Palm kernel oil polyol based shape memory polyurethane: effect of polycaprolactone and polyethylene glycol as soft segment

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Abstract
Shape memory polyurethane (SMPU) with its outstanding characteristics is categorized as smart materials and has been utilized in a wide range of applications. In this study, a series of palm kernel oil polyol (PKOp) - based SMPU with the combination of polycaprolactone (PCL) and polyethylene glycol (PEG) as soft segment was synthesized and characterized for the first time. The synthesized SMPUs were examined via several techniques such as Fourier transform infrared, x-ray diffraction, thermal analysis, tensile and shape memory test. The combination of PCL and PEG in PKOp—based SMPU has overcome the drawbacks of PKOp—based PU with only PCL or PEG as soft segment. PU-PCL4PEG4 exhibited tensile strength, Young’s modulus, and shape fixity of 5.7 MPa, 53.9 MPa, and 97%, respectively. For the variation of PEG molar ratio, PU-0.6PEG demonstrated good modulus (151.3 MPa) and shape fixity (99%) but its tensile strength and tensile strain at break were compromised as compared to other samples.

1. Introduction

In accordance with the development of science and technology, as well as the specific requirements for unique applications in the field of biomedical devices, aerospace, electronic engineering, etc, have accelerated the evolution of materials [1]. Shape memory polymers (SMPs) are polymeric materials with the capability to be fixed into a temporary shape by applying specific condition, and recover back their original shape upon the introduction of suitable external stimuli [2–5]. This behavior is also known as shape memory effect (SME) which is evaluated by shape fixity (SF) and shape recovery (SR) [6]. The SME of SMPs is due to their unique structure that comprises of so-called switching segments (reversible phase) and net points (fixed phase) [7]. The switching segments play an important role in maintaining the temporary shape whereas the net points are responsible to retain the original shape [8, 9]. Shape memory polyurethanes (SMPUs) are one of the most notable and common SMPs due to their freedom in characteristic design [10] and high processability [11]. Segmented SMPU consists of alternating sequences of hard segment (HS) serving as the net points and soft segment (SS) as the switching segments, resulting in a physically cross-linked polymeric network [12–14]. Among the prominent applications of SMPU are smart fabrics [15], electronic appliances [16, 17], and biomedical devices [11, 18].

According to Ahmad et al [19] and Firdaus et al [20], polyethylene glycol (PEG) based SMPU exhibited good SME but the mechanical properties was limited due to its brittleness. In contrary, polycaprolactone diol (PCL) is known as a flexible polyol, consequently PCL-based SMPU possesses good elastomeric mechanical properties [19, 21]. Hence, the combination of PEG and PCL as the soft segment can be lucrative and the variation of PEG/PCL molar ratio may be the key to optimize the properties of SMPU in terms of shape memory and mechanical properties. In addition, based on our previous study, the incorporation of palm kernel oil polyol (PKO-p) was found to improve the tensile and shape memory properties of the PCL-based SMPU at 10% molar ratio [22].

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Therefore, in this study, the soft segment part of SMPU which consist of PKOp and the combination of PCL and PEG was investigated systematically in order to optimize the final properties. Moreover, the degree of phase separation (DPS) and soft segment crystallinity has an essential influence on both shape memory and mechanical properties [23–25]. Hence, the effect of the PEG-PCL combination as soft segment on the DPS, soft segment crystallinity, mechanical and shape memory properties were examined.

2. Experimental

2.1. Materials
PEG with MW of 2000 and 4000 g mol\(^{-1}\) were purchased from Merk (Germany) while PCL (MW 2000 g mol\(^{-1}\)) and PCL (4000 g mol\(^{-1}\)) were supplied by Sigma Aldrich (China) and Magna Value Sdn. Bhd., (Malaysia), respectively. PKOp was supplied by Universiti Kebangsaan Malaysia (Malaysia). 4,4’-Methylenebis (cyclohexyl isocyanate) (HMDI or H12MDI), 1,4-Butanediol (BD, chain extender) and dibutyltin dilaurate (DBTDL, catalyst) were supplied by Sigma Aldrich (USA).

2.2. Synthesis of polyurethanes
PKOp—based SMPUs were prepared via two-step bulk growth polymerization process according to the method of Ahmad Zubir et al [25]. In the first step of pre-polymerization, the reaction between PEG/PCL and an excess amount of diisocyanate was taken place in a three-neck round bottom flask that was submerged in a silicon oil bath and equipped with a mechanical stirrer under a continuous stream of nitrogen gas. After 2.5 h, PKOp was injected and the reaction was carried out for another 2 h. During the pre-polymerization, the temperature and the stirring speed were maintained constant at 80 °C and 250 rpm, respectively. In the second step, the polymerization process was carried out by using Haake internal mixer. The obtained pre-polymer was reacted with BD in the presence of few drops of DBTDL at 90 °C and a rotor speed of 60 rpm. The hard segment content was kept constant at 38 wt% for all samples. The chemical structure of the monomers, the general reaction, as well as the molar ratio of the formulated samples were illustrated in figure 1 and table1, respectively. The number appeared in the sample code for sample number 1–8 is referred to the MW of polyol used in the synthesis whereas for sample number 9–14, it is referred to the molar ratio of PEG used.

2.3. Characterization
2.3.1. Fourier transform infrared analysis (FTIR)
Perkin Elmer FTIR spectrometer model Spectrum One was used to investigate the DPS in SMPU and Fityk 0.9.8 software was employed to deconvolute the carbonyl (C=O) stretching area. The test was conducted in a spectral range of 4000–600 cm\(^{-1}\) with the resolution of 4 cm\(^{-1}\) under ambient atmosphere. Each specimen was scanned 16 times. The carbonyl hydrogen index (HBI) and the DPS value was calculated according to the equations as follow [26, 27]:

![Figure 1. The chemical structure of the monomers and the general reaction scheme for the preparation of the segmented SMPU.](image-url)
Where $\Sigma A_{HCO}$ and $\Sigma A_{FCO}$ are the total areas under hydrogen bonded and free carbonyl bands, respectively.

### 2.3.2. X-ray diffraction analysis (XRD)

The diffraction pattern of SMPUs and SMPU composites were obtained using an x-ray diffractometer model BRUKER AXS GMBH D8Advance with a Cu-K$\alpha$ source ($2\theta = 1.54 \text{ Å}$) and the $2\theta$ in the range of 10° to 40° with a scan rate of 5° min$^{-1}$.

### 2.3.3. Differential scanning calorimetry (DSC)

The DSC analysis was performed using Perkin Elmer DSC Diamond series using one heating scan in the temperature range of −80 °C to 150 °C with 10 °C min$^{-1}$ heating rate under nitrogen environment. The degree of crystallinity, $X_C$, of SMPU was calculated according to the formula:

$$X_C(\%) = \frac{\Delta H_m}{\Delta H_p^0} \times 100$$

Where, $\Delta H_m$ and $\Delta H_p^0$ are heat fusion of the prepared samples and 100% crystalline polymer (PEG, 196.8 J g$^{-1}$), respectively.

### 2.3.4. Tensile properties

The tensile properties of PU were evaluated using an Instron 5982 Universal Testing Machine (UK). A dumbbell shaped specimen was prepared based on ASTM D638 - type V standard and the test was conducted at room temperature with a crosshead speed and a load cell of 50 mm min$^{-1}$ and 5kN, respectively [28, 29]. Seven specimens for each sample were tested to ensure the reliability of the data. The mean value was used to plot the bar graph and the error bar indicates the standard deviation.

### 2.3.5. Shape memory behavior

Shape fixity and shape recovery value were used to evaluate the shape memory behavior of the prepared PUs, were obtained from the bending test based on the method by Ahmad Zubir et al [25]: (1) A rectangular sheet of PU, with the dimension of $50 \times 10 \times 0.5 \text{ mm}$, was heated at 60 °C for 10 min, and afterward it was bent into a ring-liked shape; (2) The ring-shaped sample was cooled down immediately to the temperature of 0 °C using freezer and kept for 10 min while maintaining the strain to form the temporary shape; (3) The bending force was removed, the change in the angle was recorded as fixity angle ($\theta_f$); (4) The recovery angle ($\theta_r$) was obtained after heating back the sample to 60 °C. Three specimens per sample were used to perform the test. The shape memory test was described as shown in figure 2 while the shape fixity and the shape recovery were calculated according to equations below:

$$HBI = \frac{\Sigma A_{HCO}}{\Sigma A_{FCO}}$$

$$DPS = \frac{HBI}{(1 + HBI)}$$

* Table 1. Formula and molar ratio of the synthesized PUs.

| No | Sample code | PCL 2000 | PCL 4000 | PEG 2000 | PEG 4000 | PKOp | HMDI | BD |
|----|-------------|----------|----------|----------|----------|-------|-------|----|
| 1  | PU-PCL2    | 0.8      | 0.2      | 2.9      | 1.9      |       |       |    |
| 2  | PU-PCL4    | 0.8      | 0.2      | 6        | 5        |       |       |    |
| 3  | PU-PCL2    | 0.8      | 0.2      | 2.9      | 1.9      |       |       |    |
| 4  | PU-PCL4    | 0.27     | 0.53     | 6        | 4.1      | 3.1   |       |    |
| 5  | PU-PCL2PEG2| 0.4      | 0.4      | 2        | 3.2      | 2.2   |       |    |
| 6  | PU-PCL4PEG2| 0.4      | 0.4      | 2        | 6.0      | 5.0   |       |    |
| 7  | PU-PCL2PEG4| 0.53     | 0.27     | 2        | 4.1      | 3.1   |       |    |
| 8  | PU-0.1PEG  | 0.7      | 0.1      | 2        | 6.0      | 5.0   |       |    |
| 9  | PU-0.2PEG  | 0.6      | 0.2      | 2        | 6.0      | 5.0   |       |    |
| 10 | PU-0.3PEG  | 0.5      | 0.3      | 2        | 6.0      | 5.0   |       |    |
| 11 | PU-0.4PEG  | 0.4      | 0.4      | 2        | 6.0      | 5.0   |       |    |
| 12 | PU-0.5PEG  | 0.3      | 0.5      | 2        | 6.0      | 5.0   |       |    |
| 13 | PU-0.6PEG  | 0.2      | 0.6      | 2        | 6.0      | 5.0   |       |    |
| 14 | PU-0.7PEG  | 0.1      | 0.7      | 2        | 6.0      | 5.0   |       |    |
| 15 | PU-0.1PEG  | 0.2      | 0.7      | 2        | 6.0      | 5.0   |       |    |

* same composition

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HBI = $\Sigma A_{HCO}/\Sigma A_{FCO}$ (1)

DPS = HBI/(1 + HBI) (2)

Where $\Sigma A_{HCO}$ and $\Sigma A_{FCO}$ are the total areas under hydrogen bonded and free carbonyl bands, respectively.
3. Results and discussion

3.1. FTIR analysis

The FTIR spectrums of the polyols and the reaction mixture at different stage in the synthesis of PU with PEG-PCL-PKOp as multiblock soft segments are shown in figures 3 and 4, respectively. In the first step, HMDI was reacted with PEG to form urethane linkages (–NH–C=O) which can be observed via the appearance of new peaks in the range of 1600–1800 cm\(^{-1}\), and 1520–1570 cm\(^{-1}\) which represent the carbonyl stretching vibration of amide I, and the link between –NH bending and -C-N stretching vibrations of secondary amide, respectively [30]. The peak at about 1100 cm\(^{-1}\) in the HMDI-PEG mixture (figure 3(a)) was associated to ether (C–O–C) stretching vibration while the peak at about 2880 cm\(^{-1}\) was due to the aliphatic –CH stretching in the PEG chain [31, 32].
The remaining free isocyanate (–NCO) that appeared at 2260 cm\(^{-1}\) and the isocyanate terminated HMDI-PEG mixture were then reacted with –OH groups in PCL as PCL was added to the reaction, hence reduced the free NCO peak intensity (figure 4(b)). The intensity of free hydrogen bonding (F–CO) at 1725 cm\(^{-1}\) increased significantly due to the presence of typical carbonyl C=O stretching vibration of ester groups in PCL [33], with the overlapping of the amide band. The intensity of carbonyl stretching vibration of amide I, and the stretching vibrations of secondary amide increased gradually with further incorporation of PKOp (figure 4(c)).

According to the FTIR spectrum of PKOp (figure 3), the peaks appeared at about 1680 and 1790 cm\(^{-1}\) are related to carbamate (O=C=N–), and ester (C=O) in the chain of fatty acid [34]. However, in the FTIR spectrum of pre-polymer (figure 4(c)), there were no traces of those peaks which may be due to the small amount of PKOp added in the formulation. The polymerization was then continued with mixing of the pre-polymer and chain extender (BD) in internal mixer to produce the PKOp-based SMPU. The disappearance of free isocyanate stretching vibration peak at 2260 cm\(^{-1}\) and the presence of broad N–H stretching peak at 3330 cm\(^{-1}\) in the SMPU spectrum suggest that the reaction has completed [35].

### 3.2. Microphase separation behavior

#### 3.2.1. The effect of long chain polyether and polyester diol with MW 2000 and 4000 on the microphase separation

Hydrogen bonding is an important factor which affects the microphase segregation of hard segment (HS) and soft segment (SS) matrix in polyurethane (PU) [36]. It is well-known that the infrared absorbance of hydrogen-bonded urethane carbonyl appears at lower wavenumbers than that of free urethane carbonyl [37]. The band in the range of 1720–1730 cm\(^{-1}\) is associated with the stretching vibration of free carbonyl (F–CO) [38], whereas the bands with the center position at about 1695–1706 cm\(^{-1}\) and at about 1660 cm\(^{-1}\) is due to the hydrogen bonded C=O (H–CO) of the hard domains [21, 39, 40]. The band in the range of 1624–1656 cm\(^{-1}\) is associated with the H–CO groups of crystalline soft domains [37, 41].

In the case of PU-PCL samples (figures 6(a), (b)), band I at about 1730 cm\(^{-1}\) is associated with the stretching vibration of free carbonyl (F–CO) whereas the presence of broad shoulders from 1700 to 1630 cm\(^{-1}\) (band II, III, IV) is corresponding to the hydrogen–bonded carbonyl (H–CO) groups. In the case of PU-PEG sample spectrums (figures 6(c), (d)), band I appears at around 1720 cm\(^{-1}\) which is attributed to F–CO groups and the other bands are due to the H–CO stretching. The band IV (at about 1630 cm\(^{-1}\)) has raised interest because it represents the H–CO groups of the crystalline SS [37, 41]. The sharper and obvious H–CO (band IV) of PU-PEG is observed at lower frequency compared to PU-PCL, suggesting higher amount of H–CO groups, due to the higher crystalline domains of PEG [31, 42]. In the crystalline phase, the polymeric chains are aligned in parallel to form lamellae, which encouraged the stronger hydrogen bonding formation [31].

The PU-PEGs revealed higher HBI values as compared to PU-PCLs, which leads to greater DPS or lesser phase mixing due to the increase of incompatibility between the HS and SS, as tabulated in table 2 [21, 38]. Specifically, the DPS value of PU-PEG samples is about twofold compared to that of PU-PCL samples, which is also confirmed with other studies [43, 44]. The phase mixing occurred in the case of PU-PCLs indicating that the HSS may be dissolved in the SSs [45, 46]. This phenomenon can be explained by the competition of hydrogen
bonding formed between –NH groups in urethane linkages with either urethane carbonyl or oxygen functional group present in SSs. Basically, the phase separation occurs when the HSs assemble themselves via hydrogen bonding, and thus the hard domains are formed and excluded from the matrix of soft phase [47, 48]. However, in the case that the SSs possess functional groups acting as acceptors which is strong enough to interact with –NH group in HSs, phase mixing is supposed to occur [40]. The possible interactions between segments in PU are illustrated in figure 5.

As expected, the PKO—based SMPU samples whose soft segments comprised of both PCL and PEG (PU-PCLPEG) showed higher DPS value than that of PU-PCLs but still lower than PU-PEGs, as shown in table 2 and figure 6. The deconvoluted bands of PU-PCLPEG samples can be found in supporting information S1 available online at stacks.iop.org/MRX/7/025704/mmedia. The HBI increased gradually in the order of: PU-PCL < PU-PCL2 < PU-PCL4PEG2 > PU-PCL2PEG2 > PU-PCL4PEG4 > PU-PCL2PEG4 < PU-PCL4PEG2 and PU-PCL4PEG4, and consequently, the DPS of those samples went in the same trend as well. The combination of both PEG and PCL component in SS had a certain effect on the microphase separation behavior of PU. The PCL fragments enhanced the degree of phase mixing whereas the PEG fragments played an important role in promoting the formation of hard segment domain. This is due to the formation of weaker hydrogen bonding between HS -NH group with the PEG ether group as compared to the PCL ester group [12].

### 3.2.2. The effect of varying molar ratio of PEG4000 on the microphase separation

FTIR spectrum for carbonyl region and the specific value (HBI, DPS) of synthesized PKO—based SMPUs are shown in figure 7 and table 3, respectively. In this work, the amount of F-CO (1720–1730 cm⁻¹) decreased while the value of HBI increased as the amount of PEG4000 is increased, leading to a greater DPS as shown in table 3. The value of DPS increased gradually from 0.44 to 0.84 as the molar ratio of PEG is increased from 0.1 to 0.7. These results confirmed that PEG has linear effect to the increase of DPS value. As the higher the amount of PEG4000, the competitive interaction between hard segments and PCL fragments was diminished, hence HSs had more chance to align and form hard domains, and thus increase in the value of DPS.

### 3.3. Degree of soft segment crystallinity of SMPUs

The effect of polyol types and MW of soft segment on the crystallization behavior of the synthesized SMPUs was analyzed by DSC with the support of XRD results. In the range of 25 to 60 °C, PU-PEG samples showed an obvious endothermic peak, whereas a broad endothermic peak is observed for PU–PCL sample. The melting point and degree of crystallinity of PU–PEG (table 4 and figure 8) are proportional to the MW of PEG polyol. As the MW increases, from 2000 g mol⁻¹ to 4000 g mol⁻¹, the melting point and the percentage of crystallinity increase from 48 °C to 54 °C, and 15.4% to 30.4%, respectively. The MW of polyol is proportional to the length of the SS, and the higher the MW the higher the chain flexibility of SS, which makes the molecular chain of SS easier to pack into ordered arrangement and formed lamellae [19, 49].

In this study, as observed from the FTIR and DSC results, the higher the DPS, the higher crystallization capacity of SS. In this case, as the microphase separation occurred, the HS was separated from the SS matrix,
hence allow the formation of crystalline soft segment by the polyols. In contrary, the phase mixing obtained in the cases of PU-PCLs is due to the presence of HSs that were dissolved in the matrix of SS, which cause the interference in the arrangement of SS to form crystalline structure, and thus the lower degree of crystallinity obtained.

In the case of PU-PCLPEG series, the combination of PCL and PEG with different MW of SS affect the phase separation behavior as per discussed in FTIR results, the DPS of PU-PCLPEG samples was higher than that of PU-PCL samples but the value was still lower as compared to that of PU-PEG samples. Thus, there would be some significant effect on the degree of crystallinity, which was evaluated using XRD and DSC analysis (table 4, figures 8–9). According to the FTIR results of PU-PCLPEG series, PU-PCL2PEG4 possessed the highest degree of phase separation followed by PU-PCL4PEG4, PU-PCL2PEG4, and PU-PCL4PEG2, consequently the degree of crystallinity of those samples were in the order of 16.9%, 15.4%, 6.6%, 2.6%, respectively.

XRD pattern of PEG was characterized by two intense diffraction peaks which were $2\theta = 19.1^\circ$, and $2\theta = 23.0^\circ$ whereas the crystalline structure of PCL was characterized by two diffraction peaks of $2\theta = 21.7^\circ$, and $2\theta = 24.0^\circ$ (figure 10). XRD pattern of PU-PCL4PEG4 shows two obvious diffraction peaks at $2\theta = 19.1^\circ$, and $2\theta = 23.3^\circ$ which is due to the PEG crystal, and a broader hump (as compared to PU-L2G4) from $2\theta = 16^\circ$ to $24^\circ$ which is related to the amorphous phase of the PCL soft segments. The presence of PCL component with higher MW (4000 g mol$^{-1}$) in this case caused chain entanglement which restricted the crystallization of PEG fragment [21, 50]. In the case of PU-PCL2PEG4, the introduction of PCL with lower MW (2000 g mol$^{-1}$) improves the mobility of the SS, which promotes the SS to easily pack and form the crystalline structure [51]. Consequently, the amorphous region under the curve of PU-PCL2PEG4 was smaller than that of PU-PCL4PEG4 and the crystallinity value of PU-PCL2PEG4 was higher than that of PU-PCL4PEG4 as supported by DSC results (table 4).
Figure 6. Deconvoluted FTIR spectrum of the synthesized PKOp—based PUs with PCL or PEG as long chain polyol.

Figure 7. FTIR spectrum for carbonyl region of synthesized SMPUs.
The effect of PEG with MW of 4000 g mol\(^{-1}\) on the crystallinity of SMPU samples was clearly observed when the molar ratio is increased from 0.1 to 0.7. Based on the XRD pattern (figure 11), with increasing of PEG content, the peak intensity increased suggesting an increased in the SS crystallinity of SMPU samples. All samples have both the intense crystalline peak and broad amorphous peak. It is believed that the crystalline peak belongs to the PEG soft segments whereas the broad amorphous region belongs to the PCL soft segments as

![DSC curves of the synthesized PKO-p—based SMPU samples.](image)

**Table 3.** The HBI, DPS% value of the synthesized PKO-p—based SMPU samples.

| Area | Sample       | F-CO | ΣH-CO | HBI   | DPS   |
|------|--------------|------|-------|-------|-------|
|      | PU-0.1PEG    | 3.12 | 2.39  | 0.77  | 0.44  |
|      | PU-0.2PEG    | 1.85 | 2.00  | 1.08  | 0.52  |
|      | PU-0.3PEG    | 1.76 | 2.02  | 1.15  | 0.53  |
|      | PU-0.4PEG    | 1.65 | 1.96  | 1.19  | 0.54  |
|      | PU-0.5PEG    | 0.74 | 2.91  | 3.91  | 0.80  |
|      | PU-0.6PEG    | 0.51 | 2.12  | 4.16  | 0.81  |

**Table 4.** Thermal characteristic of the synthesized PKO-p—based SMPUs.

| Sample       | 1st endothermic peak | 2nd endothermic peak |
|--------------|----------------------|----------------------|
|              | \(T_{m1} (°C)\) | \(\Delta H_{m1} (J g^{-1})\) | \(X_c (%)\) | \(T_{m2} (°C)\) | \(\Delta H_{m2} (J g^{-1})\) | \(X_c (%)\) | \(\sum X_c (%)\) |
| PU-PCL2      | —                   | —                    | —                | —                   | —                   | —                | —                      |
| PU-PCL4      | —                   | —                    | —                | —                   | —                   | —                | —                      |
| PU-PCL4PEG2  | 25.0                | 3.4                  | 2.4              | 44.6                | 0.4                 | 0.2              | 2.6                    |
| PU-PCL2PEG2  | 27.1                | 3.4                  | 2.4              | 47.5                | 8.2                 | 4.2              | 6.6                    |
| PU-PCL4PEG4 (PU-0.4PEG) | 27.3 | 0.8                  | 0.5              | 50.8                | 29.4                | 14.9             | 15.4                   |
| PU-PCL2PEG4  | —                   | —                    | —                | 48.0                | 33.3                | 16.9             | 16.9                   |
| PU-PCL4PEG2  | 29.2                | 6.1                  | 3.1              | 48.4                | 24.2                | 12.3             | 15.4                   |
| PU-PCL4PEG4  | 29.3                | 0.8                  | 0.5              | 54.2                | 59.7                | 30.4             | 30.9                   |
| PU-0.1PEG    | —                   | —                    | —                | 48.9                | 6.3                 | 3.2              | 3.2                    |
| PU-0.2PEG    | —                   | —                    | —                | 47.3                | 11.9                | 6.0              | 6.0                    |
| PU-0.3PEG    | —                   | —                    | —                | 50.8                | 22.5                | 11.5             | 11.5                   |
| PU-0.5PEG    | —                   | —                    | —                | 50.6                | 36.0                | 18.3             | 18.3                   |
| PU-0.6PEG    | —                   | —                    | —                | 50.8                | 39.1                | 19.9             | 19.9                   |
| PU-0.7PEG    | —                   | —                    | —                | 54.8                | 56.9                | 28.9             | 28.9                   |

The effect of PEG with MW of 4000 g mol\(^{-1}\) on the crystallinity of SMPU samples was clearly observed when the molar ratio is increased from 0.1 to 0.7. Based on the XRD pattern (figure 11), with increasing of PEG content, the peak intensity increased suggesting an increased in the SS crystallinity of SMPU samples. All samples have both the intense crystalline peak and broad amorphous peak. It is believed that the crystalline peak belongs to the PEG soft segments whereas the broad amorphous region belongs to the PCL soft segments as
discussed previously. At low molar ratio of PEG4000 (0.1–0.3), PCL is the dominant component of SS; therefore, phase mixing occurred at a great level that hinders the crystallization of SS. As the PEG molar ratio is increased from 0.4 to 0.7, the PEG polyol became the dominant component of SS, thus the microphase separation is enhanced and the SS crystallization is increased. In general, as the PEG content is increased, both peaks shifted to lower 2θ value and the crystallite size increased with more formation of crystalline structure suggesting the occurrence of microphase separation.

The DSC curves of all the synthesized SMPUs exhibited a noticeable endothermic peak that represents the melting of SS crystalline structure, which is attributed to PEG segment (figure 12). As can be seen from the figure 12 and table 5, the heat of fusion (ΔH) is proportional to the amount of PEG4000 in SS, which can be concluded that the higher the amount of PEG4000 introduced, the higher the degree of crystallinity of SMPU. The trend observed for DSC analysis is in accordance with the trend obtained in the XRD analysis. In addition, as the PEG content is increased, the Tm of the SS is greater. This may be due to the increased of SS crystallite size, hence higher amount of energy is required to melt the bigger crystallite size.

3.4. Mechanical properties
The tensile strength, tensile strain at break, and Young’s modulus values of the synthesized SMPUs are presented in figures 13–15, respectively. The stress-strain curve of SMPU samples can be found in Supporting information.
Figure 11. XRD pattern of the synthesized PKOp—based SMPUs.

Table 5. The position of diffraction peak and the crystallite dimension of soft segment components.

| Sample      | $2\theta$ (°) | $L_{hkl}$ (nm) |
|-------------|----------------|----------------|
|             | 1st peak       | 2nd peak       | 1st peak | 2nd peak |
| PU-0.1PEG   | 20.2           | 24.3           | 17.9     | 10.6     |
| PU-0.2PEG   | 20.1           | 24.3           | 18.3     | 11.1     |
| PU-0.3PEG   | 19.9           | 24.1           | 19.6     | 10.7     |
| PU-0.4PEG   | 19.1           | 23.3           | 27.6     | 11.4     |
| PU-0.5PEG   | 19.5           | 23.6           | 18.0     | 11.5     |
| PU-0.6PEG   | 19.5           | 23.6           | 23.2     | 11.9     |
| PU-0.7PEG   | 19.5           | 23.7           | 23.6     | 12.4     |

Figure 12. DSC curves of the PKOp—based SMPUs with molar ratio of PEG4000 varied from 0.1 to 0.7.
S2. PU-PCLs exhibited higher tensile strength and elongation at break due to its chain flexibility as compared to PU-PEG. PU-PEGs possess higher Young’s modulus such that its brittleness is due to the high crystallinity of its SS as discussed in previous section, hence restricted their performance. PU-PEG4 sample was too brittle to be able to conduct the tensile test. The tensile strength of PU-PCLs is higher than that of PU-PEGs may be due to the uniform distribution of soft and hard segments as a result of phase mixing. Thus, the stress is spread uniformly across the entire polymer chains [52]. In the other hand, the low value of tensile strength of PU-PEGs can be explained by two possible reasons. First, when the phase separation occurred, the hard domains act as reinforcement which enhance the materials’ strength; however, in the case that the hard and soft segments are

Figure 13. Tensile strength of the synthesized SMPU samples.

Figure 14. Tensile strain at break of the synthesized SMPU samples.
extremely incompatible, which results in sharp phase boundary, the shear stress localization may happen at the narrow interface of these domains, hence decreased the tensile strength [39, 53]. Second, the high crystallinity of PEG soft segments makes the materials to be brittle and easier to fail.

As for the Young’s modulus, PU-PEG samples exhibited a higher value compared to that of PU-PCL samples. The Young’s modulus of PU-PEG2 and PU-PCL2 are 16.3 MPa and 2.7 MPa, respectively. This is because of the high crystallinity of PU-PEG samples as observed via XRD and DSC results. The higher the crystallinity of SS caused the PU-PEG samples to become stiffer and hence enhanced the modulus. In contrary, PU-PCL samples exhibited excellent tensile strain at break compared to that of PU-PEG samples, the strain at break of PU-PCL2 is 951% whereas PU-PEG2 is only 29%. This phenomenon can be explained by two reasons. First of all, the degree of crystallinity of PU-PCL samples is lower than that of PU-PEG samples, hence having better chain flexibility. Secondly, PU-PCLs exhibited a higher degree of phase mixing than PU-PEG samples, leading to more formation of hydrogen bonding between soft and hard segments. Hence, the chain flexibility and the strong interaction between both domains results in larger deformation of PU-PCL samples.

According to the tensile properties of PU-PCLPEG series, there are obvious differences between PU-PCL(X)PEG2 and PU-PCL(X)PEG4 samples with (X) is the MW of PCL (2000 and 4000 g mol\(^{-1}\)). As per discussed previously, PU-PEGs possessed higher DPS value and degree of crystallinity, which results in an extreme incompatibility between soft and hard segments, and brittleness; consequently, the tensile strength of PU-PEG is much lower as compared to PU-PCLs. However, with the inclusion of the PCL component, the tensile strength of PU-PCL(X)PEG4 and PU-PCL(X)PEG2 samples were improved which may be due to the enhancement of phase mixing, resulting in a higher flexibility of molecular chains as compared to PU-PEG samples.

PU-PCL(X)PEG4 showed a higher tensile strength than PU-PCL(X)PEG2 (about twofold), which is due to the presence of stronger physical crosslinking within the hard segments. The physical crosslinking plays an important role in improving the ability of the sample to withstand the load transfer during deformation. This is in agreement with the FTIR result in which the HBI value for PU-PCL(X)PEG4 is higher compared to that of PU-PCL(X)PEG2, suggesting the formation of higher degree of hydrogen bonding interactions between the HSs [54].

The Young’s modulus of PU-PCL(X)PEG2 is lower as compared to PU-PEG2 (16.3 MPa). Thus, suggesting that the PCL fragments introduced as SS not only formed the amorphous structure but also hindered the PEG fragments from crystallization. The degree of SS crystallinity decreased and leads to the reduction of the stiffness of the PU-PCL(X)PEG2 samples; hence, the Young’s modulus is reduced. In the case of PU-PCL(X)PEG4 samples, the increase of the MW of PEG improved the phase separation, as well as the degree of crystallinity. The
DPS value of PU-PCL(X)PEG4 ~ 0.6 compared to PU-PCL(X)PEG2 ~ 0.5, which leads to a higher degree of crystallinity as evident from the DSC results. The increase of DPS which results in higher physical crosslinking, together with higher degree of crystallinity contributes to the increase of the Young’s modulus.

In contrast, the tensile strain at break of PU-PCL(X)PEG2 improved significantly as compared to PU-PEG2 sample since the presence of amorphous PCL imparts the chain flexibility of the polymer backbone hence increased the elongation at break upon deformation. Due to phase mixing and a lower degree of crystallinity, the strain at break of PU-PCL(X)PEG2 increased notably as compared to PU-PCL(X)PEG4. The presence of crystalline structure and strong physical crosslinks retarded the molecular chain mobility leading to a decrease of chain flexibility and the strain at break as well. In general, the crystallinity and MW of SS have a notable effect to the tensile properties of SMPU. As compared to PU-PCL or PU-PEG samples, the tensile strength and the Young’s modulus of PU-PCLPEG samples improved significantly. The combination of the stiffness due to the crystalline PEG domains and the higher inter-molecular interaction between the soft and hard segments due to the introduction of PCL domain has enhanced the tensile properties of SMPU.

The tensile properties of the prepared SMPUs with increasing of the PEG4000 amount were analyzed to optimize the tensile properties, as well as to observe more clearly the effect of PEG4000. As the molar ratio of PEG4000 is increased from 0.1 to 0.5, the tensile strength increased and reached a maximum value at the ratio of 0.5. The tensile strain at break increased with the increase of PEG4000 molar ratio whereas the Young’s modulus decreased.

The degree of crystallinity of PEG4000 played a vital role to provide stiffness to the material. However, when the crystallinity of the material is too high (0.6 PEG molar ratio), failure occurs at lower stress level as the crystalline portion acted as the stress concentrator [19]. Therefore, with further increasing of the amount of PEG4000, the brittleness of the material increased due to the increase in soft segment crystallinity, as well as decrease of the chain flexibility provided by the PCL fragments, hence resulted in the decline of tensile strength. Similar phenomenon can be used to explained the trend of Young’s modulus obtained for the synthesized SMPUs. The increased in the modulus is due to the increased of crystalline PEG soft segment and the amount of physical crosslinking between the HSs. This is in agreement as the HBI value from FTIR analysis is also increased with increasing of the PEG content suggesting more hydrogen bonding is formed in between the urethane HSs that contributes to the formation of physical crosslinks.

The tensile strain at break of SMPU is inversely proportional to the Young’s modulus [55]. The chain flexibility of the prepared polyurethanes is provided by the presence of PCL4000 fragments in SS. Hence, when the amount of PEG is increased, the presence of higher crystalline PEG domains and less amorphous PCL chains to sustain the deformation results in the reduction of tensile strain at break.

3.5. Shape memory properties
Shape memory properties of polymers are characterized via shape memory effect, namely shape fixity and shape recoverability. While the shape fixity is responsible for retaining the temporary shape via the formation of SS crystalline structure upon quenching the sample to below transition temperature (T\text{\textsubscript{trans}}); the shape recovery is the capability to maintain the original shape after load removal at above T\text{\textsubscript{trans}}, which depends on the physical crosslinks and molecular interactions occurred in the hard segment domains [25].

As per discussed in previous paper, PU-PCL samples did not exhibit shape memory effect, the shape fixity values of PU-PCL2 and PU-PCL4 are 28.6 and 43.3%, respectively [56]. In contrary, PU-PEG2 showed a good shape fixability with the value of 96.4% whereas PU-PEG4 sample could not perform the test due to high brittleness [56]. The combination of PEG and PCL component in soft segment with different MW has significant effects on the DPS, crystallinity, and thus shape memory properties. The shape memory properties of PU-PCLPEG series are shown in figures 16 and 17. The shape fixity increased from 54% to 98% in the order of PU-PCL4PEG2 > PU-PCL2PEG2 > PU-PCL4PEG4 > PU-PCL2PEG4. This result is in good agreement with the DSC and XRD analysis, as the value of shape fixity is proportional to the degree of crystallinity. Furthermore, the shape recovery value of the synthesized PUs is maintained at 100%, which means that the SMPU can recover their original shape completely after the external load is being released and heated up to above the transition temperature. The amount of physical crosslinking within the hard segments in the samples is sufficient and remains intact after the application of bending force, hence caused the achievement of 100% recovery value (figure 18).

The PEG fragment plays an important role on the crystallinity of SMPU samples, especially with the MW of 4000 g mol\textsuperscript{-1}. The influence of PEG4000 on the shape fixity of PU can be observed clearly when its molar ratio is varied from 0.1 to 0.7 (figure 19). As the molar ratio of PEG is increased from 0.1 to 0.6, the shape fixity also increased from 60% to 98%. Once the molar ratio of PEG reached 0.3, the value of shape fixity changed slightly. The value of shape fixity is proportional with the content of PEG. This is because, the increase in PEG content resulted in the formation of more crystalline region, which plays a vital role during fixing the temporary shape of SMPU. With regards to shape recovery, all of the SMPU samples exhibited excellent recovery ability to their
Figure 16. Shape fixity (SF) and shape recovery (SR) value of the synthesized PKOp—based SMPU.

Figure 17. Shape fixity and shape recovery of (a) PU-PCL4PEG2, (b) PU-PCL2PEG2, (c) PU-PCL4PEG4, (d) PU-PCL2PEG4.

Figure 18. Mechanism of shape memory behavior during bending test (reprinted from [25], with permission from John Wiley and Sons).
original shape, as the shape recovery is 100%. The presence of sufficient amount of physical crosslinking between hard segment domains is responsible in maintaining the permanent shape of SMPUs. Our prepared PKO-p based SMPU are expected to have good biocompatibility and biodegradability since there are other similar studies that have utilized almost the same chemicals as our work [57, 58] and showed good biocompatibility and biodegradability properties. Li and his co-workers have synthesized alternating block PU based on PCL and PEG for nerve regeneration materials, and their study demonstrated that PCL/PEG plays an important role in introducing the biocompatibility and biodegradability behavior via immunocytochemistry and in vitro degradation test [57]. Hence, based on this, with the combination of good shape memory behavior and tensile properties, it is proposed that our sample is a suitable candidate for self-healing material in biomedical application.

4. Conclusions

The PKOp—based SMPU series with the combination of PCL and PEG as soft segment component was synthesized successfully. The disadvantages of PU-PCL and PU-PEG were overcome with the combination of both PEG-PCL as soft segment. PU-PCL4PEG4 is the best sample as its tensile strength, Young’s modulus, and shape fixity was increased by 148%, 3750%, and 80%, respectively, as compared to PU-PCL4PEG2. To optimize the properties of PU-PCL4PEG4, the molar ratio of PEG4000 was varied from 0.1 to 0.7. As expected, the higher the amount of PEG4000 in the soft segment, the higher the tensile strength and the Young’s modulus were obtained, accompanied with the drop of tensile strain at break. PU-0.6PEG sample exhibited good Young’s modulus and shape fixity but the tensile strength and tensile strain at break was reduced. In general, the PKOp—based SMPU produced possessed good shape memory behavior with improved tensile properties, which allows for potential application as self-healing material in biomedical application such as implant and suture.

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