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EFFECT OF METHYLENE DIPHENYL DIISOCYANATE INDEX ON PHYSICO-MECHANICAL AND MORPHOLOGICAL PROPERTIES OF PALM OLEIN-BASED VISCOELASTIC POLYURETHANE FOAMS

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ABSTRACT

This study revealed the behaviour of the effect of varying the methylene diphenyl diisocyanate (MDI) index on foaming reactivity, physico-mechanical and morphological properties of palm olein-based viscoelastic polyurethane (VE-PU) foams. The palm olein-based polyol, E-135 NOP was used from 15% to 25% (w/w) in the VE-PU foam formulations. Our study revealed that by varying the isocyanate indices, no significant changes in cream and gelling times were observed, but the rise time was slightly decreased, indicating that the rate of reaction had increased. The compression force deflection (CFD) and tensile strength with palm olein-based VE-PU foam with 25% of E-135 NOP were significantly increased as the isocyanate indices increased. However, it was observed that other mechanical properties, i.e., *density and resiliency of palm olein-based VE-PU foam decreased as the isocyanate indices increased. In terms of morphology, the average cell size determined by scanning electron microscope (SEM) also increased as the isocyanate indices increased. The finding of this study could have practical significance in the selection of the optimal isocyanate index to formulate VE-PU products.*

Keywords: bio-based polyol, isocyanate index, viscoelastic polyurethane foam.

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INTRODUCTION

Polyurethane (PU) foams are one of the most versatile polymeric materials. The chemical nature of these materials allows them to be easily tailor-made to solve challenging problems and to enhance industrial consumer products by adding comfort, warmth and convenience to our lives. PU foams are classified into three major classes, *i.e.*, flexible, rigid and semi-rigid PU foams. Globally, PU rigid foams are the most widely used in terms of application; while PU flexible foams are the fastest in terms of growing demand (Markets and Markets, 2014). Flexible PU foams are mainly used in cushioning applications, *e.g.*, automotive (seats, headrest and armrest) and furniture (pillow and mattresses) (Ionescu, 2005).

Viscoelastic (VE) PU foam is another term for memory PU foam, which constitutes a significant portion of the flexible PU foams market, and they are used primarily for high quality mattress segment and sound absorption applications (Singh *et al.*, 2003). Unlike conventional flexible PU foams, VE-PU foams are characterised by their

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slow response after compression and low resilience (below 20%, ball rebound test) (Polyurethane Foam Association, 2016). In general, parameters involved in formulating and processing VE-PU foams are more restrictive than conventional flexible PU foams. The main challenge is to obtain VE-PU foams that have open cell structure and to avoid shrinkage at a high level of foams softness (compliance) (Rajan *et al.*, 2011).

In recent years, green and bio-polyols (G&B) are becoming more popular due to consumer preference for sustainable and renewable resources. Polyols using natural oils (such as vegetable oil including soybean, castor, palm) as raw materials are known as bio-based polyols. On the other hand, polyols that are recycled from PU via glycolysis or acidolysis process and other sources are known as green polyols or recycled polyols (Markets and Markets, 2014; Sendijarevic *et al.*, 2005). Malaysia is one of the largest palm oil exporters, accounting for 18.3% (17.37 million tonnes) of the world's total vegetable oil trade and 34.3% of the total palm oil trade (Parveez *et al.*, 2021). Palm oil contains molecules with double bonds, *e.g.*, oleic acid, linoleic acid, which can be transformed into epoxy group through epoxidation and then the epoxy undergoes alcoholysis to form hydroxyl (Mohd Zan *et al.*, 2015).

The incorporation of palm oil-based polyol in PU formulation improves the microstructure and mechanical properties of flexible PU foam (Zhang and Chen, 2019). In this study, an introduction of palm oil-based polyol showed a higher closed pore ratio and increased air-flow resistivity, which enhanced the sound absorption coefficient and transmission loss of flexible PU foam. In another similar study, Prociak *et al.* (2018) formulated flexible PU foams using palm oil-based polyols with different hydroxyl numbers. They found that by introducing more than 25% (w/w) of palm oil-based polyols in the flexible PU foam formulation, the hardness, hysteresis, and support factor values of the PU foams produced increased. They also observed that addition of palm oil-based polyols up to 25% had reduced the resiliency of the flexible PU foams. A study by Nurul `Ain *et al.* (2016) discovered that having multiple polyols with different molecular weights in a formulation helped to break the molecular symmetry, which produced PU foams with low resilience. Besides an increase in the palm olein-based polyols (E-135 NOP) concentration in the VE-PU foams formulation does not influence the rate of foaming reactivity. It was also found that the foam cell size was increased and the open cell structure of VE foams was maintained.

PU foams are traditionally produced by a chemical reaction between diisocyanate and polyol. The most commonly used isocyanate (NCO) in PU foam production are aromatic NCO, namely toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI), representing about 90% of the total diisocyanate consumption (Gama *et al.*, 2018). The amount of NCO used in relation to the theoretical equivalent amount is known as the NCO index calculated using Equation (1) (Herrington and Hock, 1997):

$$\text{Isocyanate index} = \frac{\text{Actual amount of isocyanate used}}{\text{Theoretical amount of isocyanate required}} \times 100\% \qquad (1)$$

The NCO index value can have a significant impact on the properties of the PU foams. Variation of the NCO index in foam has a pronounced effect on the hardness of the final foam. The increase in hardness is directly related to increased covalent cross-linking resulting from complete consumption of NCO reactive sites caused by the presence of NCO groups (Rojek and Prociak, 2012; Sung and Byung, 2008). In the production of flexible slabstock foams, the NCO index normally ranges from 105 to 115. Within this range, the hardness of the foam can be readily and safely controlled. However, in the commercial process, foam hardness may require adjustment from mould to mould to compensate for changes in the shape of various cushions and the NCO indices in the range of 85 to 110 are common practice (Herrington and Hock, 1997).

The effect of the NCO index on the properties of palm-based flexible PU made with TDI has been previously conducted (Lee *et al.*, 2007). In this research, palm-based flexible PU foams were prepared by using a blend of polyester and petroleum-based polyols with a molecular weight of 5000 g mol^{-1} at a ratio of 1:1 (w/w) and the NCO index was varied from 90% to 110%. It was observed that at 100% NCO index, the palm-based flexible PU foam had the highest density value and lowest hysteresis, *i.e.*, 60.6 kg m^{-3} and 23.80%, respectively. Gama *et al.* (2018) reported that due to health issues, TDI has been the subject of intensive research, in terms of both human and animal toxicological studies. One important reason is that TDI may cause asthma in sensitive individuals even at extremely low concentrations. This led to the prohibition of TDI usage which is a setback to some PU producers. Recently, many studies were conducted by employing less toxic MDI as NCO instead of TDI in flexible PU foam production (Norin *et al.*, 2006).

As far as the authors are aware, only a few published studies have evaluated the performance of MDI NCO indices on palm oil-based PU foams. Thus, this study extensively investigated the effect of variation MDI NCO indices on foaming reactivity, physico-mechanical and cell morphological properties of VE-PU foams made from palm olein-based polyol (E-135 NOP). As mentioned before, the mechanical properties of VE-PU foams are greatly influenced by NCO indices. Therefore, there is a need to conduct a study on the effect of the NCO index on VE-PU foam since studies on palm oil-based VE-PU foams are limited. The NCO indices used in this study were varied at 65%, 70% and 80% because VE-PU foams are low resilience flexible foams and low NCO index are preferable (Rajan *et al.*, 2011).

MATERIALS AND METHOD

Materials

The palm oil-based polyol, E-135 NOP used in this study was obtained from the pilot plant of the Malaysian Palm Oil Board (MPOB) in Malaysia. The palm oil-based polyol was synthesised via epoxidation and alcoholysis routes as described in detail by Tuan Ismail *et al*. (2018). The E-135 NOP polyol had a hydroxyl value of 134.0 mg KOH g^{-1}, moisture content of 0.04%, acid value of 0.70 mg KOH g^{-1}, iodine value of 6.7 g I_2 100 g^{-1}, the viscosity of 4400 mPa.s at 25°C, number average molecular weight (M_n) of 2537 Da and weight average molecular weight (M_w) of 5798 Da.

Three commercial petroleum-based polyols were supplied by Monument Chemicals, Texas, USA, *i.e.*, (i) Poly-G® 76-120 (ethylene oxide capped polyether triol) with hydroxyl value: 121 mg KOH g^{-1}, moisture content: 0.08%, viscosity at 25°C: 290 mPa.s, M_w: ~1400 g mol^{-1}, equivalent weight [calculated using Equation (2)]: 463.64, (ii) Poly-G® 30-240 (oxypropylated polyether triol) with hydroxyl value: 230 mg KOH g^{-1}, moisture content: 0.05%, viscosity at 25°C; 250 mPa.s, M_w: ~700 g mol^{-1}, equivalent weight: 243.91), and (iii) Poly-G® 85-34 (ethylene oxide capped polyether triol) with hydroxyl value: 35 mg KOH g^{-1}, moisture content: 0.03%, viscosity at 25°C: 1150 mPa.s, M_w: ~6000 g mol^{-1}, equivalent weight: 1602. Lumulse POE 26 (ethoxylated glycerine) with a hydroxyl value of 29.5 mg KOH g^{-1} and the equivalent weight of 1902 were supplied by Lambent Technologies Inc., Illinois, USA. Tegostab B 8871 surfactant was purchased from Behn Meyer, Selangor, Malaysia. Diethylene glycol (DEG) was purchased from Sigma-Aldrich, Missouri, USA. Two types of amine catalysts, Dabco 33LV (A33) (triethylenediamine in dipropylene glycol) and Niax A-1 (A-1) bis(2-dimethylaminoethyl) ether in dipropylene glycol, were obtained from Air Products, Pennsylvania, USA and Momentive, New York, USA, respectively. Distilled water was used as a blowing agent. All chemicals were used as received without any modification. The equivalent weight of the polyol was calculated by using Equation (2):

$$\text{Equivalent weight of polyol} = \frac{56.1 \times 1000}{\text{OH number}} \qquad (2)$$

where 56.1 is the atomic weight of potassium hydroxide and 1000 is the number of milligrams in one gram of sample.

Two types of MDI NCO were used for this study, *i.e.*, Lupranate MI (MDI with a high content of 2,4-isomer, NCO content: 33.5%, equivalent weight: 125.37) was purchased from BASF, New Jersey, USA and Rubinate M (polymeric MDI, NCO content: 31.3%, equivalent weight: 134.19) was purchased from Huntsman, Michigan, USA. The equivalent weight of an NCO is the weight of an NCO compound per NCO site and calculated using Equation (3):

$$\text{Equivalent weight of isocyanate} = \frac{42 \times 100}{\%\ \text{NCO}} \qquad (3)$$

where 42 is the atomic weight of the NCO group.

Methods

Preparation of blends isocyanates. In this study, the NCO component of the PU system was prepared by mixing NCO Lupranate MI and NCO Rubinate M at a ratio of 1:1 (w/w) in a 1 L glass jar at 1800 rpm for 20 min. Prior to preparation, the MDI NCO blend was purged with nitrogen and the glass jar containing the MDI NCO blend was sealed. The viscosity was measured at 25°C and the calculated equivalent weight of this blend are 102.5 mPa.s and 129.78, respectively. The equivalent weight of an NCO blend of different NCOs, the net equivalent weight of the blend was calculated by using Equation (4):

$$\begin{array}{c}\text{Equivalent}\\ \text{weight}\\ \text{blend}\end{array} = \frac{100}{\dfrac{\begin{array}{c}\text{Weight \% of}\\ \text{Luranate MI}\end{array}}{\begin{array}{c}\text{Equivalent of}\\ \text{Luranate MI}\end{array}} + \dfrac{\begin{array}{c}\text{Weight \% of}\\ \text{Rubinate M}\end{array}}{\begin{array}{c}\text{Equivalent weight}\\ \text{of Rubinate M}\end{array}}} \qquad (4)$$

Preparation of VE-PU foam. The free-rise VE-PU foams were prepared by mixing the polyol component (polyols, DEG, surfactant and catalysts) and NCO component with a homogeniser mixer equipped with a 3" diameter mixing blade at 3100 rpm for 10 s. The amount of polyols and isocyanates components are listed in the VE-PU foam formulation (*Table 1*). The mixture was poured into a 34 × 20 × 12 cm polyethylene container and transferred into an air-circulating oven preheated at 70°C for 60 min to complete the polymerisation process. All the VE-PU foams prepared were aged in ambient conditions for a minimum of one week before testing, according to ASTM D3574-08; Standard Test Method for Flexible Cellular Materials-Slab, Bonded, and Molded Urethane Foams.

Foaming profiles were determined for all VE-PU foams, which included the determination of cream time, gel time, and rise time. The foaming profiles were measured using the start of mixing as time zero. Cream time is an indication of the beginning of the foaming process and at this point, the liquid mixture becomes cloudy and begins to expand. Gel time is measured as the time of string formation, at which point the mixture changes from a liquid to a soft rubbery state, indicating an onset of a cross-linked PU network. Rise time is defined as the time at which the foam rise has been completed (Kattiyaboot and Thongpin, 2016; La *et al.*, 2013).

The control VE-PUs were prepared by using a blend of three commercial petroleum-based polyols, *i.e.*, Poly-G® 30-240, Poly-G® 76-120, Poly-G® 85-34, and Lumulse POE 26. The palm olein-based VE foams containing 15%, 20% and 25% of E-135 NOP (based on the weight of total polyols) as a proportionate replacement for three petroleum-based polyols (Poly-G® 30-240, Poly-G® 76-120, Poly-G® 85-34) were prepared without any adjustment in the catalyst system. The NCO index used in this study was varied at 65%, 70% and 80%.

Characterisation of VE-PU foam. Mechanical properties of VE-PU foams were evaluated on the samples prepared with a total amount of 300 g of polyols. All the properties of VE-PU foams were determined according to ASTM D 3574-08: Foam density (Test A), resilience via ball rebound test (Test H), tensile strength and elongation at break (Test E, load cell speed: 508 mm min^{-1}), compression force deflection (CFD), (in-house modified Test C, load cell speed: 50 mm min^{-1}), hysteresis (Procedure B – CFD hysteresis loss, load cell speed: 50 mm min^{-1}). The VE-PU foam density was measured in kilograms per cubic metre as in Equation (5):

$$\text{Density} = \frac{\text{Mass of samples, g}}{\text{Volume of the samples, mm}^3} \times 10^6 \qquad (5)$$

Tear strength was measured according to ASTM D 624–00 (Test Die C) at 500 mm min^{-1} tear speed. Tensile strength, elongation at break, CFD, and hysteresis were determined using Instron Tester Model 1122 with a 500 N load cell. For each test, three to five pieces of VE-PU foam samples were used. Support factor, or the SAG-index (from the verb sag) was measured by dividing the force needed to indent the foam 65% of its original height by the force needed to indent the foam 25% of its original height. The Fourier transform infrared (FTIR) spectra of palm olein-based VE-PU foams were recorded on a Perkin Elmer FTIR Spectrum 100 MILD DTIR equipped with Universal ATR Attachment in the 650-4000 cm^{-1} wavenumber range with 64 scans using a resolution of 6 cm^{-1} for each spectrum. The cell morphology of VE-PU foam was also captured using scanning electron microscopy (SEM) (JSM-IT 100, InTouch Scope™ SEM, Tokyo, Japan) at an acceleration voltage of 10 kV. A thin foam slab was gold-coated by a sputter-coating (SCD 005) with evaporated gold (20 nm thickness), then the morphology of VE-PU foams was captured at 25x and 100x magnifications. The average cell size of the VE-PU foams was also evaluated via SEM.

TABLE 1. FORMULATION OF VE-PU FOAM

Polyol component of PU system	Amount (g)											
E-135 NOP	0.0	15.0	20.0	25.0	0.0	15.0	20.0	25.0	0.0	15.0	20.0	25.0
Poly-G® 30-240	21.0	16.0	14.3	12.7	21.0	16.0	14.3	12.7	21.0	16.0	14.3	12.7
Poly-G® 76-120	21.0	16.0	14.3	12.7	21.0	16.0	14.3	12.7	21.0	16.0	14.3	12.7
Poly-G® 85-34	18.0	13.0	11.3	9.6	18.0	13.0	11.3	9.6	18.0	13.0	11.3	9.6
Lumulse POE 26	40.0				40.0				40.0			
DEG	2.25				2.25				2.25			
Water	2.3				2.3				2.3			
Tegostab B 8871	1.5				1.5				1.5			
A33	0.1				0.1				0.1			
A-1	0.2				0.2				0.2			
Isocyanate (NCO) index (%)	65				70				80			
MDI NCO component of PU System (Lupranate MI/Rubinate) (1:1 w/w) (g)	45.76	45.88	45.90	45.67	49.56	49.61	49.61	49.76	56.64	56.69	56.69	56.76

RESULTS AND DISCUSSION

In this study, the NCO index was varied at 65%, 70% and 80%, and the E-135 NOP added into VE-PU foam formulation was varied at 15%, 20% and 25%. Based on our previous study, incorporation of E-135 NOP higher than 25% reduced the mechanical properties, *i.e.,* tensile, tear strengths of VE-PU foam and increased the size of the PU foam cells structure compared to petroleum-based VE-PU foams cell structure (Nurul `Ain *et al.*, 2016; Prociak *et al.*, 2018). Therefore, the effect of incorporating E-135 NOP at 25% and below was investigated.

Effect of NCO Index on Foaming Reactivity of Palm Olein-based VE-PU Foam

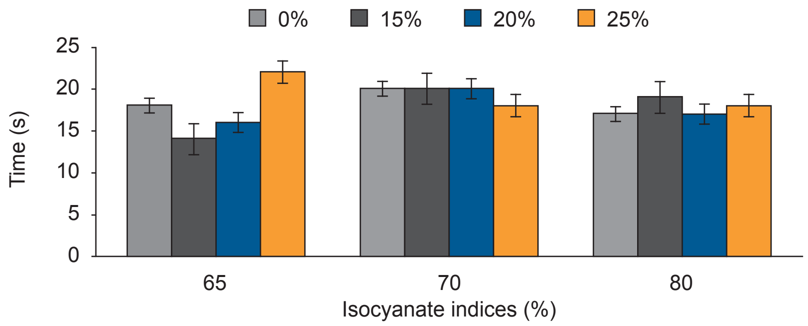
The impact of three NCO indices (65%, 70% and 80%) of palm olein-based VE-PU foams containing 15%, 20% and 25% E-135 NOP was evaluated on the foaming kinetics through the determination of cream time, gel time, and rise time. *Figure 1* demonstrates the rise time decreased, indicating that the reaction rate had increased as the NCO index increased up to 80%. This could probably be due to increased reaction between NCO and water, which resulted in a greater volume of carbon dioxide (CO_2) gas generated in a short period (Prociak *et al.*, 2016; Rojek and Prociak, 2012). The rise time of the palm olein-based VE-PU foams reached a faster rate with an increase in the E-135 NOP content which is in accordance with the studies conducted previously by La *et al.* (2013) and Lee *et al.* (2007). However, no significant changes in cream and gelling time were observed when the NCO indices were increased for all three percentages of E-135 NOP incorporated.

The changes in functional group of the different NCO index. FTIR analysis of VE-PU foams was conducted to determine functional groups that impact the properties of palm olein-based VE-PU foams with 25% E135 NOP as a result of varying the NCO index (*Figure 2*). The NCO group at the wavelength range of 2250 cm^{-1} to 2255 cm^{-1} in the palm olein-based VE-PU foam spectrum was not present as the MDI and polyol reacted to form the urethane group. It was confirmed with the presence of the N-H stretching band at a wavelength of 3299 cm^{-1} to 3334 cm^{-1} and the N-H bending at the wavelength of 1598 cm^{-1} for all palm olein-based VE-PU foams regardless of the NCO index. Increasing the NCO index from 65% to 80% reduced the unreacted -OH groups as can be seen at the absorption of -OH at 3541 cm^{-1} was shifted to 3546 cm^{-1}. The absorption bands at 1690 cm^{-1} to 1735 cm^{-1} were also of interest. It was reported that the carbonyl groups (-C=O) of urethane are divided into four types based on the degree of hydrogen bonding; 1730 cm^{-1} -free carbonyl groups from the soft domain, 1716 cm^{-1} -disordered hydrogen bonded carbonyl groups, 1704 cm^{-1} -ordered hydrogen bonded carbonyl group from hard domain and 1690 cm^{-1} -ordered hydrogen bonded carbonyl groups from crystalline phase (Liu *et al.*, 2020). In our study, the FTIR spectra of the palm olein-based VE-PU foams with 25% E-135 NOP showed the absorption bands at about 1705 cm^{-1} to 1708 cm^{-1}, depending on the NCO index used, indicating the formation of ordered hydrogen bonded carbonyl group of urethane and free carbonyl groups of urethanes, respectively. It was also observed that the intensity of the absorption band of ordered hydrogen bonded carbonyl groups of urethanes at wavelengths of 1705 cm^{-1} to 1708 cm^{-1} increased with an increase in the NCO index. The presence of ordered hydrogen bonded carbonyl groups of urethanes has been reported to improve the mechanical properties of PU (Tereshatov *et al.*, 2015). It was in agreement with the mechanical properties of VE foams in which higher mechanical properties were observed in palm olein-based VE-PU foam prepared at NCO index of 80% compared to palm olein-based VE-PU foams prepared at NCO indices of 65% and 70% (*Table* 2). The VE-PU foam evaluated in this study only contain urethane bonds and no urea bonds. Thus, the ratio of non-bonded and bonded urethane is a good indicator of the hard and soft segments separation. The extent of reaction of urethane with the increased reaction between NCO groups resulted in the formation of allophanates, biurets, and isocyanurates (Ivdre *et al.*, 2020). An isocyanurate band appears at a wavelength of 1413 cm^{-1}. The absorption band at 2923 cm^{-1} to 2927 cm^{-1} and 2859 cm^{-1} to 2869 cm^{-1} are attributed to stretching vibration of polyol soft segment (Norhayati *et al.*, 2018).

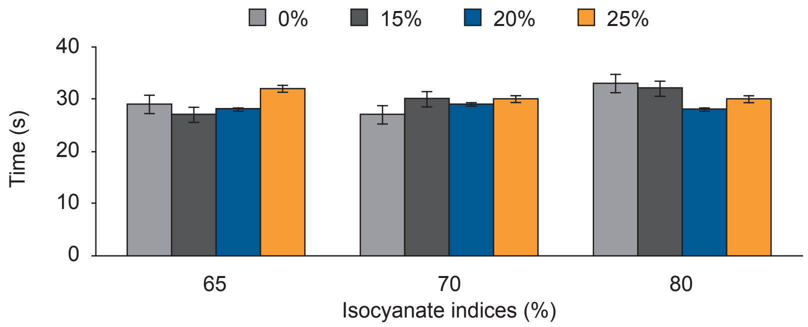
Mechanical properties of VE-PU foams. The effect of varying the NCO indices from 65%, 70% and 80% on the mechanical properties of palm olein-based VE-PU foams containing only 25% of E-135 NOP were further discussed and illustrated in *Figure 3* and *Table 2*. It was observed that the density of palm olein-based VE-PU with 25% E-135 NOP foams was in the range of 52 kg m^{-3} to 58 kg m^{-3} (*Figure 3*). However, the density of palm olein-based VE-PU foam prepared using NCO index of 70% was slightly reduced because of the combined effects of mixture mobility and additional blowing agent (other than physical blowing). These phenomena were likely promoted by increased production of CO_2 from the condensation reaction between NCO groups and water (Sung and Byung 2008). The highest hysteresis was observed at palm olein-based VE-PU foams with 25% E-135 NOP using isocyanate of 80%. This could be due to increased NCO content in the formulation indeed increased the crosslinking density because the formulation gets closer to the stoichiometric ratio (Chognan *et al.*, 2013). In addition, a high index value provides cell walls with great elasticity by allophanate crosslinks, and the walls are less vulnerable to deformation (Sung and Byung, 2008).

Effect of NCO index at 65%, 70% and 80% on other mechanical properties of palm olein-based VE-PU foam was tabulated in *Table* 2. PU foam with a higher NCO index had high hysteresis, thus, has a greater ability to absorb and dissipate energy as reflected by the increase in the resiliency of the VE-PU foam from 2.0 ± 0.7% to 7.1 ± 0.6%. Resiliency is an indicator of the surface elasticity or 'springiness' of foams. It can be explained in such a way that the hard segment content (contributed by –NCO group) in the VE-PU foams is associated with a higher NCO index (Prociak *et al.*, 2016). Therefore, the VE-PU foams with a higher NCO index had lower elasticity. However, in this study, even at the 80% NCO index, the VE-PU foams had resiliencies below 10%; ball rebound of less than 20%, which are typical characteristics desired for VE-PU foams (Singh *et al.*, 2003).

(a) Cream time



(b) Gel time



(c) Rise time

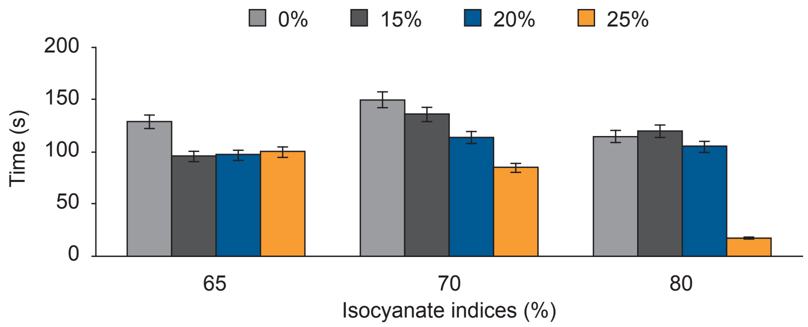


Figure 1. Reaction profiles, i.e., *(a) cream time, (b) gel time and (c) rise time of palm olein-based VE-PU foams prepared with 15% to 25% E-135 NOP at three different NCO indices.*

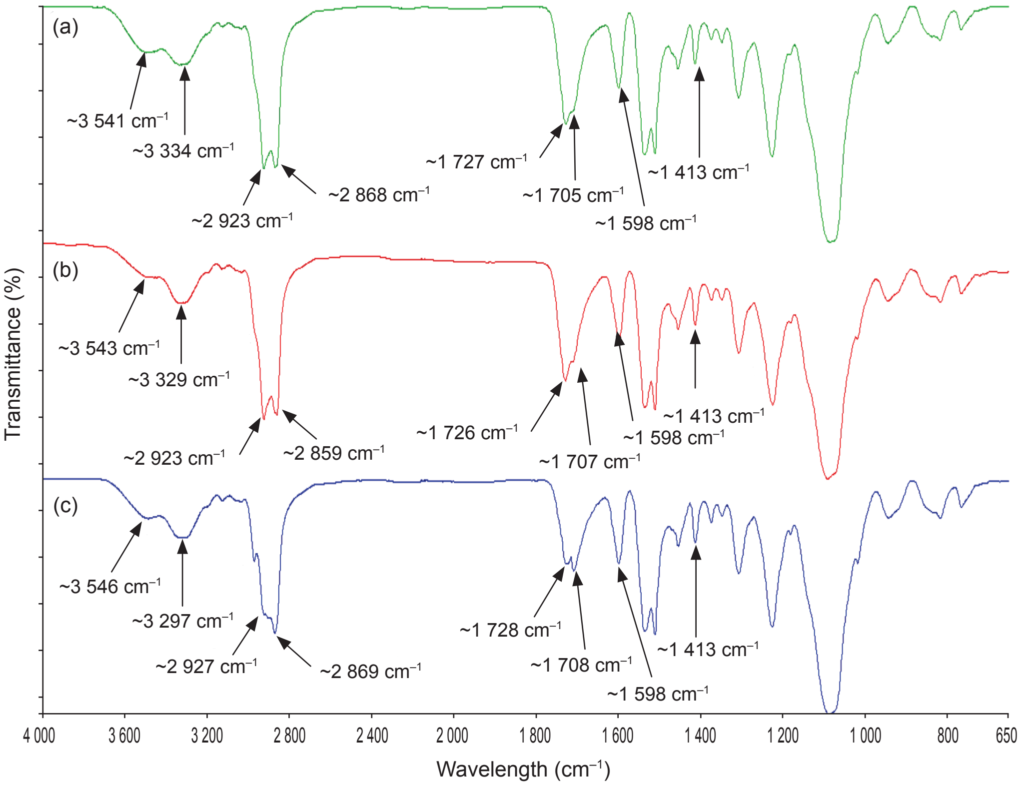


Figure 2. FTIR spectra of palm olein-based VE-PU foam with 25% E-135 NOP at three different NCO indices, i.e., *(a) NCO index at 65%, (b) NCO index at 70%, and (c) NCO index at 80%.*

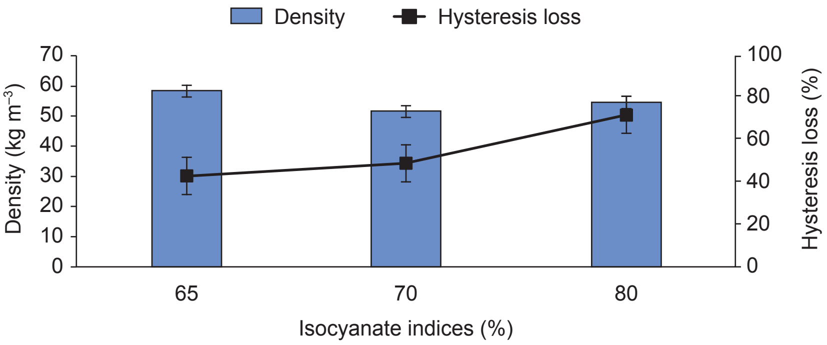


Figure 3. Effect of NCO indices on palm olein-based VE-PU foam density and hysteresis loss with 25% of E-135 NOP at three different NCO indices.

TABLE 2. MECHANICAL PROPERTIES OF VE-PU FOAMS PREPARED WITH 25% OF E-135 NOP AT THREE DIFFERENT NCO INDICES (normalised to 58 kg m^{-3})

Isocyanate indices (%)	**65**	**70**	**80**
Resilience (%)	2.0 ± 0.7	3.3 ± 0.7	7.1 ± 0.6
Compression force deflection (CFD) at 25% (kPa)	0.69 ± 0.09	0.76 ± 0.14	1.77 ± 0.14
Compression force deflection (CFD) at 65% (kPa)	1.59 ± 0.07	1.51 ± 0.07	4.19 ± 0.14
Tensile strength (kPa)	26.61 ± 8.12	36.40 ± 5.63	81.14 ± 7.52
Tear strength (N cm^{-1})	2.10 ± 4.20	2.75 ± 1.50	5.13 ± 3.70
Elongation at break (%)	242 ± 140	177 ± 28	95 ± 10
Support factor (CFD at 65%/CFD at 25%)	2.30 ± 0.78	1.99 ± 0.50	2.36 ± 1.00

Mechanical properties such as CFD and tensile strength values in *Table 2* were normalised to a randomly chosen density of 58 kg m^{-3} of VE-PU foam at 65% NCO index. A normalised value to the density is a must for properties that are dependent on density as it plays an important role in controlling the properties in the flexible PU foam production (Genova *et al.*, 2008). *Table 2* shows that resiliency increased with a higher NCO index, hence an increase in CFD (technically refers to 'hardness') at both deflections, *i.e.*, 25% and 65%. The increase in NCO indices of VE-PU foam has pronounced effect on the hardness of the final foam. Increasing the NCO content in the formulation indeed increased the crosslinking density because the formulation gets closer to the stoichiometric ratio. There are fewer unreacted -OH groups (-OH groups are incorporated in excess to all the VE-PU foam formulations in this work (Chagnon *et al.*, 2013).

Increasing the NCO indices significantly affects the strength of palm olein-based VE-PU foams. It was observed that tensile and tear strengths proportionately increased with the increase of NCO indices from 65% to 80% (*Table 2*). Palm olein-based VE-PU foams with the highest NCO index (80%) produced the highest tensile strength (81.14 kPa) but the lowest elongation at break (95%). Based on the observation above, increasing the NCO index could increase the crosslink density and cohesive strength through the hydrogen bonding, thus, introducing restrictions in the mobility of the soft segment as reflected in lower elongation at break values.

The mechanical properties of VE-PU foams prepared with 25% of E-135 NOP at three different NCO indices in *Table 2* revealed that the support factor of VE-PU foams was highest, *i.e.*, 2.36 ± 1.00 at an isocyanate index of 80%. The SAG index reflects how well the foam envelops the body contours; the better envelopment, the lower the SAG index and *vice versa*. Furthermore, higher SAG index values reflect the foam's ability to support the body and to prevent bottoming out (Soppi *et al.*, 2015). In this study, it was observed that high hysteresis loss and high SAG index which are proportional to the percent of high energy absorption, contributed to better load bearing properties. Higher load bearing properties is desirable in flexible PU foam production (Shan *et al.*, 2013).

The effect of NCO indices on the morphological properties of VE-PU foams. *Figure 4* shows the SEM morphology of the palm olein-based VE-PU with 25% E135 NOP foam cell structure at three different isocyanate indices (65%, 70% and 80%). The VE-PU foam samples were taken randomly in the centre of the foam and parallel to the foam rise. In general, it was observed that all palm olein-based VE-PU foams prepared consisted of spherical and polyhedral shapes. The SEM images also showed voids in cell windows, indicating cell windows were ruptured during the foaming reactions in palm olein-based VE-PU foams (*Figure 4*). Nevertheless, having open cell structures and ruptured windows are desirable properties of VE-PU foams, indicating that the palm olein-based VE-PU foams are fully compressible (Prociak *et al.*, 2021; Rajan *et al.*, 2011).

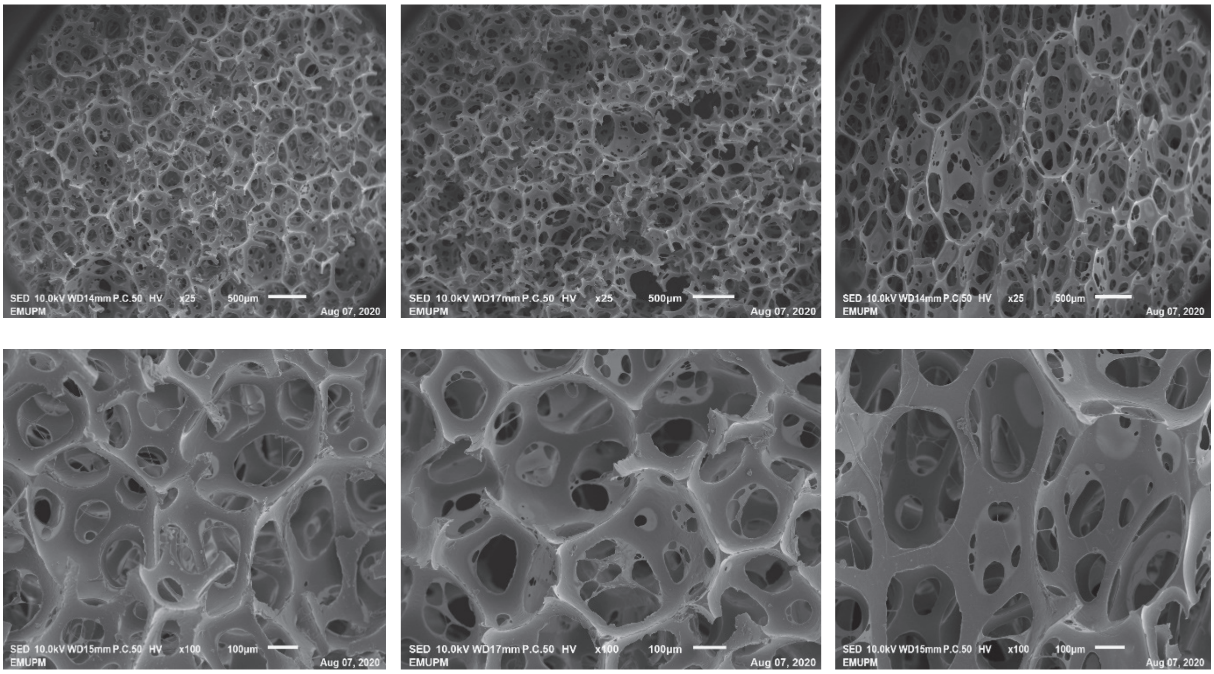


Figure 4. SEM images of palm olein-based VE-PU foam with 25% E-135 NOP at three different NCO indices. PU foams at 25x magnification top row and 100x magnification bottom row. From left to right 65%, 70% and 80% NCO indices.

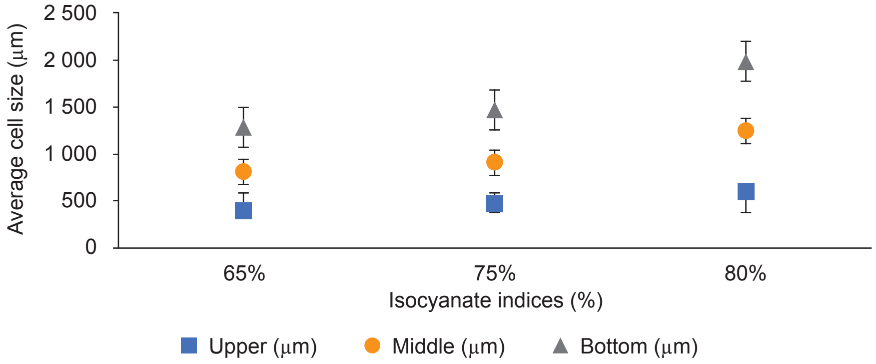


Figure 5. The average cell size of palm-based VE-PU with 25% E-135 NOP three different isocyanate indices.

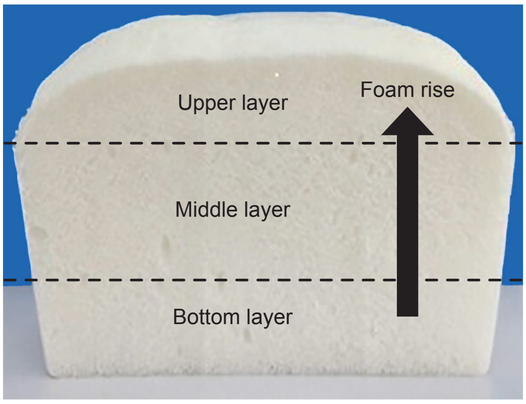


Figure 6. Photograph of a cross-section of palm olein-based VE-PU foam.

These observations were in accordance with the average cell size of palm olein-based VE-PU foam with 25% E-135 NOP at different NCO indices (*Figure 5*). The average cell size was found to increase with the NCO index increment. It was observed the average cell size of VE-PU foams increased with NCO indices from 65% (428.30 µm) to 80% (662.57 µm) at a different layer of the VE-PU foams (*Figure 6*). It is also evident from the SEM morphology of VE foams, where at a higher NCO index of 80% the cell windows of VE-PU foams are more open compared to the cell window of palm olein-based VE-PU foams prepared at NCO indices of 65% and 70%.

CONCLUSION

The effect of varying the MDI NCO indices (65%, 70% and 80%) on foaming reactivity of palm olein-based VE-PU foams containing 15% to 25% (w/w) of E-135 NOP were evaluated. This study shows that no significant changes in cream and gelling times were observed, but the rise time was slightly decreased, indicating the rate of reaction had increased as the NCO index increased up to 80%. Variation of the NCO indices affected physico-mechanical and morphological properties of palm olein-based VE-PU foams with 25% of E-135 NOP. The properties of VE-PU foams such as CFD at 65% deflection, tensile strength and average cell size increased when the NCO index increased from 65% to 80%. However, it was observed that the density and resiliency of palm olein-based VE-PU foam were slightly decreased as the NCO indices increased from 65% to 80%. Overall, it can be concluded that the NCO index of 80% gave the best mechanical properties for VE-PU foam application in comparison to other NCO indices.

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