

Rigid Polyurethane Foam Production from Palm Oil-Based Epoxidized Diethanolamides

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Abstract A new type of rigid polyurethane foam was produced by incorporating oxazolidone heterocyclic rings on to polyurethane backbones. Epoxidized diethanolamides were synthesized by reacting palm oil blends of epoxidized palm olein and refined bleached deodorized palm kernel olein with diethanolamine to produce rigid polyurethane foams. Epoxides, retained in the diethanolamides, reacted with isocyanate during foam production in the presence of AlCl_3 -THF complex catalyst to form oxazolidone linkages in the polyurethane network. The carbonyl stretch of oxazolidone was identified at $1,750\text{ cm}^{-1}$ through Fourier Transform Infra Red analysis. Chemical modifications of the polyurethane network also improved the thermal and mechanical properties of the foams. In addition, isocyanate index 1.4 was determined to be the most suitable in the production of foams from this newly synthesized epoxidized diethanolamides.

Keywords Epoxidized diethanolamides · Isocyanate index · Mechanical · Oxazolidone · Thermal

Introduction

Polyurethane foams are among the most important class of specialty polymers. It can be divided into three major

classes, namely rigid, semi-rigid and flexible polyurethane foams. The global polyurethane market in 2004 showed that rigid polyurethane foam was the second most important foam that contributed 26% to the urethane markets [1]. Rigid polyurethane foams are particularly useful in the construction field; they can be used as polymeric concrete components, insulating materials, sealants and others. Polyols play an important role in the urethane industries and conventionally, a majority of them are derived from petrochemical crude oils and coals. However, in view of the environmental and sustainability aspects, polyols have been prepared from vegetable oils, such as soybean oil, canola oil, castor oil and palm oil [2–8].

One of the important vegetable derived polyols is diethanolamides. Diethanolamides can be synthesized by reacting hydrocarbon fatty acid glyceride from vegetable oil, such as soybean, linseed and safflower oils with diethanolamine (DEA). The diethanolamides were then used in the production of rigid polyurethane foams [9]. Subsequently, modifications of the diethanolamides, in order to improve the mechanical properties of the rigid polyurethane, can be achieved by adding extra hydroxyl functional groups to the polyols. For instance, linseed and safflower hydroxymethylated oils are used in the production of diethanolamides that contained five primary hydroxyl groups per fatty acid [10]. Besides, diethanolamides were also synthesized from carboxylated linseed and soybean fatty acids and oils to increase the distribution of primary hydroxyl groups [11]. The hydroxymethylated and carboxylated diethanolamides are reported to produce better quality foam after blending with Quadrol (*N,N,N',N'*-tetrakis[2-hydroxypropyl]ethylenediamine). Foams are improved in terms of high close-cell contents, good dimensional stability and compression strength. Recently, diethanolamides has been successfully prepared from

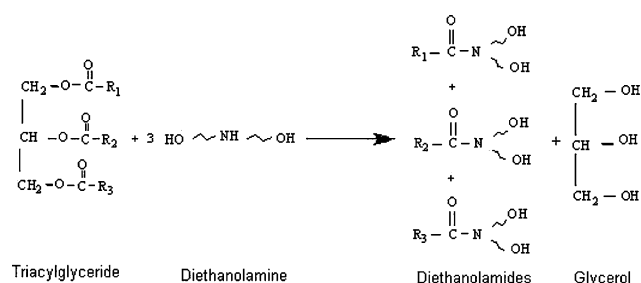
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Refined Bleached Deodorized Palm Kernel Olein (RBDPKO_o) with DEA in the presence of potassium acetate as catalyst [12]. Sieved empty fruit bunch fibres from palm tree were also added as an organic filler to improve the mechanical properties of the rigid polyurethane foam. In other words, polyurethanes prepared from diethanolamides must be modified chemically or blended with other components in order to be sufficiently strong and stable.

Several studies have also reported that the introduction of heterocyclic groups namely isocyanurate, imide, phosphazene and oxazolidone to polyurethanes, can improve the thermal and mechanical properties of the foams [13–16]. The addition of oxazolidone groups to polyurethanes was usually performed by reacting isocyanates with epoxy compounds. Yeganeh et al. reported that the introduction of oxazolidones to the polyurethane backbone from reacting glycidol with isocyanate-terminated polyurethane prepolymers improved the thermal and the stress–strain properties of the elastomers [17]. Although the epoxy groups in the middle of the fatty acid chain of triacylglycerides have lower reactivity towards isocyanate, Javni et al. found that the yield of oxazolidones is actually dependent on the type of catalyst used [18].

In the presence of an appropriate catalyst, the epoxy compounds will react with reactive isocyanate to form oxazolidone during polyurethane foam production [19, 20]. Moreover, isocyanurate can also be yielded as by-product of the reaction [21]. The thermal and physical properties of the rigid polyurethane foam can be improved by extra cross-linking of oxazolidone and isocyanurate heterocyclic rings. In this study, we report the preparation of rigid polyurethane foam using a series of epoxidized diethanolamides [22] (Scheme 1), consisting of different percentages of oxirane oxygen contents (OOC). In addition, a suitable isocyanate index for the production of polyurethane and the effects of the formation of oxazolidone on the properties of the foam were also investigated.



Scheme 1 Reaction scheme of synthesis of diethanolamides. R₁, R₂, R₃ = Alkyl chain with and without epoxides

Experimental Procedure

Materials

Refined Bleached Deodorized Palm Kernel Olein (specifications: iodine value = 26 I₂ mg/100 g sample, free fatty acid = 0.10 mg KOH/g sample, saponification value = 250 mg KOH/g sample) was obtained from Kempas Oil Sdn Bhd and Epoxidized Palm Olein (EPO_o) (specifications: oxirane oxygen contents = 3.0%, acidity = 1.1 mg KOH/g sample, iodine value = 0.65 I₂ mg/100 g sample) was obtained from the pilot plant of the Advanced Oleochemicals Technology Division (AOTD) of the Malaysian Palm Oil Board (MPOB). Potassium bromide for IR Spectroscopy (MERCK), DEA (99.3%; BASF), aluminium chloride-tetrahydrofuran complex (0.5 M solution in tetrahydrofuran; AlCl₃-THF; SIGMA ALDRICH), NIAx stannous octoate catalyst (G.E. Silicone), NIAx A33 triethylenediamine (TEDA) catalyst (G.E. Silicone), Nias silicone surfactant L6900 (G.E. Silicone) and industrial grade methylene diphenyl diisocyanate (MDI) (Cosmonate M 200, Mitsui) were used as purchased.

Synthesis of Diethanolamides

The reaction was carried out in a 1-l Pyrex glass reaction flask submerged in a silicone bath. The reaction flask was equipped with a mechanical stirrer, thermometer and condenser. Various amounts (10% to 100% w/w) of RBDPKO_o was blended with EPO_o as starting materials. The oil mixture was reacted with DEA at molar ratio of 1:3 [Triacylglyceride (TAG): DEA] (Scheme 1). The glycerol by-product was not removed from the reaction mixture as it can act as a cross-linker during rigid polyurethane foam production. The reaction was carried out at 110 °C for 5 h. The hydroxyl value [23] and OOC [24] of the synthesized diethanolamides were determined.

Foam Preparation and Evaluation

Diethanolamides, stannous octoate catalyst, AlCl₃-THF complex, TEDA catalyst, silicone surfactant and water as blowing agent were mixed together in a plastic cup and stirred vigorously at 800 rpm with a mechanical stirrer until the mixture turned creamy at room temperature. Subsequently, the stirring was stopped for the addition of MDI before continuing at the same speed until the mixture was able to rise. The mixture was then left to rise and cured at room temperature (25 °C) for 7 days before carrying out all the mechanical and thermal measurements.

The foams were varied by different isocyanate indices (NCO: OH) using epoxidized diethanolamides prepared from reacting EPO_o with DEA. The isocyanate index is a measurement of excessive isocyanate used relative to the theoretical equivalent amount that is required [25]. The selection of a suitable isocyanate index was based on the effect of the index on the compression strength, density, close cell contents and thermal conductivity of the foams. Upon selecting a suitable isocyanate index, RBDPKO_o was blended with EPO_o in a range of 10–100% (w/w) to synthesize diethanolamides under the same reaction conditions. The effects of OOC in diethanolamides on the thermal and mechanical properties of the foams were studied. Fourier Transform Infra Red (FTIR) spectra analysis was also used to study the functional groups of urethane, oxazolidone, isocyanurate, biuret and the excessive isocyanate.

FTIR Spectra Analysis

A Nicolet FTIR, Model: Magma-IR 550 spectrometer, series II (Japan) was used to monitor the functional groups of the synthesized products. The foam samples were grounded with potassium bromide powder and pelleted for analysis. An average of 64 scans were recorded for each sample.

Thermal Gravimetric Analysis

A TA Instruments SDT 2960 Simultaneous DSC-thermal gravimetric analysis (TGA) Analyzer (Newcastle, DE, USA) was used. About 4–5 mg of foam was used in the analysis of the thermal gravimetric (TG) profiles. Pyrolysis was started from 25 °C and ended at 800 °C with the heating rate of 10 °C/min under a flow of 100 ml/min of nitrogen gas. The results were plotted as percentage of weight loss against temperature in degree Celsius.

Density Measurement

The test specimens (100 mm × 100 mm × 50 mm) were weighed to determine the density in kilograms per cubic meter. Three specimens were tested and the average value was reported.

Percentage of Close-Cell Content

A Micromeritics Accu Pyc 1330 Pycnometer (Norcross, GA, USA) was used to determine the volume of the sample

block based on the pressure change of nitrogen on a calibrated volume. Two sample cubes in the sizes of 25 mm × 25 mm × 25 mm were placed into the Pycnometer cylinder and the gas displacement volume (V_{p1}) was determined. Then, each cube was cut into eight smaller cubes and placed back into the cylinder to determine the second volume (V_{p2}). Volume of open cells was determined using the following formula: $V_{oc} = 31.25 - 2 V_{p1} + V_{p2}$ and the percentage of open-cell content was calculated as: $\%V_{oc} = (V_{oc}/31.25) \times 100$, in which 31.25 was the geometric volume of the samples. Thus, the percentage of close-cell content, $\%V_{co} = 100 - \%V_{oc}$.

Compression Strength Measurement

The compression strength was tested at 10% deformation with a Zwick Universal Testing Machine (UK). Foam with the size of 50 mm × 50 mm × 30 mm was compressed between two flat plates at speed rate of 2.500 mm/min.

Thermal Conductivity Measurement

Thermal conductivity of the foam was measured by the hot-wire transient method using a Kemtherm QTM-D3 instrument (Japan).

Dimensional Stability Measurement

The samples were cut to dimensions of 100 mm × 100 mm × 25 mm. The length, width and thickness of the samples were measured using a vernier caliper. The samples were conditioned at 25 °C for 1 day before being transferred into controlled temperature chambers at 70 °C and –25 °C, respectively, for 14 days. The measurements were conducted as described in Method 5A of BS 4370: Part 1: 1998 [26].

Results and Discussion

The Effects of the Isocyanate Index on Polyurethane Foam

Alterations in the foam formulation in terms of varying amount and type of polyols, catalysts, cross-linkers, surfactants, fillers, blowing agents and others will result in different quality of foams produced. Studies have been conducted to determine the effects of water content and soy flour content, added into rigid polyurethane foam formulation, on the physical and dynamic-mechanical properties of the water-blown foam [27, 28]. In this study, we used a

typical formulation to determine the effects of different isocyanate indices (NCO: OH ratio) on the physical properties of the foam (Table 1). The rigid polyurethane foam was produced from epoxidized diethanolamides from reacting EPO_o with DEA. The synthesis and characterization of the epoxidized diethanolamides will be described in another paper. As oxazolidone linkages can only be formed at elevated temperatures, the preparation of polyurethane foam containing oxazolidone linkages at room temperature is only possible with the presence of an appropriate catalyst [20]. AlCl₃ has been reported to be the most suitable Lewis acid catalyst in the one shot preparation of oxazolidone foams and oxazolidone-isocyanurate foams. Thus, an AlCl₃-THF complex was added to the polyol mixture in addition to the regular additives, such as stannous octoate catalyst, TEDA catalyst, silicone surfactant and water during the production of polyurethane foam.

Foam with a higher density will give a higher compression stress and vice versa [29]. When the isocyanate index was varied from 1.0 to 1.7, we observed a co-relation between density and compression strength of the foam (Fig. 1). The increase in the isocyanate index from 1.0 to 1.4 had led to an increase in the density and compression strength in the foam. However, when the isocyanate index was increased to 1.5, a decrease in the density and compression strength was recorded, but when the index was further increased to 1.6 and 1.7, respectively; higher density and compression strength were recorded. Although foams produced using isocyanate indices of 1.6 and 1.7 showed higher compression strength, the foams were found to be more brittle. The increase in isocyanate index and thus the increased amounts of excess isocyanate may result in the formation of the hard segment of isocyanurate [30], biurets and allophanates [31]. The high content of isocyanurates, biurets and allophanate in turn led to a more rigid but brittle and fragile foam. Consequently, we proceeded to investigate the effects of the isocyanate index on close-cell contents and thermal conductivity of the

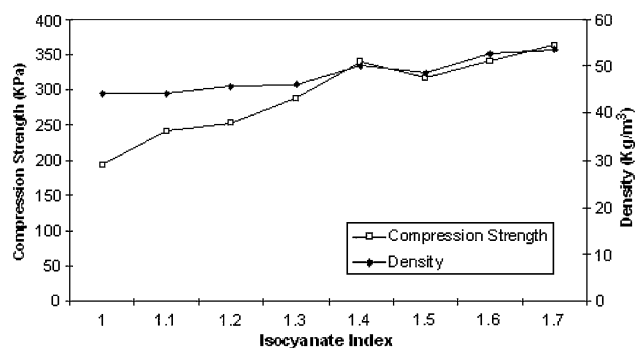


Fig. 1 Effects of different isocyanate indices on the compression strength and density of the foam. Diethanolamides used in the foam production were synthesized by reacting EPO_o with DEA at molar ratio of 1:3 at 110 °C for 5 h

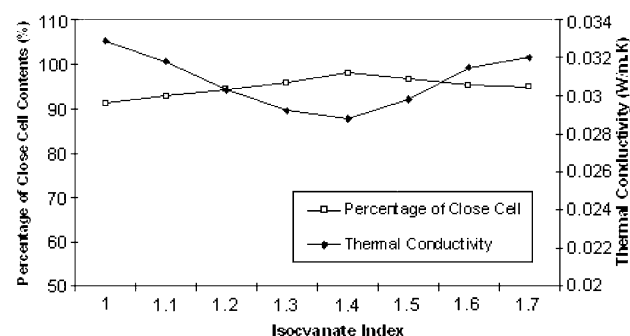


Fig. 2 Effects of different isocyanate indices on the percentage of close cell contents and thermal conductivity of the foam. Diethanolamides used in the foam production were synthesized by reacting EPO_o with DEA at molar ratio of 1:3 at 110 °C for 5 h

polyurethane foam. Results showed that foams with a higher percentage of close cell contents exhibited lower thermal conductivity (Fig. 2). Therefore, we selected an isocyanate index of 1.4 as the most suitable index to be used as it produced non-brittle foam with the lowest thermal conductivity (0.0288 W/m K) and the highest close-cell contents (97.95%) while maintaining moderate compression strength (338.8).

Table 1 Typical formulation for rigid polyurethane foam

	Part (pph)
Component A	
Diethanolamides	100.00
Stannous octoate catalyst	0.20
AlCl ₃ -THF complex	1.00
TEDA catalyst	0.40
Silicone surfactant	2.00
Distilled water	2.00
Component B	
MDI ¹ (Isocyanate index = 1.0)	111.78

¹ The isocyanate content of the MDI used was 30.80%

The Effects of OOC in Diethanolamides on Polyurethane Foam

A total of 10–100% (w/w) of RBDPKO_o was blended with EPO_o to react with DEA at molar ratio of 1:3 to produce diethanolamides. The production of foam using different OOC diethanolamides was based on the typical formulation (Table 1) with the selected isocyanate index of 1.4. Results in Table 2 showed the properties of the diethanolamides and the TG characters of the foams produced. The OOC in the diethanolamides decreased proportionately with the increasing amount of RBDPKO_o blended to EPO_o.

Table 2 Polyurethane foams produced by different OOC diethanolamides and their thermal characters

Foam code	Properties of diethanolamides				Thermal characters		
	Raw materials		OOC (%)	Hydroxyl value (mg KOH/g sample)	T _{10%} (°C)	T _{50%} (°C)	T _{90%} (°C)
	RBD	EPO _o					
	PKO _o (wt%)	(wt%)					
0	0	100	2.03	354.82	235.08	414.29	787.07
1	10	90	1.71	350.46	238.15	411.78	785.02
2	20	80	1.63	338.74	229.95	410.68	787.85
3	30	70	1.40	351.91	232.50	412.77	782.39
4	40	60	1.17	350.82	230.64	408.21	776.50
5	50	50	1.01	351.85	234.20	410.08	759.14
6	60	40	0.78	351.85	232.19	422.45	745.00
7	70	30	0.59	334.12	237.58	417.62	726.55
8	80	20	0.38	333.08	236.44	395.87	658.73
9	90	10	0.19	346.27	224.85	388.24	589.23
10	100	0	0.00	343.80	204.77	380.76	467.80

OOC oxirane oxygen contents of diethanolamides, *Thermal characters* thermal gravimetric results for the foam produced by different OOC diethanolamides, $T_{10\%}$ temperature of 10% weight loss, $T_{50\%}$ temperature of 50% weight loss, $T_{90\%}$ temperature of 90% weight loss

However, the hydroxyl values of the diethanolamides ranged from 330 to 350 mg KOH/g sample did not show significant changes when differing amounts of RBDPKO_o were blended to EPO_o. TGA recorded temperatures at 10, 50 and 90% foam weight loss resulting from the furnace pyrolysis. The initial decomposition temperature ranged from 200 to 240 °C for 10% of foam weight loss. These decompositions were related to the decomposition of the

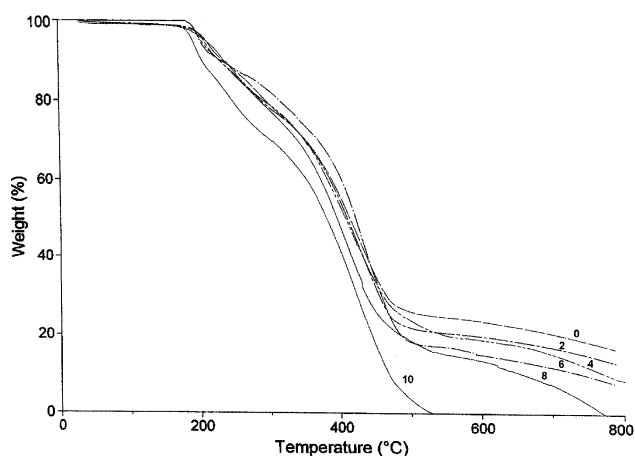


Fig. 3 Thermal gravimetric analysis curves of the polyurethane foams. Foam 0: OOC of diethanolamides = 2.03%, foam 2: OOC of diethanolamides = 1.63%, foam 4: OOC of diethanolamides = 1.17%, foam 6: OOC of diethanolamides = 0.78%, foam 8: OOC of diethanolamides = 0.38%, foam 10: OOC of diethanolamides = 0.00%. Foams were produced using isocyanate index of 1.4

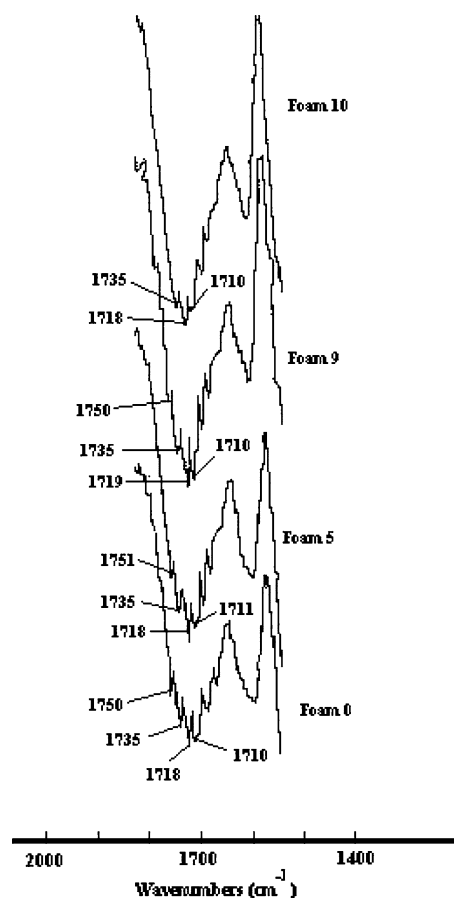


Fig. 4 FTIR spectra analysis of the polyurethane foams. A total of 1,750 cm^{-1} : carbonyl stretch of oxazolidone, 1,735 cm^{-1} : carbonyl stretch of urethane, 1,718 cm^{-1} : carbonyl stretch of biuret and 1,710 cm^{-1} : carbonyl stretch of isocyanurate. Foam 0: OOC of diethanolamides = 2.03%, foam 5: OOC of diethanolamides = 1.01%, foam 9: OOC of diethanolamides = 0.19%, foam 10: OOC of diethanolamides = 0.00%. Foams were produced using isocyanate index of 1.4

urea and urethane of the primary alcohol of the diethanolamides [32]. When it was intensified to 380–430 °C (corresponding to 50% foam weight loss), the decomposition of the polymers was based on the more thermally stable oxazolidone rings. Finally, at 90% foam weight loss, the decomposition temperature was recorded from 450 to 800 °C and could be related to the depolymerization of the isocyanurate rings. We noticed that the decomposition temperatures for 10, 50 and 90% foam weight loss decreased proportionately with the decrease in OOC in diethanolamides. Referring to Fig. 3, foam produced from higher OOC diethanolamides, which was Foam 0, exhibited markedly more thermal stability than foams with lower amounts or without the presence of epoxides (Foam 2, 4, 6, 8, 10). Higher OOC in diethanolamides allowed the formation of oxazolidones in the urethane backbones. In addition, isocyanurates can also result from reacting

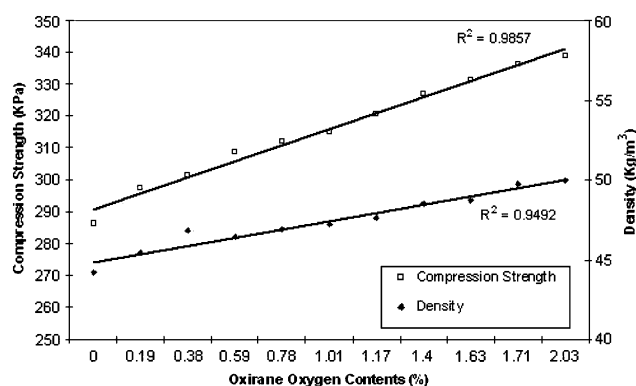


Fig. 5 Effects of OOC in diethanolamides at 10% compression strength (kPa) and density of the foam. Diethanolamides were synthesized by blending 10% (w/w) to 100% (w/w) of RBDPKO₀ to EPO₀ as starting materials to react with DEA at molar ratio of 1:3 at 110 °C for 5 h. Foams were produced using isocyanate index of 1.4

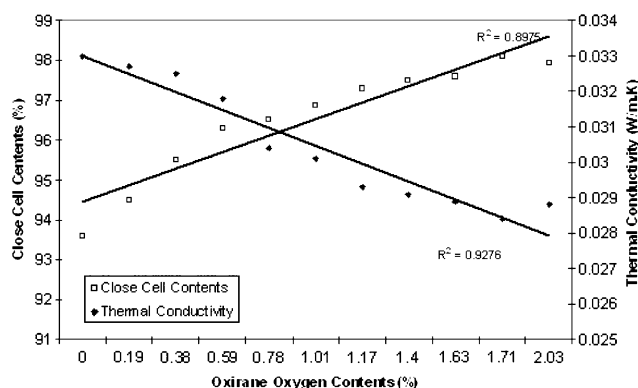


Fig. 6 Effects of OOC in diethanolamides on the percentage of close cell contents and the thermal conductivity of the foam. Diethanolamides were synthesized by blending 10% (w/w) to 100% (w/w) of RBDPKO₀ to EPO₀ as starting materials to react with DEA at molar ratio of 1:3 at 110 °C for 5 h. Foams were produced using isocyanate index of 1.4

epoxide with isocyanate at a lower temperature [21]. Both oxazolidone and isocyanurate heterocyclic rings exhibited good-heat resistance and have been used as heat resistant thermosetting resins [33]. Therefore, rigid polyurethane was noticeably improved thermally by the usage of epoxidized diethanolamides.

Fourier Transform Infra Red analysis was used to examine the functional groups present in the polyurethane foam. The carbonyl group of the oxazolidone ring appeared gradually from foam 9 to foam 0 at around 1,750 cm⁻¹ [18] (Fig. 4). But in foam 10, produced by diethanolamides synthesized by RBDPKO₀ only, the carbonyl group of oxazolidone was not detected. In the study of the reaction between aromatic isocyanate and a fatty epoxide, where the epoxy groups were in the middle of the chain, AlCl₃ Lewis acid is the most efficient converter of oxazolidone when compared with other catalysts, namely lithium chloride and zinc iodide [18]. In view of these results, we selected

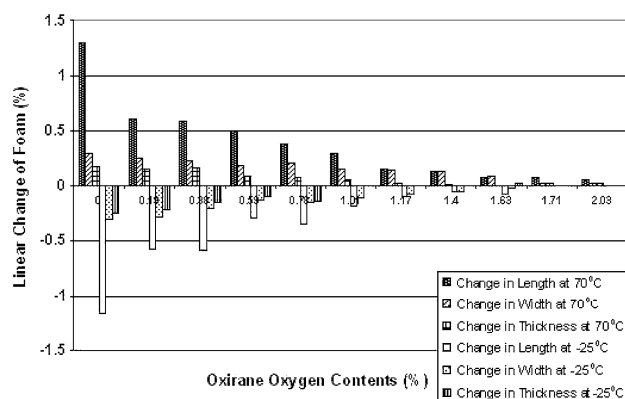


Fig. 7 Effects of OOC in diethanolamides on the linear change of the foam. Foams were conditioned at 70 °C and -25 °C for 14 days to determine the dimensional changes in length, width and thickness. Diethanolamides were synthesized by blending 10% (w/w) to 100% (w/w) of RBDPKO₀ to EPO₀ as starting materials to react with DEA at molar ratio of 1:3 at 110 °C for 5 h. Foams were produced using isocyanate index of 1.4

AlCl₃-THF complex as catalyst so that the thermally stable oxazolidone can be introduced into the polyurethane backbones. Other absorptions of the carbonyl stretch for urethane, biuret and isocyanurate have been reported at 1,735 cm⁻¹ [21], 1,718 cm⁻¹ [34] and 1,710 cm⁻¹ [35], respectively.

Results also showed that the increments in the compression strength and density of the foams corresponded to the increase in OOC in the diethanolamides (Fig. 5). Higher OOC in diethanolamides will produce polyurethane foams with higher contents of oxazolidone and isocyanurate. The hard segment of oxazolidone and isocyanurate linkages most likely contributed to the improvement of the compression strength in the rigid foam. This phenomenon was consistent with epoxy modified polyurethane foams, where the initial compressive modulus and 10% compressive strength of epoxy-PU rigid foam were higher than those of normal PU rigid foam [16]. Figure 6 shows that the increment of OOC in diethanolamides resulted in the increase of close cell contents percentage but resulted in the decrease of the foams' thermal conductivity. Close-cell contents mainly affect the thermal conductivity of rigid polyurethane foams. Foams with higher close-cell contents have better insulating properties [30]. These results reconfirmed the facts that heterocyclic oxazolidone and isocyanurate rings can improve the close cell contents of rigid polyurethane foam and therefore improve the heat retention ability by reducing the thermal conductivity of the foam.

Apart from mechanical strength and thermal stability, dimensional stability is another important characteristic of rigid polyurethane foams used in roofing, insulating or any other constructing materials. Standard specifications for dimensional stability had been reported to be less than 3%

of linear change at 70 °C for 24 h and less than 1% of linear change when tested at −15 °C for 24 h [6]. The foam produced by diethanolamides containing different OOC exhibited a linear growth that ranged from 0 to 1.3% at 70 °C for 14 days and a linear shrinkage in width, length and thickness in a range of 0–1.16% at −25 °C for 14 days (Fig. 7). Therefore, the dimensional change of all the foams were considered to be mild and is acceptable for manufacturing purposes. Lastly, foams produced by the newly synthesized epoxidized diethanolamides containing higher OOC also showed significant dimensional stability when conditioned at 70 °C and −25 °C.

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