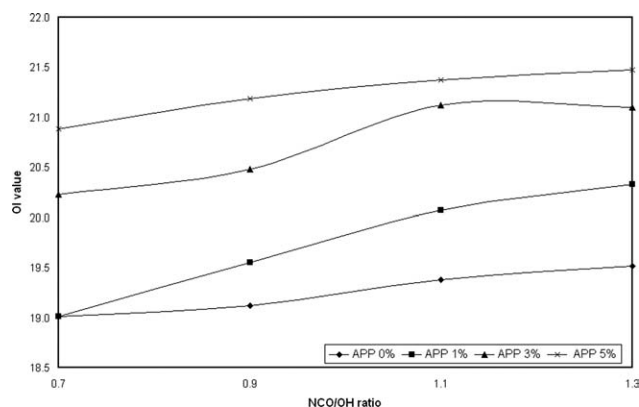


Figure 5 The effects of NCO/OH ratio and APP content on oxygen index (OI) value of PU foam with 20% EFB.

2280 cm^{-1} . Hence, it is believed that the urethane linkages had been produced from the interaction of isocyanate and hydroxyl group. The excess of the isocyanate group added (due to higher NCO/OH) is expected to react with urethane linkages (trimerization) to produce isocyanurate. In this regard, it is believed that the increase in OI value when NCO/OH ratio is increased could be due to higher isocyanurate linkages present in the foam especially for the ones produced with NCO/OH of 1.3.

The results also show that the OI value of PU foam increases as APP content is increased. According to Duquesne et al. (2001), the addition of APP to PU accelerates the decomposition of matrix which leads to an increase in the amount of high temperature residue, under an oxidative or inert atmosphere. The stabilized residue acts as a protective thermal barrier during the intumescent-fire retardancy process. Intumescent is a process when combustion occurs, a cellular charred layer on the surface of material protects the underlying materials from the action of heat flux or flame and acts as a physical barrier limiting the diffusion of combustible volatile products toward the flame and oxygen toward the polymer.²⁴ Therefore, the increase in APP addition level results in an increase in OI value due to the

TABLE III
Oxygen Index Value of PU Foam with Different EFB Content (NCO/OH = 1.1)

EFB content (%)	Oxygen index
5	19.95 (± 0.04)
10	19.37 (± 0.09)
15	19.37 (± 0.11)
20	19.36 (± 0.07)

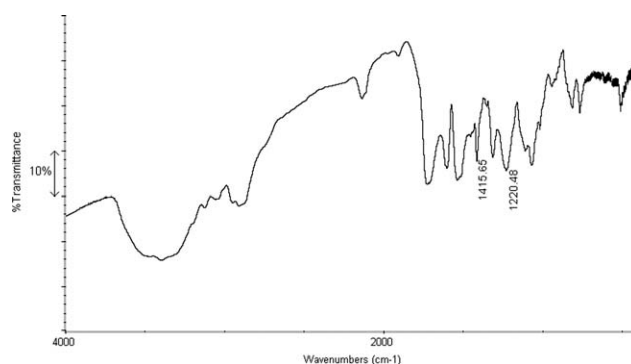


Figure 6 FTIR spectrum of EFB-PU foam prepared from 20% EFB and 1% APP with NCO/OH of 1.3.

TABLE IV
Thermal Degradation Temperature and Mass Residue at 800°C of PU Foam with Different APP Content. (NCO/OH = 1.1, 20% of EFB)

APP content (%)	Thermal degradation temperature (°C)	Mass residue (%)
0	285.73 (± 1.75)	21.22 (± 0.68)
1	285.69 (± 1.31)	20.73 (± 1.12)
3	289.09 (± 1.62)	21.49 (± 0.83)
5	296.64 (± 0.84)	30.76 (± 1.55)

increase in char formation. This result is supported with the result obtained in TGA (Table IV). It can be seen that the degradation temperature shows a slight increase as the amount of APP is increased. It also can be said that increment of APP amount in the PU foam has resulted in the increase of mass residue.

CONCLUSION

It can be concluded that the addition of EFB and APP at different percentages and NCO/OH ratios shows significant influence on the properties of PU foams. The amount of EFB incorporated in the PU foam was found to affect the compression properties. Since impact strength was reciprocal to the stiffness of the PU foam, progressive increase in EFB content resulted in a reduction in impact strength. It was evident that the inherent stiffness of EFB has contributed to the PU foam. The amount of MDI (from various NCO/OH ratios) added to the formulation influenced the properties of PU foam since the benzyl ring could also act as a hard segment and thus restricted the molecular movement in PU system. Meanwhile, the addition of APP in the formulation had increased the fire retardancy, compression, and impact properties of the PU foam.

References

- Rossi, L. [Online] [Accessed 7, July 2004]. Available from: http://www.Globalhemp.com.News/2002/November/900_million_market.shtml (2002).
- Rial, T. G.; Wolcott, M. P. *J Mater Sci Lett* 1998, 17, 317.
- Hatakeyama, H.; Hirose, S.; Nakamura, K.; Hatakeyama, T. In *Cellulosics: Chemical, Biochemical and Material Aspects*; Kennedy, J. F., Phillips, G. O., Williams, P. A., Eds.; Ellis Horwood: New York, 1993; p. 525–536.
- Desai, S. D.; Patel, J. V.; Sinha, V. K. *Int J Adhes Adhesiv* 2003, 23, 393.
- Wang, H.; Chen, H. Z. *J Chin Inst Chem Eng* 2007, 38, 95.
- Wang, T.; Zhang, L.; Li, D.; Yin, J.; Wu, S.; Mao, Z. *Biores Technol* 2008, 99, 2265.
- Ferrer, M. C. C.; Babb, D.; Ryan, A. J. *Polymer* 2008, 49, 3279.
- Tay, G. S.; Rozman, H. D. *J Appl Polym Sci* 2008, 108, 995.
- Rozman, H. D.; Tay, G. S. *J Appl Polym Sci* 2008, 110, 3647.
- Rozman, H. D.; Tay, G. S.; Abubakar, A.; Kumar, R. N. *Eur Polym J* 2001, 37, 1759.
- Yao, Y.; Yoshioka, M.; Shiraishi, N. *J Appl Polym Sci* 1996, 60, 1939.
- Kwon, O. J.; Yang, S. R.; Kim, D. H.; Park, J. S. *J Appl Sci* 2007, 103, 1544.
- Yan, Y.; Pang, H.; Yang, X.; Zhang, R.; Liao, B. *J Appl Polym Sci* 2008, 110, 1099.
- Chen, F.; Lu, Z. *J Appl Polym Sci* 2009, 111, 508.
- Chang, L.-C.; Xue, Y.; Hsieh, F. H. *J Appl Polym Sci* 2001, 80, 10.
- Strong, A. B. *Plastics: Materials and Processing*; Prentice Hall; Bew Jersey, OH, 2000.
- Folkes, M. J. *Short Fibre Reinforced Thermoplastic*; Research Studies Press: New York, 1982.
- Cheradame, H.; Detoisien, M.; Gandini, A.; Pla, F.; Roux, G. *Brit Polym J* 1989, 21, 269.
- Hatakeyama, H.; Kosugi, R.; Hatakeyama, T. *J Therm Anal Calorimet* 2008, 92, 419.
- Tanaka, R.; Hirose, S.; Hatakeyama, H. *Biores Technol* 2008, 99, 3810.
- Stael, G. C.; Tavares, M. I. B.; Almeida, J. R. M. D. *Polym Test* 2001, 20, 869.
- Landrock, A. H. *Handbook of Plastic Foams: Types, Properties, Manufacture and Applications*; Noyes Publication: Park Ridge, NJ, 1995.
- Bhattacharjee, D.; Engineer, R. *J Cell Plast* 1996, 32, 260.
- Duquesne, S.; Bras, M. L.; Bourbigot, S.; Delobel, R.; Camino, G.; Eling, B.; Lindsay, C.; Roels, T.; Vezin, H. *J Appl Polym Sci* 2001, 82, 3262.