The Malaysian Journal of
ANALYTICAL SCIENCES
ISSN 1394-2506

PALM-BASED POLYURETHANE WITH SOYBEAN PHOSPHATE ESTER AS A FIRE RETARDANT

(Poliuretana Sawit dengan Ester Fosfat Soya Sebagai Perencat Api)

Nor Rabbi'atul 'Adawiyah Norzali[1], Khairiah Haji Badri[1,2]*, Ong Soo Ping[1], Ishak Ahmad[1,2]

[1]*School of Chemical Sciences and Food Technology*
[2]*Polymer Research Center*
Faculty of Science and Technology
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

**Corresponding author: kaybadri@ukm.edu.my*

Abstract

Palm-based polyurethane (PU) with soybean oil phosphate ester (PE) as a fire retardant was prepared. The effect of PE to the mechanical and burning properties of the PU was investigated. The PE was synthesized via ring-opening hydrolysis between *o*-phosphoric acid (*o*-H_3PO_4) and epoxidized soybean oil. The synthesis was conducted at 60-70 °C. The concentration of *o*-H_3PO_4 was varied at 2.5, 5.0 and 7.5 wt%. PE with 2.5 wt% H_3PO_4 showed the lowest acid value ($2.8\ mg \cdot g^{-1}$) but high hydroxyl value ($351.6\ mg \cdot g^{-1}$). PU containing PE (PU-PE) has higher density ($60\text{-}61\ kg \cdot m^{-3}$) compared to control PU ($49.7\ kg \cdot m^{-3}$). Burning rate decreased from $2.16 \times 10^{-3}\ m \cdot s^{-1}$ for control PU to $1.26 \times 10^{-3}\ m \cdot s^{-1}$, $1.06\ 10^{-3}\ m \cdot s^{-1}$ and $0.6 \times 10^{-3} m \cdot s^{-1}$ for PU-PE at 5, 10 and 15 wt% PE respectively. However, the addition of PE into the PU system gradually decreased the compression stress and modulus of the PU-PE.

Keywords: Epoxidized soybean oil, fire retardant, palm-based polyurethane, phosphate ester

Abstrak

Poliuretana sawit (PU) mengandungi ester fosfat minyak soya (PE) sebagai perencat api telah berjaya dihasilkan. Kesan PE terhadap sifat mekanik dan kebakaran PU telah dikaji. PE disintesis melalui tindak balas hidrolisis pembukaan gelang antara asid fosforik (o-H_3PO_4) dan minyak soya terepoksida. Sintesis dijalankan pada 60-70 °C. Kepekatan o-H_3PO_4 divariasikan pada 2.5, 5.0 dan 7.5 bt%. PE dengan 2.5 bt% o-H_3PO_4 menunjukkan nilai asid yang rendah ($2.8\ mg \cdot g^{-1}$) tetapi tinggi nilai hidroksil 351.6 $mg \cdot g^{-1}$). PU yang mengandungi PE(PU-PE) mempunyai ketumpatan yang tinggi ($60\text{-}61\ kg \cdot m^{-3}$) berbanding PU kawalan (49.7 $kg \cdot m^{-3}$). Kadar kebakaran menurun dari $216 \times 10^{-3}\ m \cdot s^{-1}$ untuk PU kawalan kepada $1.26 \times 10^{-3}\ m \cdot s^{-1}$, $1.06\ 10^{-3}\ m \cdot s^{-1}$ and $0.6 \times 10^{-3} m \cdot s^{-1}$ masing-masing untuk PU dengan 5, 10 and 15 bt% PE. Walau bagaimanapun, penambahan PE ke dalam sistem PU menyebabkan kekuatan dan modulus mampatan menurun secara berperingkat.

Kata kunci: Minyak soya terepoksida, perencat api, poliuretana sawit, ester fosfat

Introduction

Palm-based polyurethane (PU) exists in various forms such as foams (in rigid and flexible form), coating, elastomers, sealant and adhesive [1]. It consists of polyol and polyisocyanate in the structural chain to form urethane linkage (NHC(O)O). Polyols are industrially produced from petroleum derivatives. Higher demand and consumption of petroleum and its derivatives has led to depletion and escalation in petroleum prices [2]. Furthermore, petroleum is a nonrenewable material. Sustainable technologies were developed to produce PU by using renewable resources such as vegetable oil as an alternative to petroleum [3]. Soybean oil, sunflower oil, safflower oil, and palm kernel oil has been used in many researches to produce eco-friendly PU [2,4-9]. Triacylglycerol (TAG), the main component in vegetable oils can be converted into high value polymers with some modifications in their chains [2]. Eco-PU is comparable to synthetic PU in term of strength.

PU is flammable when in direct contact with heat or fire [10]. Flame retardants (FR) are introduced to the PU system to overcome this problem. Although they improve the fire resistivity of the polymer, their presence deteriorates the mechanical properties. This is due to the interphase separation that occurred between FR and the polymer. FR with high degree of compatibility with the polymer was synthesized in order to improve the flammability as well as the mechanical properties of the PU. Liquid FRs i.e. commercial halogenated FR tris(1-chloro-2-propyl) phosphate (TCPP) or tris (mono-chloro-propyl) phosphate (TMCP) are manufactured as an alternative to improve the mechanical properties [11]. However, these liquid FRs are mostly halogenated compounds. They are potentially toxic and create environmental problem during storage, transportation and combustion [12-13]. Phosphorus-containing compound has been considered as an alternative to replace the halogenated FRs.

Soybean oil-based phosphate ester (PE) was produced via acid hydrolysis of soybean oil in the presence of phosphoric acid. Phosphoric acid was used in the preparation of PE from epoxidized soybean oil for coatings, elastomers and rigid polyurethane foams [4,14-17]. In this reaction, phosphoric acid not only initiates the reaction but also chemically becomes part of the product which is the PE [4]. This paper reported the effect of PE loading on the mechanical and burning properties of palm-based PU.

Materials and Methods

Materials

For epoxidation: Soybean oil (SO) (iodine value, IV of 124.4 $I_2 \cdot 100\ g^{-1}$) was purchased from Mewah Oleoindustries, Malaysia while hydrogen peroxide (H_2O_2 with concentration of 30–32 wt%) was distributed by Friendemann Schmidt Chemicals, German. Glacial acetic acid (CH_3COOH with concentration of 99.8 wt%) and sulphuric acid (H_2SO_4 with concentration of 98 wt%) were purchased from Merck, Malaysia. For esterification: *o-p*hosphoric acid, H_3PO_4 (85 wt%) was purchased from Merck, Malaysia and *tert*-butyl alcohol was produced by BDH Limited Poole, England. *For polyurethane preparation:* Palm-based polyester polyol (PKO-p) was supplied by UKM Technology Sdn Bhd, Pekan Bangi Lama, Malaysia. Silicone surfactant (Niax L5440) was supplied by Witco Ltd, Singapore. Glycerol ($C_4H_8O_3$) was supplied by BHD Laboratory Supplies, Poole England, while tetramethyl hexanediamine (TMHDA) and pentamethyl dietilenetriamine (PMDETA) were distributed by Cosmopolyurethane (M) Sdn Bhd, Port Klang, Malaysia. Crude isocyanate of type 2, 4-methylene diphenyldiisocyanate (MDI) was supplied by Cosmopolyurethane (M) Sdn Bhd, Port Klang, Malaysia.

Epoxidation of SO

About 300 g soybean oil and 44.0 g glacial acetic acid were placed in a 500 ml three-necked reactor equipped with a thermometer, mechanical stirrer and a condenser. A sufficient amount of H_2O_2 and 3.85 ml of H_2SO_4 was dropped into the mixture at 40 °C. After the final dropping, the temperature was raised to the reaction temperature of 50–60 °C and allowed to react for 6 h. The stirring speed was fixed at 400 rpm. Upon completion of reaction, the bilayer mixture was separated using a separation funnel and neutralized with saturated sodium chloride and distilled water until it reached pH 7. The top part was then retrieved for acid hydrolysis.

Hydrolysis and Esterification of Epoxidized SO

Ring-opening hydrolysis of epoxidized soybean oil (eSO) was conducted based on the study by Guo et al.[4]. In a glass reactor equipped with a thermometer, dropping funnel, water cooled condenser and mechanical stirrer, an amount of *o*-H_3PO_4, a portion of 50 wt% *tert*-butyl alcohol and 10 wt% distilled water were charged. The mixture was heated to 30 °C at a slow heating rate under mechanical stirring at 400–500 rpm for 30 min. The eSO was dissolved in a portion of *tert*-butyl alcohol and added drop wise into the mixture over the period of 45 min. After the final dropping of the eSO, the temperature was increased to 80–90 °C for 6 h or until the oxirane oxygen content (OOC) content reached below 0.2%. Upon completion of the reaction, the mixture was separated using a separation funnel. The yellow oily phase (PE) was retrieved. The amount of *o*-H_3PO_4 was varied at 0, 2.5, 5.0 and 7.5 wt% of the eSO.

Preparation of palm-based polyurethane containing PE

The resin was prepared prior to polymerization by mixing 90 wt% of PKO-p with 10 wt% glycerol, 2 wt% Niax L5440, 0.45 wt% TMHDA, 0.40 wt% PMDETA and 4.00 wt% of water. The polyurethane containing PE (PU-PE) was prepared by mixing the resin with PE at varying amount of PE at 0, 5, 10 and 15 wt% before the reaction with MDI. The mass ratio of the resin to MDI was 1:1. The mixture was mechanically stirred at 1000 rpm for 10 s. The mixture was then poured into a mold and demolded after 15 min. The molded PU foam was then conditioned for 16 h according to BS 4370 Part 1: 1988: Method 3 (*Method of Test for Rigid Cellular Material: Compression*) standard before characterization.

Characterization of SO, eSO, PE and PU-PE: Fourier Transform Infrared Spectroscopy Analysis

The functional groups in SO, eSO, PE and PU-PE were determined using Fourier transform infrared (FTIR) Spectroscopy analysis. This test was conducted using Perkin Elmer spectrometer model Spectrum BX with sodium chloride (NaCl) method for SO, eESO and PE samples and potassium bromide (KBr) pellet method was used for PU-PE samples. Samples were analyzed at a wavenumber ranging from 700 to 4000 cm^{-1}.

Compression Test

The compression test was conducted according to BS 4370: Part 1: 1988 *(Method of Test for Rigid Cellular Material):* Method 3 *(Compression)* standard. Samples were cut into dimension of 50 mm × 50 mm × 50 mm. The test was carried out using Instron Universal Test Machine model 5566 at cross-head speed of 50 mm·min^{-1} until the thickness was reduced to 90% of its original thickness. The compression stress and modulus were recorded as an average of five readings.

Burning Test

The burning test was carried out to determine the fire resistivity of the PU according to ASTM D 5048-09 Procedure B method 2 (*Standard Test Method for Measuring the Comparative Burning Characteristics and Resistance to Burn-Through of Solid Plastics Using 125-mm Flame*) standard. The PU foam was cut into samples of dimension 125 mm × 30 mm × 10 mm (length×width×thickness). The test sample was then clamped at one end so that its position was at 30°. A Bunsen burner with blue flame was positioned within the range of 25–30 mm from the test samples for 5 s and was then removed. The burning rate was determined using equation (1):

$$\text{Burning rate} = \frac{\text{(final length of specimen - initial length of specimen), m}}{\text{Total burning time, s}} \tag{1}$$

Bomb Calorimetry Analysis

Bomb Calorimetry analysis was conducted using oxygen bomb calorimeter model Parr 6100 coupled to a built-in printer with star SP700 software that automatically calculate the enthalpy of combustion (ΔH_c) of the PUs. This test was in accordance to ASTM D240-09 (*Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter*) standard.

Results and Discussion

FTIR Spectroscopy Analysis

Figure 1 shows the FTIR spectra for SO, eSO and PE respectively. The SO spectrum (Figure 1(a)) showed stretching vibration peak for C=C at 3009 cm^{-1} and HC=CH bonding peak at 1652 cm^{-1} [18]. Upon completion of epoxidation, these peaks disappeared and a new peak was observed at 824 cm^{-1} indicated the formation of epoxide ring [19]. It verified the ring-opening of the alkene group. The peak at 1746 cm^{-1} belongs to the carbonyl group (C=O) in the fatty acid. After epoxidation, the peak shifted to the right (1744 cm^{-1}) to the carbonyl group of the ester. The disappearance of epoxide group in the PE as shown in Figure 1(c) indicated that the epoxide group has undergone hydrolysis. The presence of P-O-C of the PE was detected at 1025 cm^{-1} upon completion of the hydrolysis reaction of the eSO. On the other hand, the presence of the hydroxyl (-OH) group in the PE was observed at 3394 cm^{-1} as a strong and intense peak [4]. The FTIR spectrum of the PU comprised of 0, 5, 10 and 15 wt% PE are as shown in Figure 2 and further summarized in Table 1. The inclusion of PE showed insignificant difference in the spectrum of the PU containing PE (PU-PE). The presence of PE did not affect the polymerization reaction and the formation of the urethane linkages.

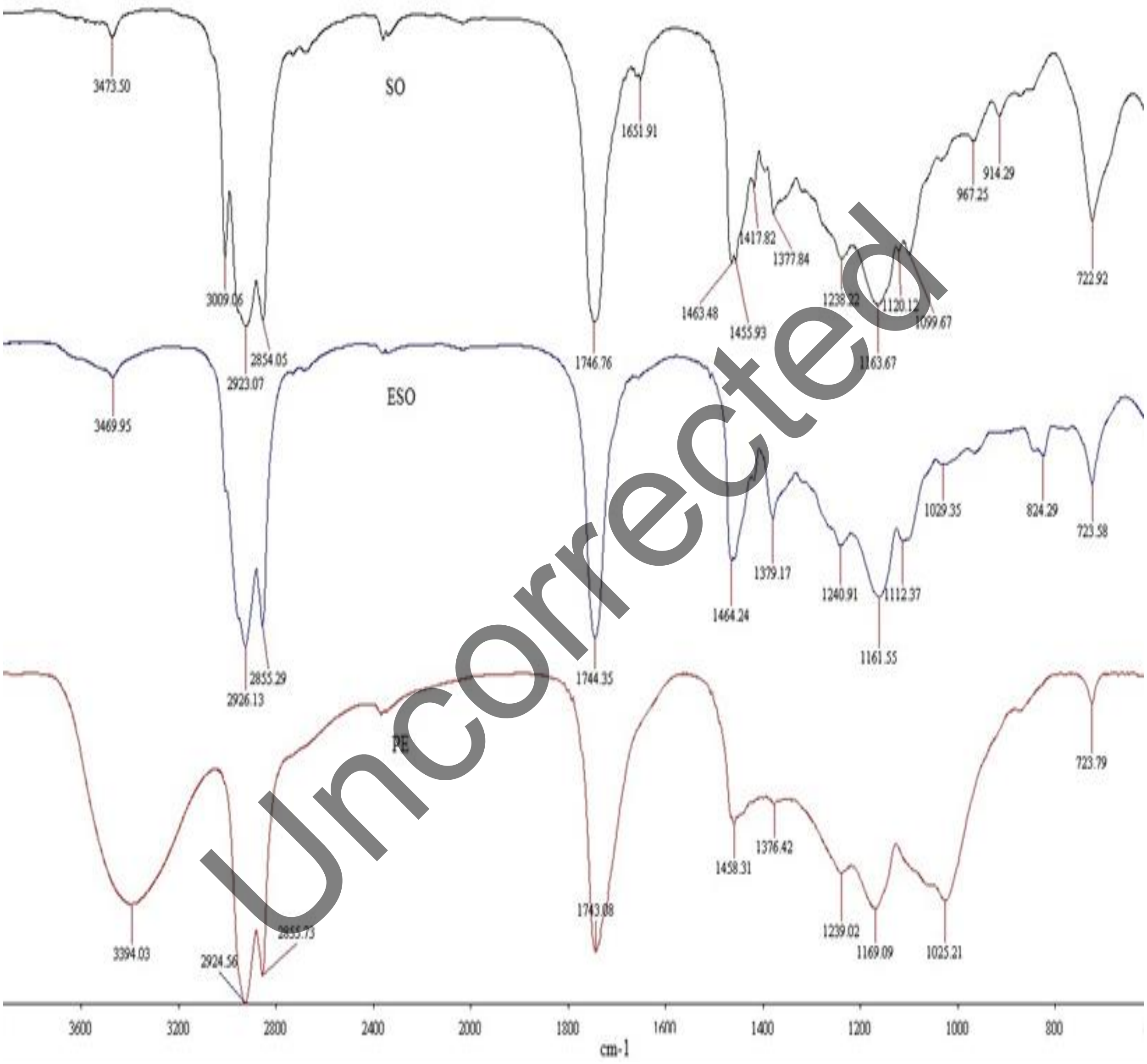

Figure 1. FTIR spectra of SO, eSO and PE

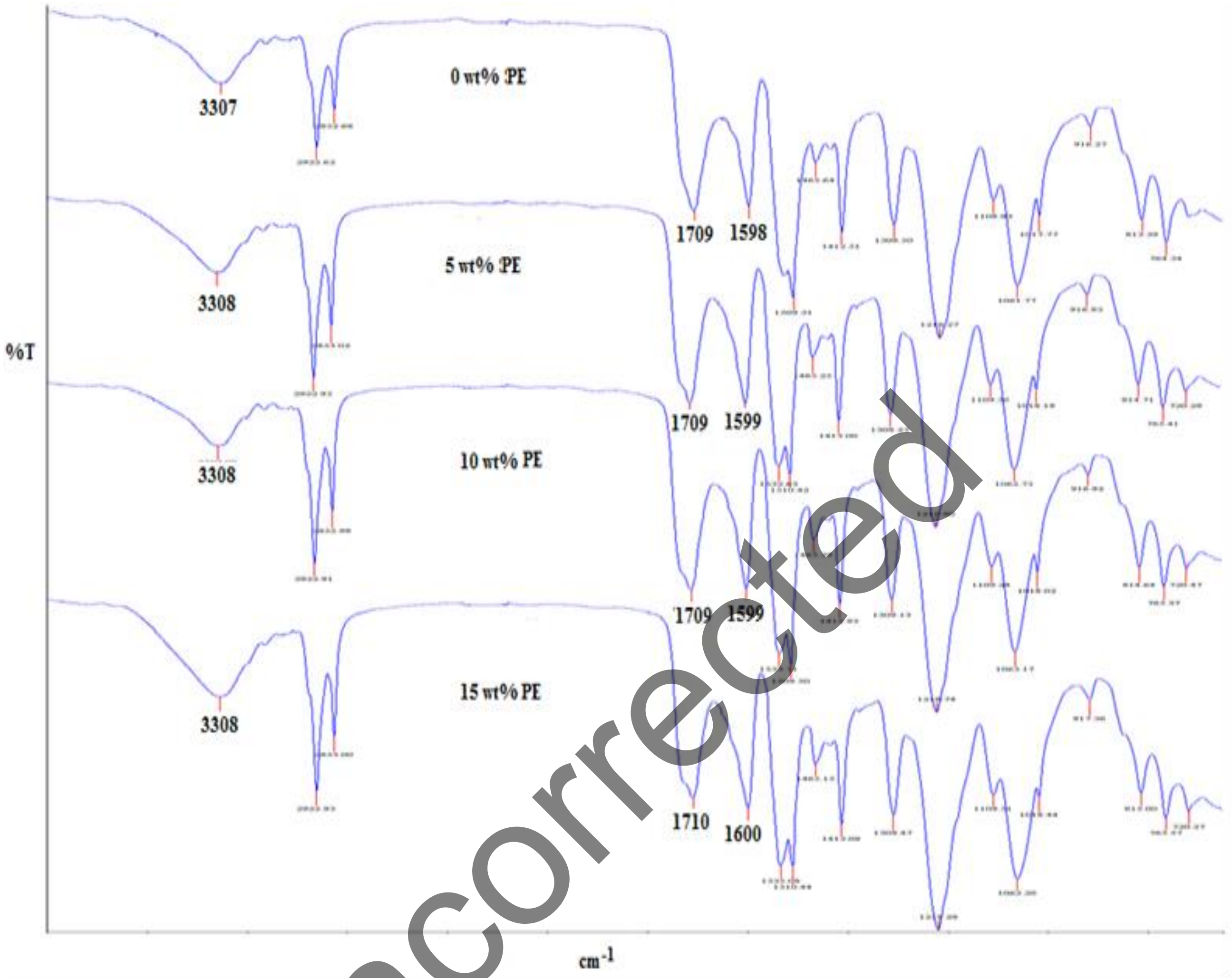

Figure 2. FTIR spectra of PU comprised of 0, 5, 10 and 15 wt% PE

Table 1. Summarised data from the FTIR spectrum of PU and PU-PE

Stretching or vibration peaks	**Wavenumber, cm^{-1}**			
	0 wt% PE	**5 wt% PE**	**10 wt% PE**	**15 wt% PE**
Amine (N-H)	3307	3308	3308	3308
Isocyanate (-NCO)	-	-	-	-
Carbonyl (-C=O)	1709	1709	1709	1710
Carbamate (-C-N)	1598	1599	1599	1600

Mechanical Properties

Figure 3 shows the effect of PE loading on the compression stress and modulus of the PU foam. Addition of PE to PU has decreased the compression stress and modulus. Compression stress and modulus for pristine PU was at 225 ± 43 kPa and 804 ± 203 kPa respectively. Further addition of PE at 5 to 15 wt% decreased the compression stress dramatically to 105 ± 11 kPa (15 wt% PE). Addition of 10 wt% PE has slightly increased the compression modulus to 130 ± 19 kPa from 122 ± 23 kPa (5 wt% PE). According to Fan et al. [16], compression stress and modulus are depending on density and degree of cross-linking of the polymer network. Higher density and degree of cross-linking give higher compression stress and modulus. The PE has secondary hydroxyl in the middle chain of the TAG. The bulky chain in the PE when reacted with isocyanate produced dangling chain. This dangling chain created plasticizing effect in the PU. When stress was loaded to the PU, the plasticizing effect weaken the networks by limiting the movement of the PU molecules and thus decreased the mechanical properties [20].

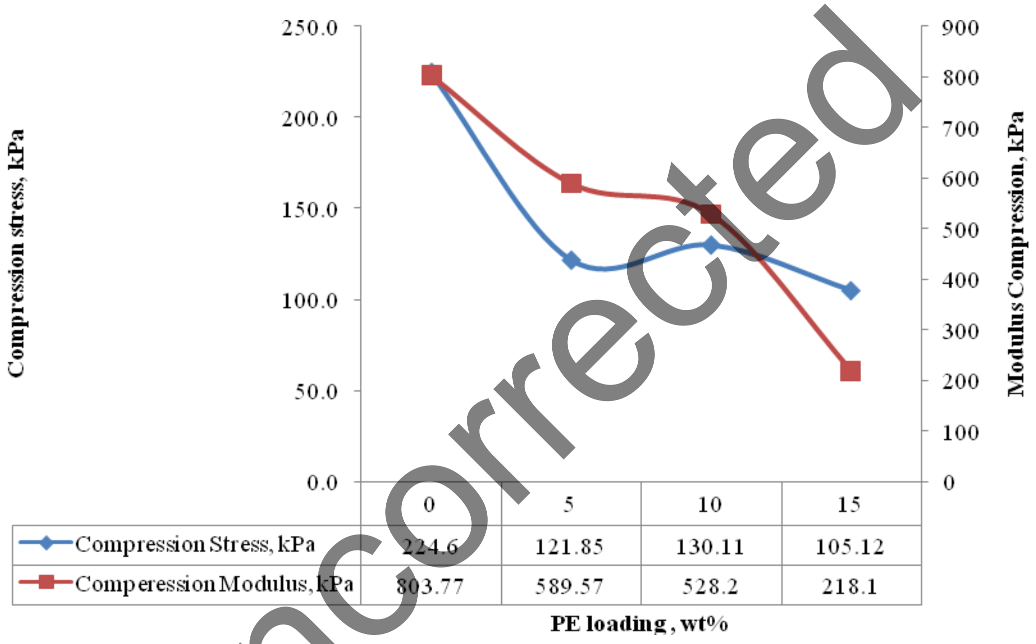

Figure 3. Compression stress and modulus of PU containing PE at 0, 5, 10 and 15 wt%

Burning Properties

Figure 4 showed that control PU showed higher burning rate at 2.16 × 10^3 m·s^{-1}. Addition of PE to the PU has decreased the burning rate (Figure 4). The flammability of PU was contributed by the soft segment in the PU structure (Figure 5). The soft segment in PU tends to degrade at lower temperature than the hard segments. It starts to dissociate and produces alcohol. During degradation, the combustible compound evaporates and mixes with air and thus forms flammable air. When this mixture is saturated, and the temperature reached flammability limits, PU starts to burn [21]. Phosphorus in PE (Figure 6) decomposes to produce phosphoric acid. Further decomposition of phosphoric acid leads to dehydration of PU and produces phosphorus-rich layer. This phosphorus-rich layer prevents PU surface from heat and oxygen [22]. The carbon layer forms on the surface of PU acts as a barrier and prevents combustible gases and oxygen from diffusing to the inner layer of the PU [23]. It protects the underneath layer of PU from any contact with heat [24].

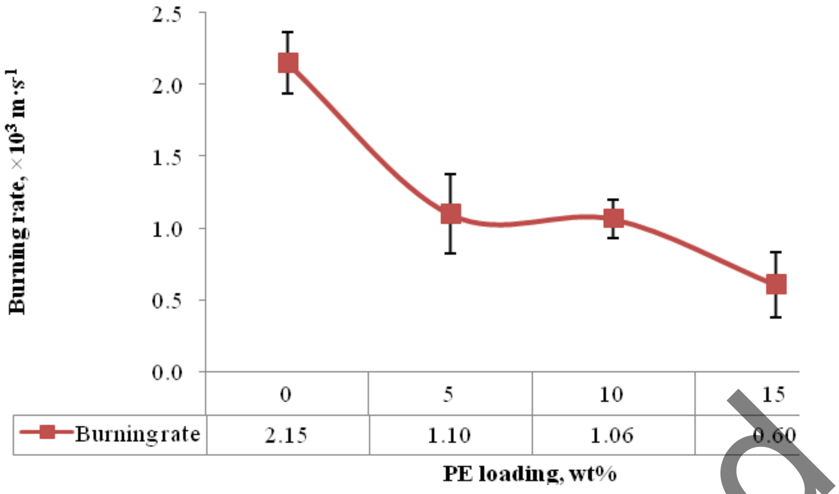

Figure 4. Burning rate of PU-PE at varying loading percentage of PE

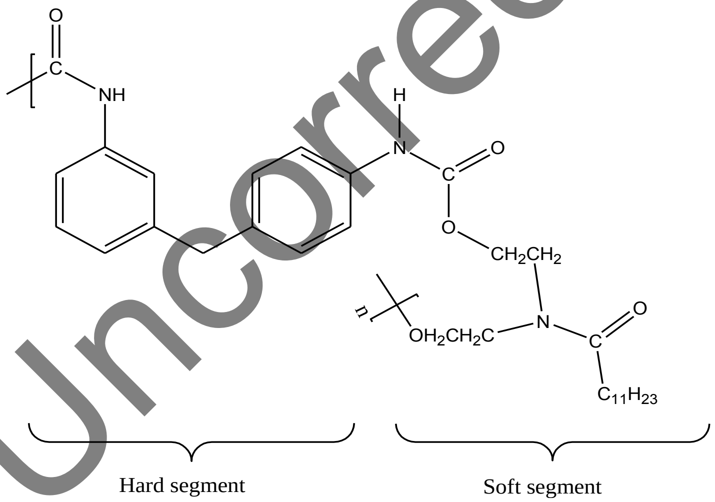

Figure 5. The hard and soft segments in the polyurethane structure

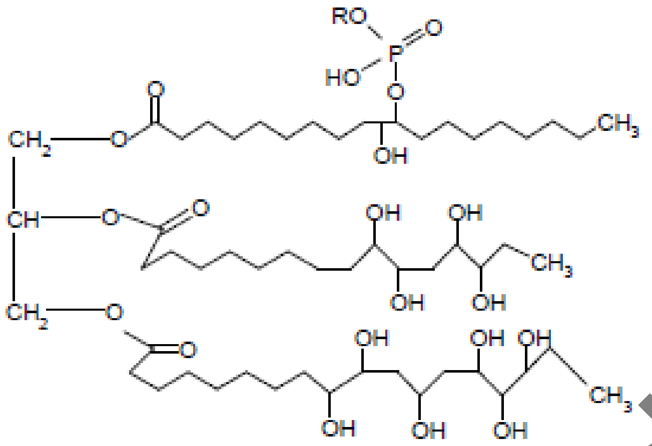

Figure 6. Structure of soybean oil-based phosphate ester (PE)

Bomb Calorimetry

Bomb calorimetry was conducted to support the fire characteristic by determine the enthalpy of combustion for PU and PU-PE. Figure 7 showed the enthalpy of combustion of the PU and PU-PE. Enthalpy of combustion for PU was 2.66×10^4 kJ·kg^{-1}. The enthalpy of combustion decreased for PU-PE compared to PU. Further addition of PE at 10 and 15 wt% into the PU system exhibited insignificant difference. Lower heat of combustion indicated that there was a small interaction between PE and PKO-p with MDI. Phosphorus in the PE thermally decomposed to phosphoric acid during the pyrolyzing process [25]. Kuryla [26] stated that further thermal decomposition of phosphoric acid leads to the formation of polyphosphoric acid. Polyphosphoric acid dehydrates the pyrolyzing polymer and at the end of the process, char was formed on the polymer (PU). Char formation occurs through cross-linking reaction. It reduces the production of combustible and volatile materials. The char layer restricted the flow of heat to below surface of the PU and it obstructs permeation of combustible gases from the pyrolyzing polymer [27].

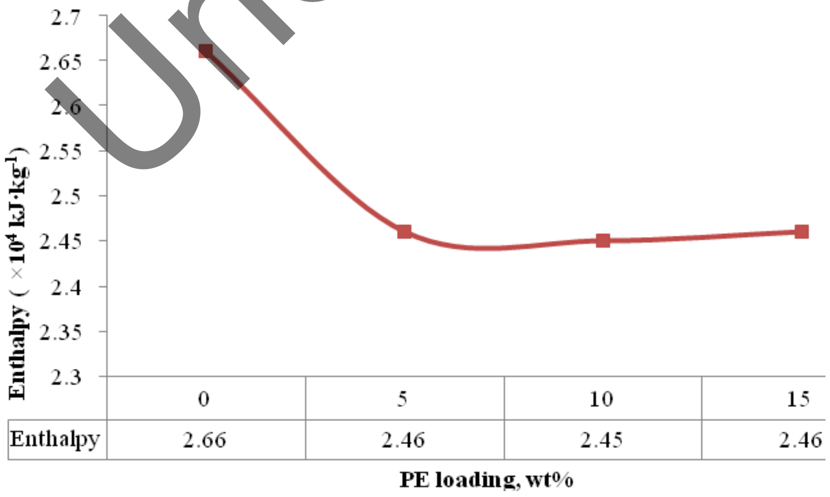

Figure 7. Combustion enthalpy of PU-PE at varying loading percentage of PE

Conclusion

PE has proved to increase the fire resistivity of the palm-based polyurethane. Optimum loading of the PE was detected at 5 wt% based on the mechanical properties where higher compression stress and modulus were observed. However, higher loading of PE to PU system decreased the compression stress and modulus. Lower heat of combustion indicated that there was an interaction between PE with PKO-p and MDI.

Acknowledgement

The authors would like to thank Polymer Research Center and School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia for the laboratory facilities and working space; Ministry of Science, Technology and Innovation (MOSTI) for funding of this research via Sciencefund Project No. 03-01-02-SF0949 and Ministry of Higher Education for the financial support via MyPhd grant for the graduate research assistant.

References

1. Ferrer, M.C.C., Babb, D. & Ryan, A.J. (2008). Characterisation of polyurethane networks based on vegetable derived polyol. *Polym*. 49: 3279-3287.
2. Badri, K.H. (2012). Biobased Polyurethane from Palm Kernel Oil-Based Polyol. Polyurethane. InTech.
3. Beltran, A. A. & Boyaca, L.A. (2011). Preparation of Oleochemical Polyols Derived from Soybean Oil. *Lat. Am. Applied Research*. 41: 69-74.
4. Guo, Y., Hardesty, J.H., Mannari, V.M. & Jr, J.L.M. (2007). Hydrolysis of Epoxidized Soybean Oil in the Presence of Phosphoric Acid. *J. Am. Oil Chem. Soc*. 84: 929-935.
5. Jia, L.K., Gong, L.X., Ji, W.J. & Kan, C.Y. (2011). Synthesis of vegetable oil based polyol with cottonseed oil and sorbitol derived from natural source. *Chinese Chem. Let.* 22 (11): 1289-1292.
6. Montero de Espinosa, L. & Meier, M.A.R. (2011). Plant oils: The perfect renewable resource for polymer science *European Polym. J*. 47 (5): 837-852.
7. Pfister, D.P., Xia, Y. & Larock, R.C. (2011). Recent Advances in Vegetable Oil-Based Polyurethanes. *ChemSusChem*. 4 (6): 703-717.
8. Norzali, N.R.A., Badri, K.H. & Nuawi, M.Z. (2011). Effect of Aluminum Hydroxide Loading on the Compression Stress and Modulus, Thermal Conductivity and Acoustic Properties of Palm-Based Polyurethane Hybrid Composite. *Sains Malaysiana*. 40 (4): 379-384.
9. Badri, K.H., Othman, Z.B. & Razali, I.M. (2005). Mechanical properties of poyurethane composites from oil palm resources. *Iranian Polym. J.* 14 (5): 441-448.
10. Chung, Y.-j., Kim, Y. & Kim, S. (2009). Flame retardant properties of polyurethane produced by the addition of phosphorous containing polyurethane oligomers (II). *J. Ind. Eng. Chem*. 15 (6): 888-893.
11. Ashida, K., (2007). Polyurethane and Related Foams: Chemistry and Technology. Taylor & Francis: New York.
12. Liang, S., Neisius, M., Mispreuve, H., Naescher, R. & Gaan, S. (2012). Flame retardancy and thermal decomposition of flexible polyurethane foams: Structural influence of organophosphorus compounds. *Polym. Deg. Stab*. 97 (11): 2428-2440.
13. Van der Veen, I. & De Boer, J. (2012). Phosphorus flame retardants: Properties, production, environmental occurrence, toxicity and analysis. *Chemosphere*. 88 (10): 1119-1153.
14. Guo, Y., Mannari, V., Patel, P. & Massingill, J. (2006). Self-emulsifiable soybean oil phosphate ester polyols for low-VOC corrosion resistant coatings. *J. Coatings Tech. and Research*. 3 (4): 327-331.
15. Firdaus, F.E. (2011). Relationship od ReactionTemperature on Phosphate Oligomers Reactivity to Properties of Soy-Poyurethane. *World Academy of Science, Engineering and Technology*. 76: 230-234.
16. Fan, H., Tekeei, A., Suppes, G.J. & Hsieh, F.-H. (2012). Physical Properties of Soy-Phosphate Polyol-Based Rigid Polyurethane Foams. *Int. J. Polym. Sci*. 2012: 1-8.
17. Latere Dwan'Isa, J.-P., Mohanty, A.K., Misra, M., Drzal, L.T. & Kazemizadeh, M. (2003). Novel Biobased Polyurethanes Synthesized from Soybean Phosphate Ester Polyols: Thermomechanical Properties Evaluations. *J. Polym. and the Environment*. 11 (4): 161-168.

18. Derawi, D. & Salimon, J. (2010). Optimization on Epoxidation of Palm Olein by Using Performic Acid. *e-Journal of Chemistry*. 7 (4): 1440-1448.
19. Pavia, D.L., Lampman, G.M. & Kriz, G.S., (2001). Introduction to Spectroscopy. Brooks/Cole: California.
20. Narine, S.S., Kong, X., Bouzidi, L. & Sporns, P. (2007). Physical Properties of Polyurethanes Produced from Polyols from Seed Oils: II. Foams. *J. Am. Oil Chem. Soc*. 84: 66-72.
21. Badri, K.H. & Redwan, A.M. (2010). Effect of Phosphite Loading on the Mechanical and Fire Properties of Palm-Based Polyurethane. *Sains Malaysiana*. 39 (5): 769-774.
22. Zhang, L., Zhang, M., Hu, L. and Zhou, Y. 2014. Synthesis of Rigid Polyurethane Foams with Castor Oil-based Flame Retardant Polyols. *Industrial Crops and Products*. 52: 380-388.
23. Pan, L.L., Li, G.Y., Su, Y.C. and Lian, J.S. 2012. Fire retardant mechanism analysis between ammonium polyphosphate and triphenyl phosphate in unsaturated polyester resin. *Polym Deg Stab*. 97 (9): 1801-1806.
24. Chattopadhyay, D.K. and Webster, D.C. 2009. Thermal stability and flame retardancy of polyurethanes. *Prog. Polym. Sci*. 34 (10): 1068-1133.
25. Hörold, S. 1999. Phosphorus flame retardants in thermoset resins. *Polym. Deg. Stab*. 64 (3): 427-431.
26. Kuryla, W.C. and Papa, A.J. 1978. Flame Retardancy of Polymeric Materials. Vol. 4. Marcel Dekker, Inc: New York
27. Shih, Y.-F., Wang, Y.-T., Jeng, R.-J. and Wei, K.-M. 2004. Expandable graphite systems for phosphorus-containing unsaturated polyesters. I. Enhanced thermal properties and flame retardancy. *Polym. Deg. Stab*. 86 (2): 339-348.