The Role of Phosphate Ester as a Fire Retardant in the Palm-Based Rigid Polyurethane Foam

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SUMMARY

Palm-based polyurethane containing phosphate ester (PE) as fire retardant has been developed. This study was conducted to investigate the effect of PE inclusion into palm-based polyurethane (PU) system onto the mechanical and burning property of the PU. The PE was synthesized *via* ring-opening hydrolysis between phosphoric acid (H_3PO_4) and epoxy. The synthesis was conducted at 60-70 °C with varying concentration of H_3PO_4 at 2.5, 5.0 and 7.5 wt.%. It was then added into the PU system at 0, 5, 10 and 15 wt.%. Density of the PU foam was in the range of 45-50 kg·m^{-3}. PE increased the compression strength and modulus of the PU. The highest compression stress (1441 kPa) and modulus (7733 kPa) were discovered with the addition of 10 wt.% PE. Burning properties showed that the addition of PE has decreased the burning rate of the PU foam. PU with PE synthesized from 5.0 wt.% H_3PO_4 showed excellent burning properties with the lowest burning rate (0.047 cm·s^{-1}) compared to control PU which was at 0.119 cm·s^{-1}.

Keywords: Epoxidized palm kernel oil, Palm-based polyol, Phosphate ester, Phosphorus fire retardant, Polyurethane

1. INTRODUCTION

Polyurethane (PU) is a versatile class of polymers due mainly to their rapid and easy processing and to some excellent chemical and physical properties which can be tailored to suit a wide range of applications including elastomers, fibers, foams, surface coatings, and adhesive products. PU is a polymer with urethane linkage in their structure that is produced from the reaction of polyalcohol (-OH) with polyisocyanate (N=C=O) as shown in **Figure 1**[1]. PU has been widely used as insulated material due to its low thermal conductivity[2]. However, it is easily caught fire. PUs are flammable when in direct contact with heat or fire[3]. This drawback limits PU foam as building materials and in automobile industries without specific lamination or interfaces. The flammability of PU becomes particularly severe when it undergoes degradation to form flammable monomers or active products[4].

In order to improve its fire property, flame retardant (FR) was introduced into the PU system. FR is defined as a chemical compound that modifies the pyrolysis reactions of polymers or oxidation reactions implied in the combustion by slowing down or by inhibiting them[4]. Although it improves the flammability of the polymer, its presence deteriorates mechanical properties of the PU foam. Norzali and co-workers[5] has found that the incorporation of mineral-type FR (aluminium hydroxide) into the PU system has decreased mechanical properties of the PU even though it has successfully enhanced the burning properties. This is due to the interphase separation that occurred between FR and the polymer. FR with high degree of compatibility with the polymer has intensively been designed to improve the flammability as well as the mechanical properties of the PU.

Commercial halogenated FR namely tris(1-chloro-2-propyl)phosphate (TCPP) or tris(monochloro-propyl) phosphate (TMCP) that exists in the form of liquid is manufactured as an alternative to improve the mechanical properties[6]. However, these liquid FRs are mostly halogenated compounds. Halogenated FR produces halide metal and halogen acid when heated and creates environmental issues. Halide metals and halogen acid release from the reaction have greater tendency to deplete the ozone layer. They are potentially toxic and create environmental problem during storage, transportation and combustion[7]. Phosphorus-containing compound has been considered as an alternative to replace the halogenated FR. Fan *et al.*[8], Firdaus[9], Guo *et al.*[10]

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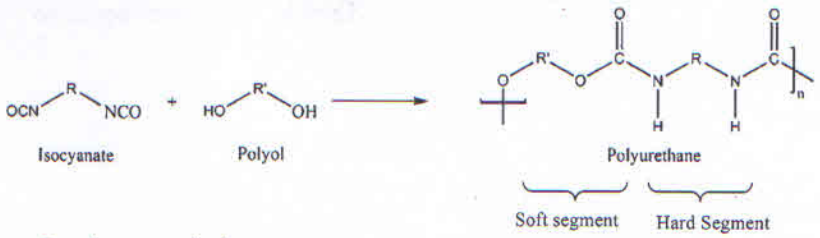
Figure 1. The chemical pathway for the formation of urethane linkage



and Norzali *et al.*[11] have synthesized phosphate esters FR from soybean oil. They have found that the phosphate esters improved the flammability of the PU. This paper investigated the effect of palm-based phosphate ester loading on the burning and mechanical properties of the rigid PU foam. This paper discussed the role of PE as FR in the palm-based PU system.

2. MATERIALS AND METHOD

2.1 Materials

Epoxidized palm kernel oil (EPKO) was supplied by Malaysia Nuclear Agency, Selangor, Malaysia. *Ortho*-phosphoric acid H_3PO_4 (85 wt.%) was purchased from Merck, Malaysia and *tert*-butyl alcohol (*t*BOH) was manufactured by BDH Limited Poole, England. Palm-based polyol (PKO-p) was supplied by UKM Technology Sdn Bhd, UKM/MPOB Station, Pekan Bangi Lama, Malaysia. Silicone surfactant (*Niax L5440*) was supplied by Witco Ltd, glycerol was supplied by BHD Laboratory Supplies, Poole England. Tetramethylhexanediamine (TMHDA), pentamethyl-dietilenetriamine (PMDETA) and the hardener 4,4-methylenediphenyl diisocyanate (MDI) were purchased from Cosmopolyurethane (M) Sdn Bhd, Port Klang, Malaysia.

2.2 Method

2.2.1 Hydrolysis of the EPKO

Hydrolysis of EPKO was conducted based on the method suggested by Guo *et al.* (2007). An amount of H_3PO_4, a portion of 50 wt.% *t*BOH and 10 wt.% distilled water were charged in a glass reactor equipped with a thermometer, dropping funnel, water cooled condenser and mechanical stirrer. The mixture was heated to 30 °C at a slow heating rate under mechanical stirring at 400–500 rpm for 30 min. The EPKO was dissolved in a portion of *t*BOH and added drop-wise into the mixture over the period of 45 min. After the final dropping of the EPKO, the temperature was raised to 80–90 °C for 6 h or until the epoxide content reached below 0.2%. Upon completion of the reaction, the mixture was separated using a separatory funnel. The yellow oily organic phase (PE) was then neutralized with sodium chloride and hot distilled water until pH7. The amount of H_3PO_4 was varied at 2.5, 5.0 and 7.5 wt.% of the EPKO.

2.2.2 Development of Rigid PU Foam With the Addition of PE

Table 1 showed the formulation of PU with varying amount of PE. The resin was prepared by mixing PKO-p with glycerol, surfactant, catalysts and water. PE was added into the resin at varying amount of 0, 5, 10 and 15 wt.% prior to reacting with MDI. The mass ratio of resin to MDI was fixed at 100:140. The mixture was mixed at 1000 rpm for 10 s before being poured into the mould and allowed to cure for 15 min. The moulded polyurethane was then conditioned for 16 h according to BS 4370 Part 1: 1988: Method 3 (*Method of Test for Rigid Cellular Material: Compression*) before further characterizations.

2.3 Characterization of the PU Foam

2.3.1 Fourier Transform Infra-red Spectroscopy Analysis

The presence of the functional groups in the PU was analyzed by Fourier Transform Infra-red spectroscopy (FTIR) using a spectrometer model Perkin Elmer Spectrum 400. Samples were analyzed by Attenuated Total Reflectance technique at wave number of 4000-700 cm^{-1}. Amine (N-H), carbamate (C-N) and carbonyl (C=O) peaks were identified.

Table 1. Formulation of the rigid PU foam with the inclusion of PE

Component	PU Control (0 wt.% of PE)	Amount of PE, wt.%		
		5	10	15
PKO-p	90	85	80	75
PE	–	5	10	15
Glycerol	10	10	10	10
Surfactant	3	3	3	3
TMHDA	0.45	0.45	0.45	0.45
PMDETA	0.40	0.40	0.40	0.40
Water	4	4	4	4

2.3.2 Density

Density of the PU foam was measured according to BS 4370 Part 1: 1988 Method 2 (*Determination of Apparent Density*). PU-PE block was weighed and measured and the density was determined using Equation (1):

$$\text{Density, kg} \cdot \text{m}^{-3} = \frac{\text{mass of PU, kg}}{\text{volume of PU, m}^3} \quad (1)$$

2.3.3 Compression Test

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

2.3.4 Burning Test

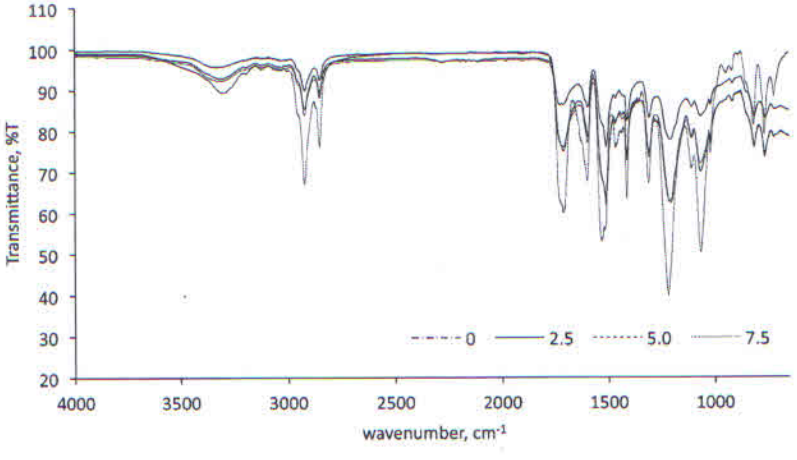
The burning test was carried out to determine the fire resistivity of the PU foam according to ASTM D 5048-90 Procedure B method 2 (*Standard Test Method for Measuring the Comparative Burning Characteristics and Resistance to Burn through of Solid Plastics Obsolete*). The PU foam was cut into test samples with the dimensions of 125 mm × 30 mm × 10 mm (length × width × thickness). The test samples were then clamped at one end so that its position was at 30°. The 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 (2):

$$\text{Burning rate, m} \cdot \text{s}^{-1} = \frac{(\text{final length of specimen - initial length of specimen}), \text{m}}{\text{overall burning time, s}} \quad (2)$$

2.3.5 Bomb Calorimetry

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*).

Figure 2. FTIR spectra of PU-PE at PE content of 2.5, 5.0 and 7.5 wt.%



2.4 Determination of Hydroxyl Value (OHV) and Acid Value (AV) of PE

The hydroxyl value test was conducted according to ASTM E 1899–97 *(Standard test method for hydroxyl groups using reaction with p-toluenesulfonyl isocyanate (TSI) and potentiometric titration with tetrabutylammonium hydroxide)* standard. Acid value test was conducted according to PORIM p2.5 (1995) Acidity (*Methods of Test for Palm Oil and Palm Oil Products)* standard and moisture content test was according to ASTM D 2672– 91 Method B (*Polyurethane Raw Materials: Determination of Water Content Polyols*) standard.

3. RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectroscopy Analysis

Spectra of PU-PE are shown in **Figure 2**. Urethane carbonyl (O-C=O) was detected at 17091729 cm^{-1}, carbamate (-C-N) at 1597-1600 cm^{-1}, C-O vibration at 1065 cm^{-1}, N-H bending at 1509 cm^{-1} [11-13]. C-O-P peak was detected at 1018 cm^{-1}. The carbonyl, carbamate and amine peaks of PU-PE were shown in **Figure 3**. Broad band near 1710 cm^{-1} is attributed to the H-bonded and free C=O urethane group. Peak at 1726 cm^{-1} is attributed to the free C=O group. The intensity increased with increasing amount of PE in the PU system. The non-bonded urethane group increased with the increase in the hard segment content. The presence of amine (N-H) stretching group was detected from the increased in intensity of the urethane peak. This N-H stretching peak indicated association of hard segment in the PU system[14]. **Figure 4** showed the structure of PE.

Figure 3. FTIR spectra of PU-PE indicating carbonyl, carbamate and amine peaks belong to PU-PE

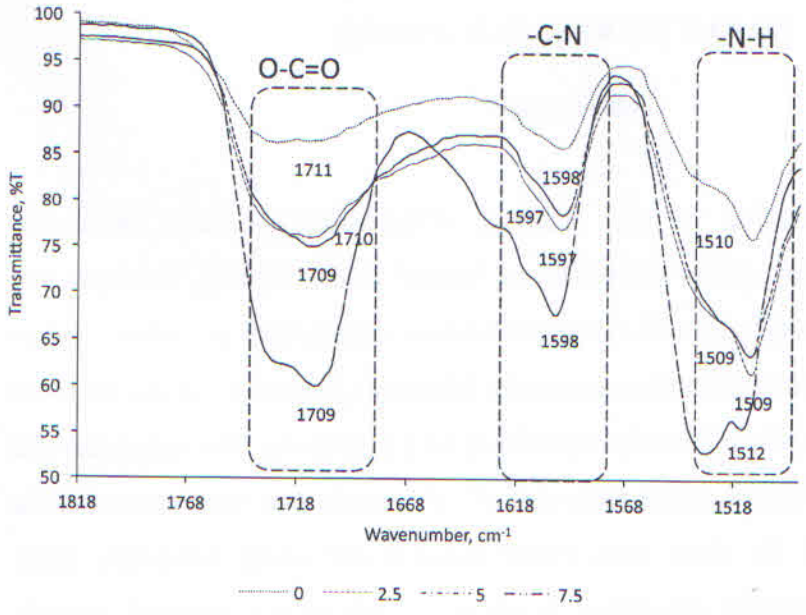
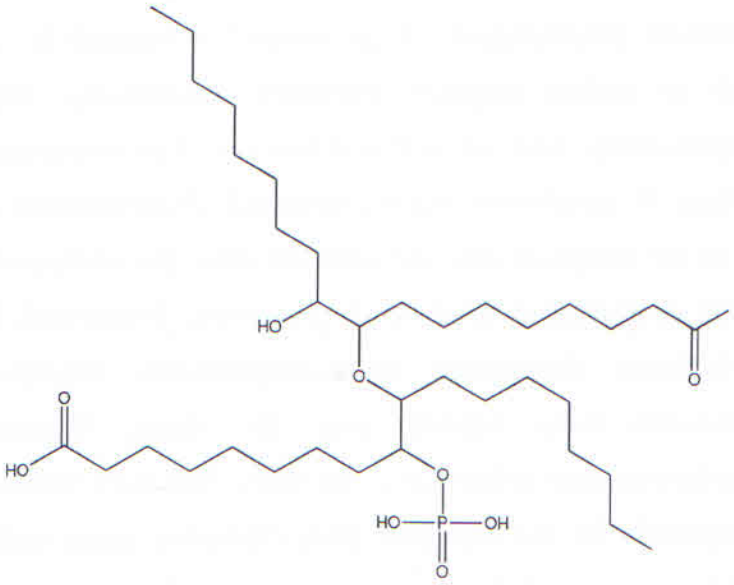


Figure 4. Probable structure of PE



3.2 Density and Compression Stress of the Rigid PU Foam

Table 2 tabulated the density and reaction stages of PU-PE foams. The cream time (CT) and tack-free time (TFT) illustrated the reactivity of the PU foams. CT and TFT became slower with increasing loading amount of PE. CT is related to the starting point of reaction with nucleation of cellular structure (with the aid of released carbon dioxide) during the polymerization. The amine catalyst activity was reduced due to the high acidity of PE. The polymerization occurred in a very slow manner due to retarding activity of the amine catalysts. The amine catalysts act as a buffer in the presence of an acid[15]. CT was delayed from 35 s to 90 s at increasing amount of PE. TFT on the other hands is the time when the surface of the foam is tack-free upon finger pressure. TFT has also been affected by the addition of PE. PE slower the TFT and thus makes it longer for the PU foam to completely cure. In addition, Septevani and co-workers[16] has reported that the position of hydroxyl group in the ester structure affected the TFT. The hydroxyl group is position in the middle of the PE chain as shown in **Figure 4**. The terminal hydroxyl group was sterically hindered and it leads to longer curing time (dangling effect).

Density of PU-PE is shown in **Table 2**. The density of controlled PU (0 wt.% PE) was 55 kg·m^{-3}. For PU-PE 2.5, increasing loading amount of PE from 0 to 5, 10 and 15 wt.% decreased the density from 55 to 54, 50 and 45 kg·m^{-3} respectively. Addition of 5 wt.% and 10 wt.% PE 5.0 does not showed difference from controlled PU. Increasing loading amount of PE to 15 wt.% has slightly decreased the density to 48 kg·m^{-3}. The density of PU-PE 7.5 with 5 wt.% PE showed the same density as the controlled PU while addition of 10 wt.% and 15 wt.% PE 7.5 into the PU system decreased the density to 49 and 50 kg·m^{-3} respectively. Because PE has lower hydroxyl number (OHV), it requires less isocyanate to react. Furthermore, the same amount of CO_2 was generated during the foaming process with the amount of water was fixed at 4.0 wt.%. The production of CO_2 also depends on the amount of moisture in the PE. Because the foam was more expandable and the foam weights essentially the same, the density was reduced[17]. **Table 3** shows the acid number, hydroxyl number and moisture content of PE.

Effect of PE loading to the PU system on the compression stress and modulus is shown in **Figure 5** and **Figure 6** respectively. The compression stress of controlled PU was 476 kPa. Addition

Table 2. The reaction stages of the PU-PE polymerization and its effect on the density of the foams

	PU control	PU-PE 2. 5			PU-PE 5. 0			PU-PE 7. 5		
	0	5	10	15	5	10	15	5	10	15
CT, s	35	36	38	37	45	53	66	63	65	90
TFT, s	79	107	109	112	115	175	240	140	215	380
Density, kg·m^{-3}	55	54	50	45	55	55	48	55	49	50

of PE into the PU system has increased the compression stress of PU-PE. Highest compression stress (1441 kPa) was found at PU-PE 2.5 with 10 wt.% loading. From **Figure 6**, compression modulus showed the same trend as compression stress. Compression modulus was referred to the rigidity of the PU foam. Compression modulus for controlled PU was 1008 kPa. Highest compression modulus was found at PU-PE 2.5 with 10 wt.% loading.

Density and cellular structure i.e. cell struts, cell walls or membranes, cell structures and properties of liquid in the cell are factors affecting the mechanical properties[8,18]. The compression stress and modulus was linerly proportional to the density of PU-PE. Higher density gives higher compression stress and modulus. When load was applied to the PU foam, the struts at the edge of the cell will deformed and bend. After that, the cell will compress. The stress onto the PU system creates energy that was absorbed by the PU molecules. The energy was transferred to the neighbouring molecules continuously and dispersed in the system. Incorporation of PE into the PU system improved the stiffness of the PU-PE. Interaction between hydroxyl group from PE and isocyanate created more crosslinking system and increased the degree of crosslinking[19]. The chemical structure of PU has blocks of alternating segment linked together in covalent bond as shown in **Figure 1**. Hard segment was contributed by the high polarity isocyanate group while soft segment was associated to the low polarity of the polyol. Secondary structure based on the segregation of hard segments into the domain can occurred due to hydrogen bonding. Incompatibility between the

Table 3. Acid number, hydroxyl number and moisture content of PE

Parameters	PE, wt.% H_3PO_4		
	2.5	5.0	7.5
Acid number, mg KOH/g	10.62	31.34	110.95
Hydroxyl value, mg KOH/g	35.33	16.16	26.90
Moisture content, %	1.92	3.02	2.64

Figure 5. Compression stress of PU-PE

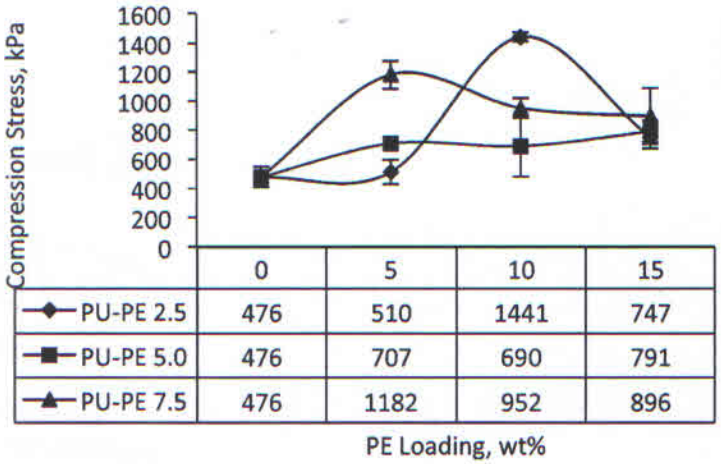
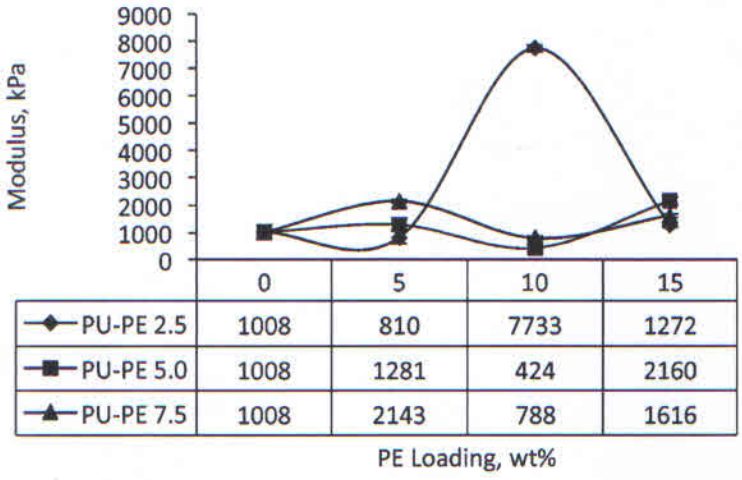


Figure 6. Modulus compression of PU-PE



chemically dissimilar blocks prevent from forming homogenous mixture. The urethane and the PE segments cluster into separate domain forming two phase system. Hard segment acts as filler and crosslinks to restrain the soft segment movement[20]. This mechanism enhances the mechanical properties of the PU system.

3.3 Burning Properties

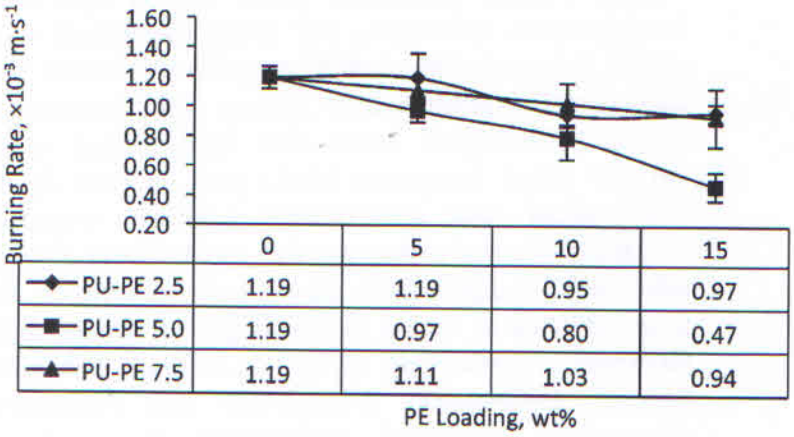
The flammability of polyurethane was contributed by the soft segment in the polyurethane structure (**Figure 1**). When PU was being heated with rising heat, it began to degrade. Burning rate of PU and PU-PE is shown in **Figure 7**. Higher burning rate was observed when PE at 0 wt.% (Controlled PU) which was 1.19 $\times 10^{-3}$ m·s^{-1}. After the addition of the PE, the burning rate reduced. The lowest burning rate was found at PU-PE 5.0 with 15 wt.% PE loading (0.47$\times 10^{-3}$ m·s^{-1}). The burning rate was reduced by 30%. Burning of PU was exothermic process. Applying rising temperature to the PU system results in the thermal excitation of the covalent bond in the PU chain. Once the PU system reached critical temperature, the PU chain starts to decompose and produced small molecules in gaseous phase. The combustible compound evaporated and diffused into the flame region above the polymer/air interface and formed flammable mixtures. When the concentration of these mixtures and the temperature crosses the flammability limits, it started to burn. The exothermic heat from the burning process fed back to the condensed phase, causing further degradation of the polymer[21,22].

Addition of PE to the PU system has decreased the burning rate. When heat is supplied to the PU, the urethane linkage from PE and isocyanate began to dissociate and degrade. The phosphorus in the structure starts to degrade and formed phosphoric acid as shown in **Figure 8**[23]. During thermal and oxidative degradation, the hydrolysis reaction will produce acidic products, since it is the –O-C- bond that is attached. The hydrolysis proceeds stepwise yielding alcohol and substituted phosphoric acid ester. Phosphoric acid and the starting material will be generated when the reaction was driven to completion[23]. Further decomposition of phosphoric acid leads to dehydration of PU and produced phosphorus-rich layer. This phosphorus-rich layer prevents the PU surface from heat and oxygen[19].

3.4 Bomb Calorimetry

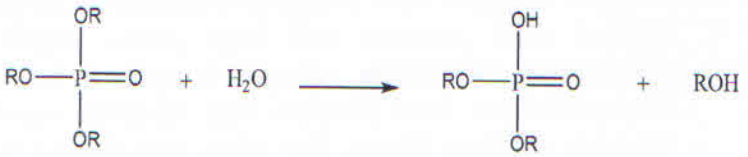
Bomb calorimetry was conducted to support the fire characteristic by determining the enthalpy of combustion for PU-PE. **Figure 9** showed the enthalpy of combustion (ΔH_c) PU-PE. ΔH of Controlled PU was 32.65 kJ·kg^{-1}. The ΔH_c decreased when PE was introduced into the PU system. PU-PE 2.5 with 5 wt.%, 10 wt.% and 15 wt.% loading showed ΔH_c of 30.85, 29.59 and 30.72 kJ·kg^{-1} respectively. PU-PE 5.0 with 5 wt.%, 10 wt.% and 15 wt.%

Figure 7. Burning rate of PU-PE



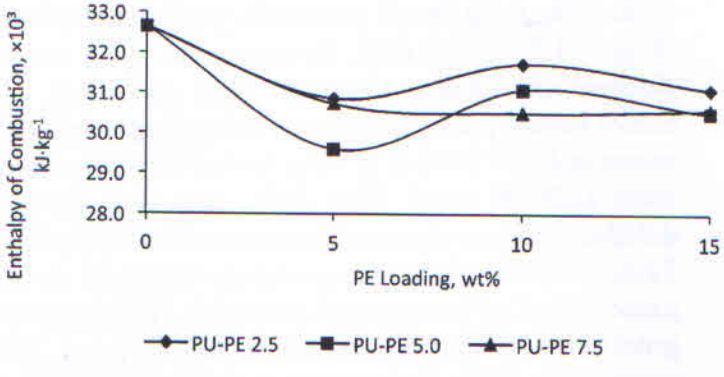
	0	5	10	15
PU-PE 2.5	1.19	1.19	0.95	0.97
PU-PE 5.0	1.19	0.97	0.80	0.47
PU-PE 7.5	1.19	1.11	1.03	0.94

Figure 8. Decomposition of phosphate ester



R - alkyl group

Figure 9. Enthalpy of combustion PU-PE



loading showed ΔH_c of 31.72, 31.07 and 30.50 kJ/kg respectively. PU-PE 7.5 with 5 wt.%, 10 wt.% and 15 w% loading showed ΔH_c of 31.08, 30.49 and 30.58 $kJ \cdot kg^{-1}$ respectively. The ΔH_c proved the interaction between PE and isocyanate. When PU was heated with rising temperature, the chemical structure starts to degrade. Lower ΔH_c attributed to the formation of protective charred layer[19]. The formation of this layer reduces the combustible and volatile products that will further the combustion process. Phosphorus linkage in the PE structure decomposed into phosphoric acid that diluted the combustible gases from further pyrolisis[11].

4. CONCLUSIONS

Polyurethane with palm kernel oil phosphate ester (PU-PE) was successfully produced and the mechanical and burning properties have been determined. Urethane linkage in the PU-PE structure was proved by FTIR spectroscopy analysis. Addition of different amount of PE into PU system has increase the intensity of the carbonyl group indicated that there was an interaction between PE and isocyanate. Compression stress and modulus showed that addition of PE into the PU system has increased the compression stress and modulus especially at PU-PE 2.5 with 10 wt.% loading. Burning test showed that the flammability of PU with PE has improved by decreasing the burning rate with increasing amount of PE into the PU system. PU-PE 5.0 with 15 wt.% loading showed lowest burning rate. Optimum loading of PE was found at PU-PE 5.0 with 15 wt.% where lowest burning rate was observed. The mechanical properties of PU-PE 5.0 with 15 wt.% loading showed higher compression stress and modulus compared to control PU. Lower heat of combustion proved that there was an interaction between the PE and the isocyanate.

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