

STRUCTURE AND COMPATIBILITY STUDY OF MODIFIED POLYURETHANE/Fe₃O₄ NANOCOMPOSITE FOR SHAPE MEMORY MATERIALS

Dick Ferieno Firdaus*, Masrudin, Dessy Ayu Lestari, Mutya Rahmah Arbi, and Mochamad Chalid

Department of Metallurgy and Materials Engineering, Universitas Indonesia,
UI Depok New Campus, Depok 16424, West Java - Indonesia

Received January 8, 2015; Accepted March 17, 2015

ABSTRACT

Shape Memory Polymer (SMP) is one of smart materials class that has the ability to recall a given shape before deformation in the transient state. The development of SMP is dominated by polyurethane which is currently focused on the optimization of manufacturing-related research (ease of processing), and the extraction of the potential for biomedical applications. In this study, Shape Memory Polyurethane (SMPU) with Polyethylene Glycol-based material (PEG mw: 6000) as soft segment, 4,4'-Methylenebis (Cyclohexyl isocyanate) (HMDI) as a hard segment and 1,1,1-Trimethylol propane (TMP) as a chain extender were used as a candidate for Vascular Stents. Materials used for the fillers were nano particles of magnetite (Fe₃O₄) which have 20–50 nm diameters. Variations of the composition were used as a variable. Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance (NMR) were conducted to investigate the polymer chains which were formed during polymerization, Field Emission Scanning Electron Microscopy (FE-SEM) was used to analyze the interface between the filler and the composite matrix. Manual physical actuation was conducted to analyze the physical recovery and transition temperature of the SMPU. Composition and fillers effect on the performance of SMPU composite were discussed in detail along with analysis of its structure and molecular design.

Keywords: HMDI; magnetite; PEG; SMPU; TMP

ABSTRAK

Shape Memory Polymer (SMP) merupakan salah satu kelas dari material cerdas (smart material) yang memiliki kemampuan untuk mengingat bentuk yang diberikan sebelum deformasi dalam keadaan sementara. Perkembangan Shape Memory Polymer didominasi oleh penggunaan Polyurethane yang saat ini diarahkan kepada penelitian terkait optimalisasi manufaktur (ease of processing) dan penggalan potensi aplikasi biomedis. Dalam penelitian ini, Shape Memory Polyurethane (SMPU) dengan bahan dasar Polyethylene Glycol (PEG mw: 6000) sebagai macrodiol atau soft segment, 4,4'-Methylenebis(cyclohexyl isocyanate) (HMDI) sebagai hard segment dan 1,1,1-Trimethylol Propane (TMP) sebagai chain extender akan digunakan sebagai material kandidat Vascular Stents. Bahan yang digunakan untuk filler adalah partikel nano magnetit (Fe₃O₄) yang memiliki ukuran diameter sebesar 20–50 nm. Variasi komposisi digunakan sebagai variabel. Fourier Transform Infrared Spectroscopy (FTIR) dan Nuclear Magnetic Resonance (NMR) digunakan untuk menginvestigasi rantai polimer pada saat proses polimerisasi, Field Emission Scanning Electron Microscopy (FE-SEM) digunakan untuk melihat antarmuka matriks dengan filler pada bahan komposit. Untuk uji sifat mekanis, aktuasi fisik secara manual dilakukan untuk menganalisis physical recovery dan temperatur transisi dari SMPU yang telah difabrikasi. Efek komposisi dan material filler terhadap performa SMPU didiskusikan secara mendetil dengan analisis pada struktur dan disain molekular.

Kata Kunci: HMDI; magnetit; PEG; SMPU; TMP

INTRODUCTION

Shape memory effect that has been observed in polymeric materials has recently been the subject of significant attention in the category of smart materials. Category of new polymer materials that can have a shape memory effect is generally referred to as a shape memory polymer (SMP). Shape memory polymer material can be defined as intelligent, who has the ability

to remember the shape when triggered by an external stimulus. Until now, research on shape memory polymers has grown rapidly since its first publication in 1984. It has been nearly 30 years after the first publication, a shape memory polymer research has focused on the optimization of the manufacturing process, cost and mechanical properties. Progress to date, provide a very large contribution to many areas of science and applications ranging from sensors,

* Corresponding author. Tel/Fax : +62-87885655058
Email address : dick_ferieno@nano.or.id

materials for packaging to the application of biomaterials.

For biomaterials industry, the development of shape memory polymer directed towards innovation and improvement to facilitate its biocompatibility. Quite numbers of polymeric materials that can be categorized as a shape memory polymer. The very first research of SMP was Polynorbornene-based SMP (Kuraray Company, Japan) and the Trans-isopolyprerme-based SMP (company ASAHI, Japan), both materials appeared to have SMP properties but unfortunately their processability are poor. Other studies, investigate that Polyurethane also have SMP properties and yet it have good processability properties and low price which is highly desired by biomaterials industry. Another advantage possessed by the polyurethane is very well-known biocompatibility. Nevertheless SMPU has a very significant shortcomings such as thermal conductivity and poor mechanical properties, for that the addition of composite materials to SMPU is needed to correct the weaknesses.

Researchers typically use a conductive filler to develop thermal and electrical conductivity of SMPU like adding nickel nanostrand [1], the nanotube fibers [2], nanocarbon particles [3] and carbon nanotubes [4]. Other studies have also been done not only to increase the conductivity but also to improve its mechanical properties as well as developing the shape memory effect properties. Some researchers have been able to speed up the recovery time using high molecular weight polyols or the use of soft segment in high presentation [5]. Researchers are also able to slow down the recovery time using hard segment in high presentation [6]. Long-time recovery process is usually needed in the application of biomedical implants to reduce the risk of shock to the body's response, while on the other hand the process of accelerating the recovery time is usually used for biomedical applications of electrical actuator or sensor.

The latest approach in developing SMPU located to the observations regarding its ability to be triggered not only due to thermal or moisture but also to the magnetic field. Research has recently developed by researchers is to create a composite SMPU based magnetic nanoparticles [7] and aligned carbon nanotubes [8]. Due to its good biocompatibility, magnetite nanoparticles (Fe_3O_4) can also be a material considered for researchers in developing SMPU properties that could be triggered by magnetic field [9].

As we already know that the two mechanisms SMPU segment (dual segment mechanism), namely, the soft segment and hard segment in the process of generating a shape memory effect is, therefore, play an important subject to design SMPU material. Soft segment of SMPU known as macrodiol or polyols

generally contain such high molecular weight poly (ethylene glycol) (PEG), poly (Caprolactone) (PCL) and poly (tetrahydrofuran) PTHF [10], while the hard segment of SMPU usually known as a diisocyanate. Diisocyanate derivatives which can be used as a hard segment generally is 4,4'-diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), 4,4'-diisocyanate Dibenzyl (DBDI) [10] and 4,4'-Methylenebis (Cyclohexyl isocyanate) (HMDI). T_{max} in the application of biomedical materials should be low but it should have a pretty good impact value anyway. Therefore HMDI used in this study because of HMDI and other derivatives such as DBDI have lower T_{max} , although not as low as the TDI but has a pretty good impact value. This is due to both HMDI and DBDI structure that makes it has high mobility than the other diisocyanate derivative because of the rotation between the two benzene rings amid $-\text{CH}_2-\text{CH}_2-$ but not as much as the TDI with two phenyl rings [10].

The use of macrodiol such as PEG, PTHF and PCL in SMPU have different properties [5]. As we have seen, SMPU applications for biomedical materials should have slow enough recovery actuation time, to reduce the risk of body shock, and because of that, in this study HMDI is used as a hard segment with a fairly high mobility, this study used PEG as the soft segment for the maintain the slow actuation time. Another important aspect of SMPU is chain extender with 1,4-Butanediol (BDO) is one type that is often used, but 1,1,1-trimethylol propane (TMP) is usually used to improve the stiffness and mechanical properties of SMPU [10].

Based on several studies [11] hard segment used by 20 or 25 wt% towards the SMPU will decrease the physical cross-link composition due to the low presentation of hard segment, so SMPU will lost its shape memory effect. Meanwhile, polyurethane that used 50 wt% of hard segment did not also show the shape memory effect, it is caused by the massive interaction between the hard segment and it will make the structure more rigid. So based on this study, the exact amount of hard segment used should only about 30–45 wt% to keep the optimality of SMPU shape memory effect.

For SMPU triggered by the magnetic field, the magnetite nanoparticles can be used at 1.0 wt% to maintain the optimality of SMPU performance [12]. The addition of magnetite will speed the actuation time in magnetic field ($f = 45 \text{ kHz}$, $H = 35.7 \text{ kA M}^{-1}$), but it can reduce its shape memory effect [13].

Therefore, based on the consideration of composition that has been previously explained, we can conclude that, to make SMPU capable to be triggered by magnetic field used for biomedical implantation it must be contained 4 and 6 mol HMDI for

Table 1. Sample compositions comparison

Sample Code	Specifications				Comparison (mol)
	Macrodiol	Diisocyanate	Chain Extender	Filler	
SMPU-PEG-01	PEG 6000	4,4'-Methylenebis(cyclohexyl isocyanate) (HMDI)	1,1,1-TriMethylol Propane (TMP)	Nano Fe ₃ O ₄	1:4:2:0,5
SMPU-PEG-02	PEG 6000	4,4'-Methylenebis(cyclohexyl isocyanate) (HMDI)	1,1,1-TriMethylol Propane (TMP)	Nano Fe ₃ O ₄	1:4:2:1
SMPU-PEG-03	PEG 6000	4,4'-Methylenebis(cyclohexyl isocyanate) (HMDI)	1,1,1-TriMethylol Propane (TMP)	Nano Fe ₃ O ₄	1:6:2:1

Table 2. Sample compositions

Sample Code	Quantity			
	PEG 6000	HMDI	TMP	Fe ₃ O ₄
SMPU-14205	0.0025 mol	0.01 mol	0.005 mol	0.00125 mol
	15 g	2.45 mL	0.67 g	0.27875 g
SMPU-1421	0.0025 mol	0.01 mol	0.005 mol	0.0025 mol
	15 g	2.45 mL	0.67 gr	0.575 g
SMPU-1621	0.0025 mol	0.015 mol	0.005 mol	0.0025 mol
	15 g	3.675 mL	0.67 g	0.575 g

the hard segment, 2 moles of TMP for the chain extender and 1 mol of PEG Mw: 6000 for soft segment with the addition of composite materials magnetite nanoparticles as small as possible (about 0.5 and 1 mol) as a filler to maintain a slow actuation properties. Magnetite is used only to make SMPU able to be triggered by a magnetic field without accelerating the actuation process. The purpose of this study was to investigate the structure and interface between matrix and filler of SMPU magnetic nanocomposite with shape memory effect.

EXPERIMENTAL SECTION

Materials

The material used in this study is divided into four types of materials, namely polyethylene glycol (PEG) Mw: 6000 obtained from Sigma-Aldrich as a soft segment, 4,4'-Methylenebis (Cyclohexyl isocyanate) (HMDI) obtained from Sigma-Aldrich as a hard segment, 1,1,1-TriMethylol propane (TMP) obtained from Sigma-Aldrich as chain extender and nano particles of magnetite (Fe₃O₄) obtained from Inframat USA with the size of 20–50 nm as composite materials or filler. With each composition can be seen at Table 1.

Instrumentation

The research products were tested with Non-Destructive Test as follows: SEM (Scanning Electron Microscope) Inspect F50 at DTMM FTUI to determine the topography of the sample, FTIR (Fourier Transform Infrared Spectroscopy) PerkinElmer Frontier at DTMM FTUI, to determine the chemical bonding and molecular

structure formed qualitatively and NMR (Nuclear Magnetic Resonance) Agilent 500 MHz at ITB for testing the molecular structure quantitatively. Actuation test was also conducted to determine the physical recovery time of the products.

Procedure

The process started by the preparation of three three-neck round-bottom flasks each filled with 15 g of PEG-6000 and dissolved in 25 mL of DMF. After that, all of the three flasks containing a solution of PEG-6000 was fluxed using vacuum suction machine and nitrogen gas three times. All of the flasks were then dipped into the oil bath and then heated. The temperature is then raised to 75 °C and stirring for 1 h until the solution became clear.

After 1 h, HMDI (see each composition in Table 2) were injected into the flasks in a nitrogen atmosphere. After that, 2 drops of Dibutyltin Dilaurate (DD) catalyst were added into each flask. Then stirring were conducted for 2 h at a constant temperature at 75 °C.

After the solution became as white as milk, a 10 mL solution from each tube was then separated and terminated using 20 mL of water. The terminated initial product then taken for initial analysis and characterization using FTIR and NMR. For the rest of the solution at the tubes, chain extender TMP which was dissolved in DMF was added to the solution to form a physical crosslink on SMPU. The temperature was then raised to 80 °C. After 2 h, the magnetite nanoparticles which was diluted with DMF was added to the solution and then underwent stirring at a constant temperature of 80 °C for 1 h.

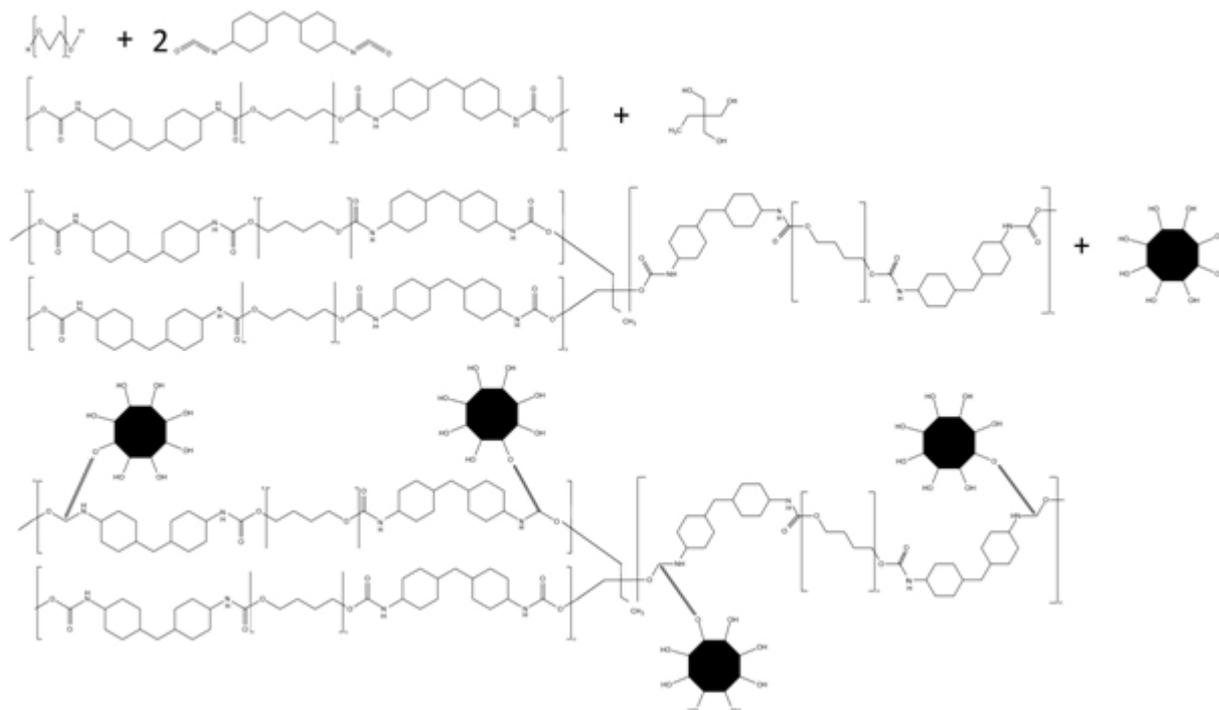


Fig 1. Full reaction route

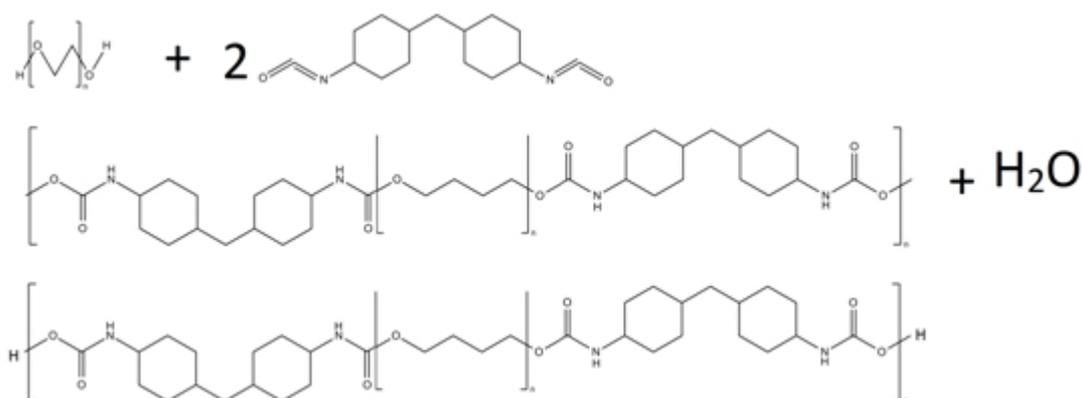


Fig 2. Water terminated reaction route

After the solution became slightly blackish, the solution was then heated in a vacuum state at a temperature of 85 °C for 2 h to evaporate the DMF solvent. After that, the solution will turn into a gel-like that then do the casting into a dog bone shape Teflon mold (ASTM D1708 (Microtensile)) for physical actuation testing.

RESULT AND DISCUSSION

Reaction Route

Reaction process as can be seen at Fig. 1, initiated by the formation of urethane linkage between PEG and

HMDI inside of the DMF solvent with nitrogen atmosphere, the linkage form the basis of polyurethane and then it continue to react with TMP which provide the chain extension space. Modified Fe_3O_4 which created from the solution of DMF then added to create a contact with the polyurethane to make nanocomposite. PEG take part as soft segment while HMDI as hard segment with semi-crosslink formed between them.

The formation of $-\text{COOH}$ functional groups are the consequence of the addition of water as the reaction terminator. The initial products were characterized to confirm the molecular design for our modified polyurethane.

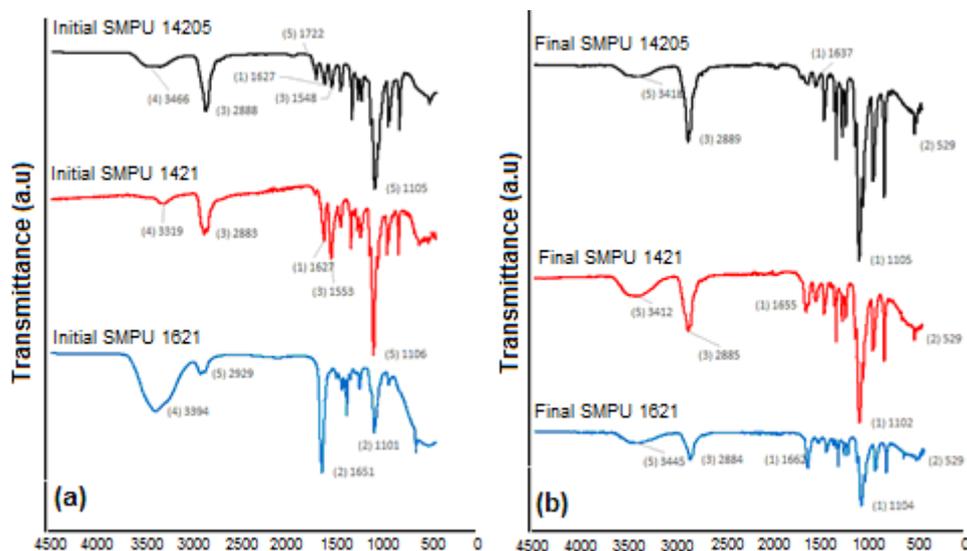


Fig 3. (a) FTIR spectra of initial products of SMPU 14205; SMPU 1421; SMPU 1621 (b) FTIR spectra of final products of SMPU 14205; SMPU 1421; SMPU 1621

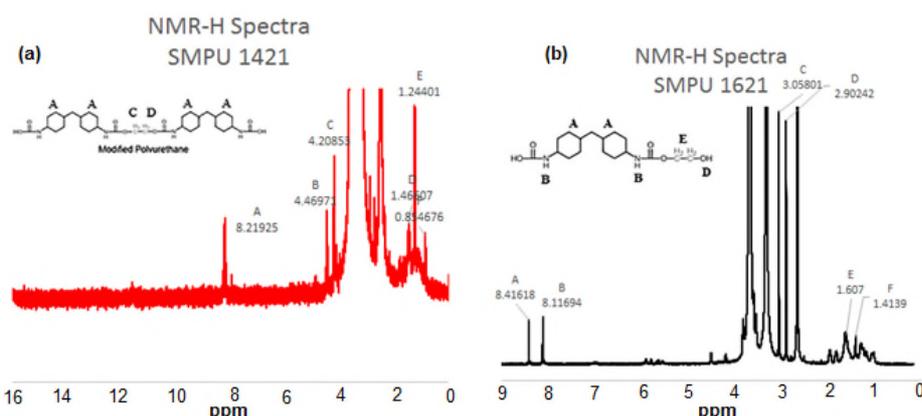


Fig 4. (a) $^1\text{H-NMR}$ spectra of initial product of SMPU 1421 (b) $^1\text{H-NMR}$ spectra of initial product of SMPU 1621

FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ Spectra Analysis

As mentioned earlier, there are two types of products being characterized, which are initial product (terminated by water, without the presence chain extender) and final product (with the presence of chain extender and filler Fe_3O_4). The FTIR spectra as seen at Fig. 3 (a) and (b) do not show an absorbance band at 2270 cm^{-1} arising from residual $\text{N}=\text{C}=\text{O}$ groups. However, both initial and final products have two principal vibrational regions related to the urethane group appear at $2855\text{--}3312\text{ cm}^{-1}$ for the ν_{NH} and $1621\text{--}1703\text{ cm}^{-1}$ from the $\nu_{\text{C}=\text{O}}$ stretching vibration, respectively. The main difference between initial product and final product by means of FTIR spectra are the presence of urea linkage. The observed urea linkage is formed from the excess diisocyanate reaction during the water termination step of initial product as can be seen at the Fig. 6.

However, the initial product has been successfully match with our molecular design. On the other hand, urea linkage is not visible at FTIR spectra of final product because it is assume that all of the diisocyanate has been reacted with chain extender and the remainders of PEG.

The spectra for both ^{13}C and ^1H NMR for the entire sample including initial and final product have been matched with our molecular design for modified polyurethane. NMR characterization only conducted to initial products of SMPU 1421 and SMPU 1621. SMPU 14205 initial products are considered similar with SMPU 1421 because the composition (without the addition of chain extender and Fe_3O_4 filler) and the process of synthesis are same. All of the final products have not been tested by NMR but only by FTIR because the presence of Fe_3O_4 filler will make a magnetic disturbance to the NMR.

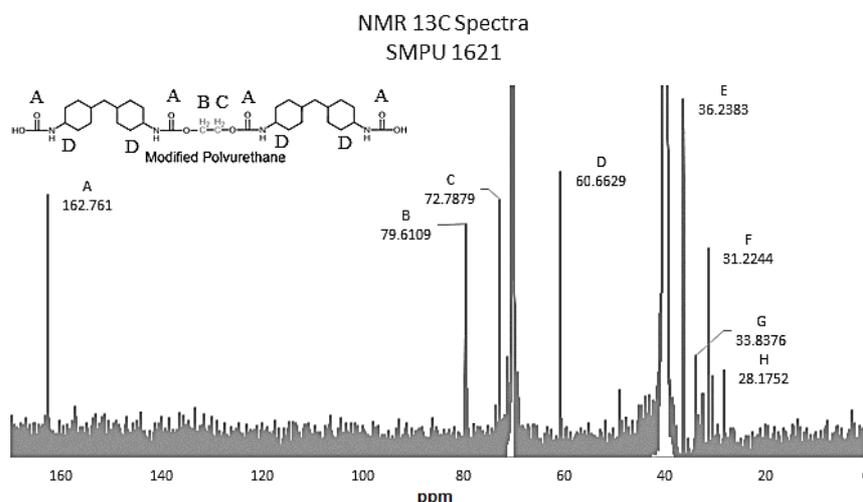


Fig 5. ¹H-NMR spectra of initial product of SMPU 1421 (b) ¹H-NMR spectra of initial product of SMPU 1621

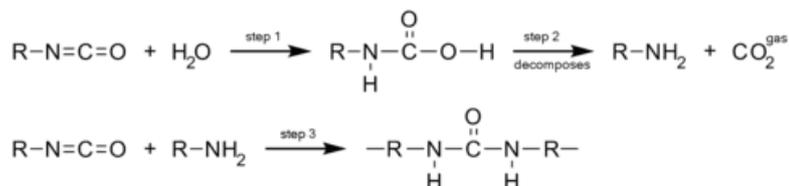


Fig 6. Isocyanate and water reaction to form urea linkage

The important spectra for ¹H-NMR for all of the product are δ 8.2–8.5 ppm for the C aromatic structure; δ 1.41–1.469 ppm for the C-C of the soft segment and δ 4.469 ppm for the C-N-H which refer to urethane structure. Detailed analytical data are shown in Table 4. According to M. Chalid et al. [28] reported that free –NH groups are at 3266–3312 cm⁻¹ whereas hydrogen-bonded –NH groups appear at 2855–2976 cm⁻¹ and similarly, free –C=O groups are present at 1682–1703 cm⁻¹ and hydrogen-bonded –C=O groups at 1621–1643 cm⁻¹. All of the initial product has both hydrogen-bonded and free –C=O and –NH groups, those groups are free because chain extender as the cross-linking agent has not been added. After the addition of chain extender (final product) there are no visible free –C=O and –NH groups at SMPU 14205 and SMPU 1421 samples, it is considered that all of the groups has been hydrogen cross-linked that makes the materials very brittle. For SMPU 1621 the case is quite different, the numerous addition of excess MDI certainly creates a phase separation between hard segment and soft segment. There are still visible free groups of –C=O and –NH at FTIR spectra. This case is due to the phase separation, large amount of diisocyanate make globular-like structure (as can be seen at SEM images later on) and leave some of trapped diisocyanate at intermolecular spacing which formed free groups of –C=O and –NH. The distributed phase separation is good for shape

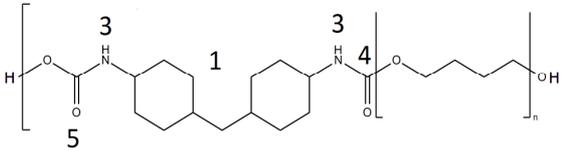
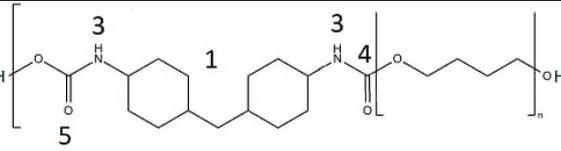
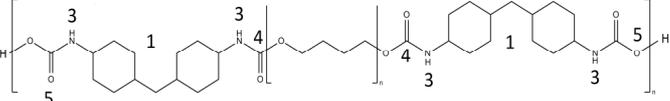
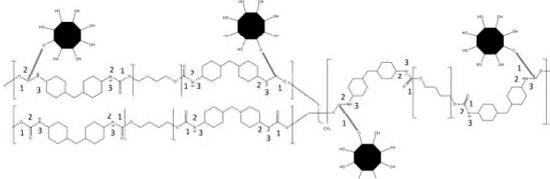
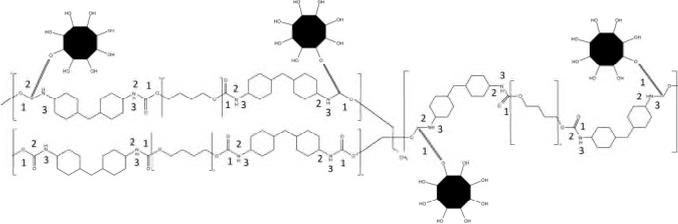
memory effect so that soft segment and hard segment can work separately but still in reasonable limits.

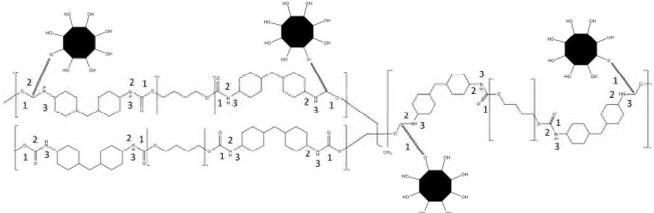
Based on the calculation of the amount of data, comparison of hard and soft segments of each sample in Table 5. Using a reference to the results of NMR in Fig. 4 and 5, this result is quite unusual because as we know SMPU 1621 has more HMDI composition (as the source of the formation of the hard segment) than SMPU 14205 and SMPU 1421 but it have small hard segment percentage. This phenomena can be explained by the phase separation process in which precisely happened by the addition of massive composition of HMDI. The excess of the addition of HMDI will be able to mobilize the hard segment into a separate phase in which will reduce the probability of crosslink formation (minimum crosslink formation can contribute to better properties) whereas it is the core of the hard segment. The results of this percentage then be linked to the mechanical strength and the speed of actuation of the final product which will be discussed in the next section.

SEM Image Analysis

SEM analysis are conducted towards Fe₃O₄ nanoparticle to know about the actual size of the nanoparticle and SMPU 14205; SMPU 1421; SMPU 1621 to know about the morphology, filler interface and

Table 4. Analytical data of polyurethane products

Product	Chemical Structure Appearance & Elemental Analysis	¹ H- Chemical Shift (ppm)	¹³ C- Chemical Shift (ppm)	FTIR (cm ⁻¹)
SMPU 14205 (Initial)	 <p>CHNO white solid Separated phase → low hydrogen bonding</p>	(1) 8,2 (2) 1,469 (3) 4,469 (4 & 5) 1,650	n/a	(1) 1627 (Aromatic C-C, s) (hydrogen bonded C=O urethane) (Urea) (3) 1548 (stretched C-N & bended N-H, s) (4) 3466 (carboxylic acid, O-H, s) (5) 1722 (free C=O urethane, s) (5) 1105 (C-O Stretch) (3) 3323-3499 (free N-H, br) (bertindihan dengan spektrum (4)) (3) 2888 (H bonded N-H, m)
SMPU 1421 (Initial)	 <p>CHNO white solid Separated phase → low hydrogen bonding</p>	n/a	n/a	(1) 1627 (Aromatic C-C, s) (hydrogen bonded C=O urethane) (Urea) (3) 1553 (stretched C-N & bended N-H, s) (4) 3319 (carboxylic acid, O-H, s) (5) 1105 (C-O Stretch) (3) 3323-3499 (free N-H, br) (bertindihan dengan spektrum (4)) (3) 2883 (H bonded N-H, m)
SMPU 1621 (Initial)	 <p>CHNO white solid Separated phase → low hydrogen bonding</p>	(1) 8,4 (3) 1,416 (4) 1,827	(1) 35,80 (2) 162,32	(2) 1651 (Aromatic C-C, s) (hydrogen bonded C=O urethane) (Urea) (2) 1105 (C-O Stretch) (5) 3286-3384 (free N-H, br) (5) 2929 (H bonded N-H, m) (5) 3319 (free N-H, br) (bertindihan dengan spektrum (4)) (4) 3394 (carboxylic acid, O-H, s)
SMPU 14205 (Final)	 <p>CHNO brownish solid Dispersed phase → high hydrogen bonding</p>	n/a	n/a	(1) 1637 (Aromatic C-C, s) (hydrogen bonded C=O urethane) (1) 1105 (C-O Stretch) (2) 529 (Fe-O stretch) (3) 2889 (H-bonded N-H vibration, urethane) (5) 3418 (free N-H, br)
SMPU 1421 (Final)	 <p>CHNO brownish solid Dispersed phase → high hydrogen bonding</p>	n/a	n/a	(1) 1655 (Aromatic C-C, s) (hydrogen bonded C=O urethane) (1) 1102 (C-O Stretch) (2) 529 (Fe-O stretch) (3) 2885 (H-bonded N-H vibration, urethane) (5) 3412 (free N-H, br)

SMPU 1621 (Final)		n/a	n/a	(1) 1662 (Aromatic C-C, s) (hydrogen bonded C=O urethane) (1) 1104 (C-O Stretch) (2) 529 (Fe-O stretch) (3) 2884 (H-bonded N-H vibration, urethane) (5) 3445 (free N-H, br)
CHNO brownish solid Separated phase → low hydrogen bonding				

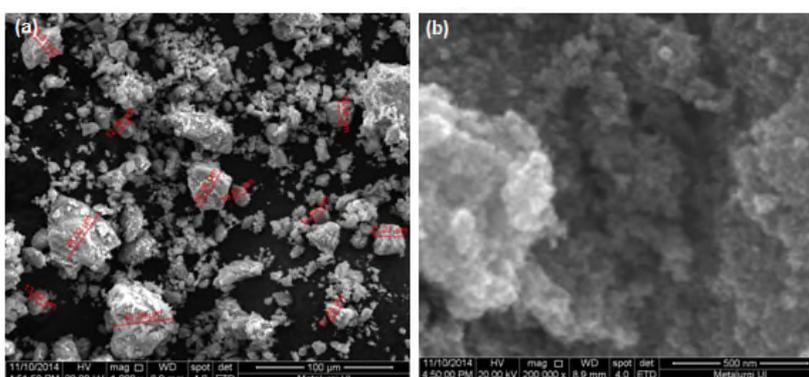


Fig 7. (a) Fe_3O_4 nanoparticle 1.000x magnification; (b) Fe_3O_4 200.000x magnification

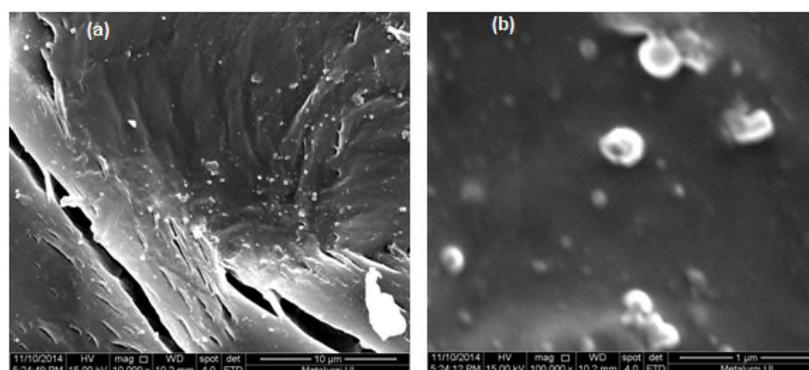


Fig 8. (a) SMPU 14205 10.000x magnification; (b) SMPU 14205 100.000x magnification

Table 5. Data calculation of the amount of hard and soft segment ratio of each sample (SMPU 14205; SMPU 1421; SMPU 1621)

Sample Code	Soft : Hard Segment Comparison
SMPU 14205	1: 0.588
SMPU 1421	1: 0.588
SMPU 1621	0.89: 1

phase separation. As can be seen at Fig. 7(a) as received Fe_3O_4 nanoparticle are agglomerated with the average size of $40 \mu\text{m}$, however the agglomerated particle are composed of smaller nanoparticles about 20–50 nm as can be seen at Fig. 7(b). The agglomeration occurred due to the presence of humid

air, however the agglomerated particle can be broken up at the solvation process with the addition of DMF.

Related to the SEM image of SMPU 14205 and SMPU 1421 as can be seen at Fig. 8 and 9. There are a lot of spindle-like micro pores at the surface of the materials, while there are no visible micro pores at SMPU 1621. The micro pores found at SMPU 14205 and SMPU 1421 were formed during the process of solvent evaporation while the solvent evaporated the curing happened. Because SMPU 14205 and SMPU 1421 have lack of diisocyanate, both have 4 moles of diisocyanate, while SMPU 1621 has 6 moles, phase separation process cannot be done fully, so that all of the $-\text{C}=\text{O}$ and $-\text{NH}$ groups are hydrogen bonded inside of PEG matrix, this curing brittleness caused by cross-linking resulted in the formation of micro pores which

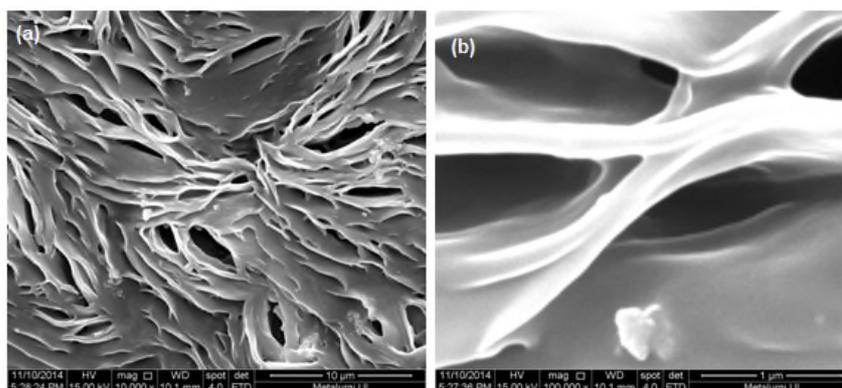


Fig 9. (a) SMPU 1421 10.000x magnification; (b) SMPU 1421 100.000x magnification

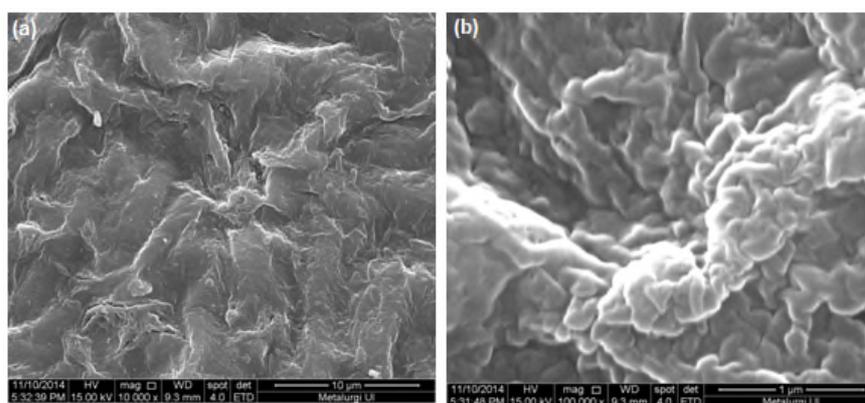


Fig 10. (a) SMPU 1621 10.000x magnification; (b) SMPU 1621 100.000x magnification

Table 5. Mechanical properties data

Sample Code	Tensile Strength (MPa)	Strain at Break (%)	Actuation Speed (s)	Rf (%)	Rr (%)
SMPU 1621	0.61	7.36	30	94.4	97.22

makes the material becomes more brittle, it's why SMPU 14205 and SMPU 1421 cannot undergo physical actuation testing because it is too fragile.

For the phase separation, Fig. 8 and 9 shows the amorphous form of polyurethane, it is proved that very little hard segment were formed and proved that the curing process was uncompleted. Whereas in SMPU 1621 which can be seen in Fig. 10, there are some visible globular shape, this shape shows that many of urethane hard segment were formed and the phase separation process can take place fully which of course enhance the mechanical and shape memory properties of the polyurethane. As can be seen at Fig. 8, 9 and 10 some Fe_3O_4 agglomerated nanoparticle nodules are visible, while gap between nanoparticles and the polyurethane are not visible, therefore the interface physically can be considered appropriate, this data corroborate with the NMR data which C=O interface

were formed between Fe_3O_4 nanoparticles and polyurethane matrix.

Physical Actuation Analysis

The sample made for physical actuation analysis has the size of 1 cm x 3 cm. The test conducted by using bending force to the SMPU sheet (180°) at elevated temperature (40°C) until fully deformed to 10° . After that, the sample was cooled to 10°C and stored for 30 min while maintaining the bending force. And then, the sample was put into 40°C water while the time for the materials to transform back to original shape (180°) was quantified using stop watch. The sample used for this analysis only applicable for SMPU 1621, because SMPU 14205 and SMPU 1421 are too brittle to be deformed as mentioned earlier at SEM Image analysis.

Rf and Rr can be calculated using equation 1, which Rf is shape retention rate and Rr shape recovery rate.

$$R_f(\%) = \frac{180^\circ - \theta_f}{180^\circ} \times 100$$

$$R_r(\%) = \frac{\theta_f}{180^\circ} \times 100$$
(1)

$$R_f(\%) = \frac{180^\circ - 10^\circ}{180^\circ} \times 100 = 94.4\%$$

$$R_r(\%) = \frac{175^\circ}{180^\circ} = 97.22\%$$

The mechanical properties for the SMPU 1621 have a very good result, however the tensile strength and strain at break are considered low. This is because of the brittleness of the polyurethane caused by under-cured mechanism that has been mentioned earlier at SEM Image analysis.

CONCLUSION

The three compositions of the base materials (PEG 6000, HMDI and TMP) and the additives (Fe_3O_4) is influential in the formation of cross-links and the partial crystallinity of the polymerization process that will affect the performance of SMPU. SMPU 14205, SMPU 1421 and SMPU 1621 have been successfully synthesized as the urethane linkages were formed during the synthesis process. However, SMPU 14205 and SMPU 1421 cannot complete their phase separation because of the lack of diisocyanate (HMDI) so that the surface contains significant spinel-like micro pores which affect the mechanical properties of the polyurethane (brittleness). On the other hand, SMPU 1621 can perform the shape memory effect with R_f 94.4% and R_r 97.22%, but the tensile strength is considered low because still the diisocyanate was less added. Overall, the interface between Fe_3O_4 nanoparticles is physically and chemically compatible proven by the SEM images and FTIR spectra.

ACKNOWLEDGEMENT

The authors express their gratitude and thanks to the research project assistance granted by DIKTI (Indonesian Directorate General of Higher Education) through the grant of PKM-P (Student Creativity Program-Research), dated July, 2014, and CMPFA (Center of Materials Processing and Failure Analysis) Department of Metallurgy and Materials Engineering, Universitas Indonesia, through equipment grant.

REFERENCES

- Lu, H., Liang, F., and Gou, J., 2011, *Soft Matter*, 7(16), 7416–7423.
- Viry, L., Mercader, C., Miaudet, P., Zakri, C., Derré, A., Kuhn, A., Maugey, M., and Poulin, P., 2010, *J. Mater. Chem.*, 20(17), 3487–3495.
- Leng, J., Lv, H., Liu, Y., and Du, S., 2007, *Appl. Phys. Lett.*, 91(14), 144105.
- Jung, Y.C., Yoo, H.J., Kim, Y.A., Cho, J.W., and Endo, M., 2010, *Carbon*, 48(5), 1598–1603.
- Sokolowski, W., Chmielewski, A., Hayashi, S., and Yamada, T., 1999, "Cold hibernated elastic memory (CHEM) self-deployable structures", *SPIE '99 International Symposium on Smart Structures and Materials*, Newport Beach, CA.
- Ahmad, M., Xu, B., Purnawali, H., Fu, Y., Huang, W., Mirafteb, M., and Luo, J., 2012, *Appl. Sci.*, 2(2), 535–548.
- Schmidt, A.M., 2006, *Macromol. Rapid Commun.*, 27(14), 1168–1172.
- Lu, H., Gou, J., Leng, J., and Du, S., 2011, *Appl. Phys. Lett.*, 98, 174105.
- Yakacki, C.M., Satarkar, N.S., Gall, K., Likos, R., and Hilt, J.Z., 2009, *J. Appl. Polym. Sci.*, 112(5), 3166–3176.
- Buckley, C.P., Prisacariu, C., and Caraculacu, A., 2007, *Polymer*, 48(5), 1388–1396.
- Lee, B.S., Chun, B.C., Chung, Y.C., Sul K.I., and Cho, J.W., 2001, *Macromolecules*, 34(18), 6431–6437.
- Cai, Y., Jiang, J-S., Zheng, B., and Xie, M-R., 2013, *J. Appl. Polym. Sci.*, 127(1), 49–56.
- Kalita, H., and Karak, N., 2013, *Polym. Adv. Technol.*, 24(9), 819–823.
- Jacoby, M., 2001, *Chem. Eng. News*, 79(6), 30–35.
- Mantovani, D., 2000, *JOM-J. Min. Met. Mater. Soc.*, 52(10), 36–44.
- Deurig, T., Pelton, A., and Stöckel, D., 1999, *Mater. Sci. Eng., A*, (273-275), 149–160.
- Ölander, A., 1932, *Z. Kristallogr.*, 83(1), 145–148.
- Sokolowski, W., *CHEM Structure for Mars Exploration*, Internal JPL Presentation, August 15, 1997.
- Hayashi, S., 1993, *Proc. SPI Polyurethanes Div. 35th Annual Cong.*, Vancouver, B.C. Canada.
- Andelman, D., and Rosensweig, R.E., 2009, "The Phenomenology of Modulated Phases: From Magnetic Solids and Fluids to Organic Films and Polymers", in *Polymers, liquids and colloids in electric fields: interfacial instabilities, orientation and phase transitions*, Tsori, Y., and Steiner, U., eds., World Scientific, 1–56.
- Kunzelman, J., Cung, T., Mather, P.T., and Weder, C., 2008, *J. Mater. Chem.*, 18(10), 1082–1086.
- Habib, A.H., Ondeck, C.L., Chaudhary, P., Bockstaller, M.R., and McHenry, M.E., 2008, *J. Appl. Phys.*, 103, 07A307.
- Okawa, K., Sekine, M., Maeda, M., Tada, M., Abe, M., Matsushita, N., Nishio, K., and Handa, H., 2006, *J. Appl. Phys.*, 99, 08H102.
- Hergt, R., Andra, W., d'Ambly, C.G., Hilger, I., Kaiser, W.A., Richter, U., and Schmidt, H., 1998, *IEEE Trans. Magn.*, 34(5), 3745–3754.
- Bahadur, D., and Giri, J., 2003, *SĀDHANĀ*, 28(3-4), 639–656.

26. O'Handley, C., 2000, *Modern Magnetic Materials: Principles and Applications*, Wiley, New York.
27. Pankhurst, Q.A., Connolly, J., Jones, S.K., Dobson, J., 2003, *J. Phys. D: Appl. Phys.*, 36(13), R167–R181.
28. Chalid, M., Heeres, H.J., and Broekhuis, A.A., 2012, *Appl. Mech. Mater.*, 229-231, 297–302.