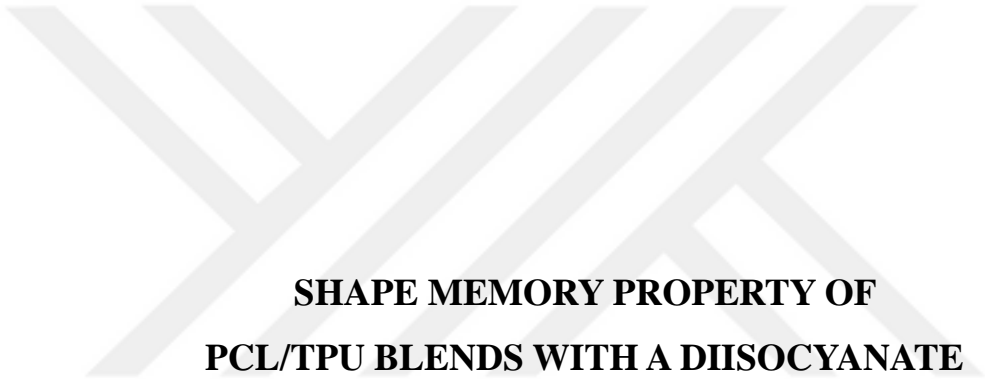


KOCAELI UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES

DEPARTMENT OF POLYMER SCIENCE AND TECHNOLOGY

THE MASTER'S THESIS



**SHAPE MEMORY PROPERTY OF
PCL/TPU BLENDS WITH A DIISOCYANATE
COMPATIBILIZER**

NAYEON LEE

KOCAELI 2018

KOCAELI UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES

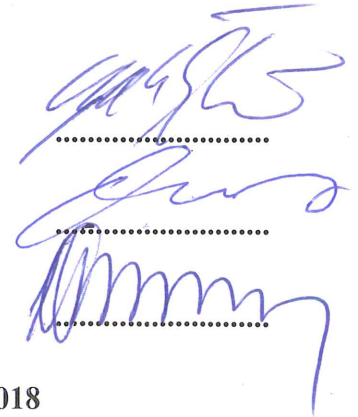
DEPARTMENT OF
POLYMER SCIENCE AND TECHNOLOGY

THE MASTER'S THESIS

SHAPE MEMORY PROPERTY OF
PCL/TPU BLENDS WITH A DIISOCYANATE
COMPATIBILIZER

NAYEON LEE

Assoc. Prof. Dr. Gralp ZKO
The Supervisor, Kocaeli University
Assoc. Prof. Dr. Baėdagl KARAAėA
The Jury Member, Kocaeli University
Prof. Dr. Mustafa KSZ
The Jury Member, Yalova University



The Date of the Thesis Defense: 21.06.2018

ACKNOWLEDGMENTS

Foremost, I would like to thank my thesis advisor Assoc. Prof. Dr. Gralp zko of the Polymer Science and Technology Department at Kocaeli University. Even with his busy schedule he gladly helped me and gave advice for researching and writing this thesis in all the time. I was fortunate in having this great advisor during my master study.

I would also like to thank my fellows in the lab group, Ezgi Bier, Esra Bařaran, Nazlı Yazıcı, Glřen Kurt Demir, Fatma Gler and others. They always lend a hand without slightest hesitation and make school life enjoyable. Thanks to them, I was easily able to get used to the new circumstances in Turkey.

Lastly, I must express my heartfelt gratitude to my parents and to friends of mine for giving me boundless support and encouragement every moment throughout my years of study. It would be much harder to put the final touch on the master's course without them. Thanks a lot.

May - 2018

Nayeon LEE

TABLE OF CONTENTS

ACKNOWLEDGMENTS	i
TABLE OF CONTENTS	ii
LIST OF FIGURES	iii
LIST OF TABLES	v
SYMBOLS AND ABBREVIATIONS	vi
ABSTRACT	vii
Ö ZET	viii
INTRODUCTION	1
1. GENERAL INFORMATION	4
1.1. Poly ϵ -caprolactone (PCL)	4
1.2. Thermoplastic Polyurethane (TPU)	5
1.3. Diisocyanate	6
1.4. Shape Memory Polymer (SMP).....	7
1.5. Test Technique and Equipment Information	9
1.5.1. Technique for processing	9
1.5.1.1. Twin-screw compounder	9
1.5.1.2. Injection molding	10
1.5.2. Characterization	10
1.5.2.1. Tensile test	10
1.5.2.2. Thermal gravimetric analysis (TGA)	12
1.5.2.3. Differential scanning calorimeter (DSC)	13
1.5.2.4. Rheometer.....	15
1.5.2.5. Scanning electron microscopy (SEM)	15
1.5.2.6. Shape memory test	16
2. LITERATURE REIVEW	18
3. EXPERIMENTAL.....	20
3.1. Materials	20
3.2. Blends Preparation	21
3.3. Characterization	22
4. RESULTS AND DISCUSSION	25
4.1 Mechanical Properties	25
4.2 Thermal Properties	29
4.3. Rheological Properties	34
4.4. Morphological Properties	37
4.5. Shape memory Properties	40
4.5.1. Shape fixity ratio	42
4.5.2. Shape recovery ratio	43
4.5.3. Effect of programming temperature to shape memory properties.....	45
5. CONCLUSIONS AND SUGGESTION	48
REFERENCES	50
ACADEMIC ACHIEVEMENT.....	56
PROFILE	57

LIST OF FIGURES

Fig. 1.1.	The structure of PCL.....	4
Fig. 1.2.	The reaction of active hydrogen and diisocyanates	6
Fig. 1.3.	The schematic of reaction with diisocyanate and [-OH]	7
Fig. 1.4.	The schematic of reaction with diisocyanate and polyurethane.....	7
Fig. 1.5.	The mechanism of SMP. Black dots indicate net points, blue lines indicate molecular chains below T_{trans} and red lines indicate molecular chains having high mobility above T_{trans}	8
Fig. 1.6.	Diagram form of twin-screw extruder.....	10
Fig. 1.7.	The example of the stress-strain curve of a semi-crystalline polymer	11
Fig. 1.8.	TGA curves and decomposition curves according to the effect of heating rate.....	13
Fig. 1.9.	Typical DSC curve of polymer with T_g , T_c and T_m	14
Fig. 3.1.	Schematic diagram of the fold- deploy shape memory test.....	23
Fig. 3.2.	The measuring the angle of fixation (θ_{fixed}) after waiting the samples being cooled down at the room temperature.....	24
Fig. 3.3.	The measuring the angle of fixation (θ_{final}) after waiting the samples being full recovered at the test temperature.....	24
Fig. 4.1.	Stress-strain curves of TPU/PCL blends without PDI.....	25
Fig. 4.2.	Stress-strain curves of TPU70/PCL30 blends depending on the percent of PDI	26
Fig. 4.3.	Stress-strain curves of TPU50/PCL50 blends depending on the percent of PDI.....	27
Fig. 4.4.	Tensile strain at break of TPU/PCL blends.....	28
Fig. 4.5.	Tensile strength at break of TPU/PCL blends.....	28
Fig. 4.6.	DSC thermogram of samples depending on the PCL/TPU ratio.....	30
Fig. 4.7.	DSC thermogram of PCL30 samples with different ratio of PDI.....	30
Fig. 4.8.	DSC thermogram of PCL50 samples with different ratio of PDI.....	31
Fig. 4.9.	TGA thermogram of samples depending on the PCL/TPU ratio.....	32
Fig. 4.10.	The onset point of decomposition of the samples.....	32
Fig. 4.11.	The variation of complex viscosity with respect to angular frequency(a) PLA/TPU blends without PDI (b) PLA TPU blends with PDI	35
Fig. 4.12.	Storage and loss modulus to frequency of the PCL 50 samples (with 2% of PDI and without PDI)	36
Fig. 4.13.	SEM results on the cryo-fractured surfaces of samples (magnifications:1000x).....	38
Fig. 4.14.	SEM results on the cryo-fractured surfaces of samples (magnifications:5000x)	39
Fig. 4.15.	SEM images on the cryo-fractured surfaces of PCL20PDI2 (magnifications:10000x)	40
Fig. 4.16.	The pictures on the shape memory test of the PCL50 PDI2 sample with different condition of the temperature ((A)is under	

	40°C (B) is under 50°C, and (C) is under 65°C)	41
Fig. 4.17.	Shape retention ratio of the samples	42
Fig. 4.18.	Shape recovery ratio of the samples (under the condition of 40, 50 and 65°C).....	44
Fig. 4.19.	Shape retention ratio depending on different pre-deformation temperature.....	46
Fig. 4.20.	Shape recovery ratio at 55°C with different pre-deformation temperature.....	47



LIST OF TABLES

Table 3.1. Used materials, supplier and characters.....	20
Table 3.2. Blending ratio of the samples.....	21
Table 4.1. The temperature at the highest degradation peak of the samples.....	33
Table 4.2. The chart of onset and endset temperature.....	33



SYMBOLS AND ABBREVIATIONS

T_{trans}	: the Transition temperature, ($^{\circ}\text{C}$)
T_{g}	: the Glass transition, ($^{\circ}\text{C}$)
T_{m}	: the Melting temperature, ($^{\circ}\text{C}$)
M_{w}	: Molecular weight
M_{n}	: Number-average molecular weight
R_{f}	: Shape fixation ratio, (%)
R_{r}	: Shape recovery ratio, (%)
σ_{max}	: The maximum recovery stress, (MPa)
ϵ_{max}	: The maximum recoverable strain
C_{p}	: Heat capacity, ($\text{J/g}^{\circ}\text{C}$)
T_{c}	: Crystallization temperature, ($^{\circ}\text{C}$)

ABBREVIATIONS

DMA	: Dynamic Mechanical Analysis
DSC	: Differential Scanning Calorimeter
PCL	: Poly(ϵ -caprolactone)
PDI	: 1,4-Phenylene Diisocyanate
SEM	: Scanning Electron Microscopy
SMA	: Shape Memory Alloy
SME	: Shape Memory Effect
SMP	: Shape Memory Polymer
TGA	: Thermal Gravimetric Analysis
TPU	: Thermoplastic Polyurethane

SHAPE MEMORY PROPERTY OF PCL/TPU BLENDS WITH A DIISOCYANATE COMPATIBILIZER

ABSTRACT

Shape memory polymers are a smart material which is able to memorize the specific shape with a particular stimulus. In this study, thermal stimuli-responsive shape memory polymers based on blends of thermoplastic polyurethane (TPU) and poly(ϵ -caprolactone) (PCL) are investigated in the presence of a diisocyanate (1,4-phenylene diisocyanate, PDI) compatibilizer. Mechanical, thermal, rheological and morphological characteristics of the blends are investigated. Shape memory properties are also studied with the fold deploy shape memory test. PCL also provides thermal stability and higher tensile strength. PDI acts as the chain extender, which potentially reacts with ends groups of PCL and/or TPU. The blends with PDI tend to exhibit high elongation in comparison to the blends without PDI. PCL affects the crystallinity of the blends and results in providing high fixity of the materials. Contrarily, the presence of PCL negatively influences the shape recovery ratio. The presence of PDI regulates the aforementioned behavior. Optimal shape memory polymer can be designed by regulating the ratio of the components.

Keywords: Compatibilization, Polymer Blending, Poly(ϵ -caprolactoe), Shape Memory Polymers, Thermoplastic Polyurehtane.

POLİ(ε-KAPROLAKTON)(PCL) / TERMOPLASTİK POLİÜRETAN(TPU) KARIŞIMLARININ DIISOCYANATE İLAVESİ İLE ŞEKİL HAFIZA DAVRANIŞININ İNCELEMESİ

Ö ZET

Şekil hafızalı polimerler, bir dış uyaran ile önceden hafızalanan şekle geçebilen akıllı malzemelerdir. Bu çalışmada 1,4-fenilendiizosiyanat (PDI) ile uyumlaştırılmış poli(ε-kaprolakton) (PCL) ve termoplastik poliüretan (TPU) bazlı, şekil hafızalı polimer karışımları üretilip, mekanik, termal, reolojik ve morfolojik özellikleri incelenmiştir. Şekil hafıza özellikleri ise katlanma-açılma testi ile incelenmiştir. PCL ilavesi, TPU'nun çekme dayanımı ve termal kararlılığını arttırmıştır. PDI ise hem uyumlaştırıcı hem de zincir uzatıcı gibi davranmış, PCL ve/veya TPU'nun zincir uç grupları ile etkileşmiştir. PDI içeren karışımların kopma uzama değerleri diğerlerine göre daha yüksek olarak elde edilmiştir. PCL, karışımların kristalinitesini etkileyerek daha yüksek şekil sabitleme oranı sağlamıştır. Tersine, PCL içeren karışımlarda şekil geri dönüş oranı düşmektedir. PDI ilavesi ile bu olumsuz durum düzenlenebilmektedir. Optimum şekil hafıza özelliği bileşenlerin oranlarının ayarlanması ile elde edilebilir.

Anahtar Kelimeler: Uyumlaştırma, Polimer Harmanlama, Poli(ε-kaprolakton), Şekil Hafızalı Polimerler, Termoplastik Poliüretan.

INTRODUCTION

Shape memory polymers (SMPs) have been received a great deal of attention for decades. Due to the ability of shape changing under different conditions, it has been studied and developed with an expectation of wide potential applications [1-3]. SMPs are stimuli-responsive materials, which “actively move” in response to an external stimulus like heat or light [4]. SMPs are able to “memorize” a permanent shape (original shape). After it is manipulated and “fixed” in the intended temporary shape with applied external mechanical force by cooling under the transition temperature, T_{trans} , which process is called “programming” [2, 5-7]. When the temperature heats up above T_{trans} , it gets back to the original shape by restoring the random coil from the oriented and crystalline chains. T_{trans} is usually the glass transition, T_g or the melting temperature T_m . Melting point as T_{trans} shows relatively a sharper transition compare to the glass transition as T_{trans} [7]. SMPs can be applied widely in various fields. Above all, attention is concentrated in biomedical applications. In comparison with shape memory alloys (SMAs), SMPs possess large recovery strains and low recovery stress [2, 7]. In addition to this, it is biocompatibility and shows cost-efficient. Since It is also tunable a compliant range of actuation temperature as well as glassy elastic modulus, It is applied for a human body, where the use of high temperature needs to be avoided [8-10].

Some SMPs are known for suitable to be decomposed in a body, such as polyurethane, polyesters (like poly(ϵ -caprolactone) (PCL), PLA, PGA), polyether urethane, polylactic acid and their blends or block copolymers. Especially, PCL, semi-crystalline aliphatic polyester, is noticeable biodegradable soft materials for biomaterial applications as SMP [11-13]. PCL based SMP shows fast response and a small range of transition temperature since it is operated under “ T_m -based system” [14]. Lendlein and Langer [15] also refer a PCL-based biodegradable polymer and demonstrate the potentiality of using medical area. Salvekar, A., V., et al. [16] studied the shape and temperature memory phenomena with uncross-linked poly(ϵ -caprolactone) and proposed promising development possibility of PCL as SMP.

Even though PCL was uncross-linked, it showed proper shape memory properties. PCL-based SMPs have limitations that durability is weak after the shape is restored. Polyesters generally have low strength and stiffness, which put a limit on making enough recovery force, and consequently to restricted being applied properly.

Polymer blending is the readily accessible way to control properties and overcome limitations such as mechanical characters and degradation rate, which is a mixing process of more than two polymers with different ratios. Thermoplastic polyurethane (TPU) is able to complement weakness of PCL by blending. Polyurethane has used for shape memory blending and applied to the biomedical field because of their mechanical properties-flexibility and potentially biocompatibility. Furthermore, the soft domain of polyurethane is possible to be tailored for shape memory. TPUs are copolymers consisting of three parts. These are hard domain derived from diisocyanate, which memorizes a permanent shape, soft domain derived from the polyol, which stores external force for a reversible process, and chain extender [17, 18]. PCL is one of the polyesters which has been usually used in soft blocks applied in TPU synthesis [5, 19] and combining properties of PCL and TPUs might be advantageous to create new biodegradable SMPs. TPU acts as the net point, which is recovering the permanent shape, and PCL acts as the switch phase [20, 21].

Jing et al. [21] recently studied the blending of TPU and PCL as SMP for applying self-knotting sutures. As adjusting the weight ratios of two materials, they found the best ratio having shape memory effect. Ajili, Ebrahimi and Soleimani [22] also investigated shape memory properties of PU and PCL blend for cardiovascular implants. They arranged the research in the range near body temperature. As outcome, the sample showed superior biocompatibility and applicability of the target field. Their previous research is conducted to see the miscibility of blending with polyurethane and PCL through rheological study. They suggested the possibility of partial dissolution of PCL, the state of semi-miscible, because of the differential molecular weight between PCL and soft block in PU, even though they have a microstructural similarity [23].

Partially miscible might be the reason of a slow recovery in shape memory effect [7]. Because of that, enhancing miscibility between PCL and TPU is considered. Dogan

et al. [24] made an attempt to overcome this problem as adding diisocyanate to PLA/TPU blends and study reactive compatibility. Harada et al. [25] also studied the increasing the compatibility of poly(lactic acid)/Poly(butylene succinate) blend by using isocyanate in the reactive processing. Diisocyanates as compatibilizer potentially interacts with –OH of TPU and -OH/-COOH of PCL during compounding.

To the best of our knowledge, the function of diisocyanates in PCL/TPU blends is not studied yet. PDI might function as compatibilizer as like the case of PLA and TPU blends [24], or it might contribute to other functions because PCL already have high and homogeneous miscibility to TPU. Therefore, the aim of the current study is to investigate the effects of PDI on the mechanical, thermal, morphological and shape memory properties of PCL/TPU blends. PDI was added from %0 to %3 to each different composition of PCL/TPU. The shape memory properties were investigated by means of ‘fold-deploy shape memory test’ [26, 27]. The mechanical and thermal properties are measured by tensile test, TGA and Differential Scanning Calorimetry (DSC), respectively. The compatibility of the blends in the presence of PDI was examined through rheometry and scanning electron calorimeter (SEM) analysis.

The following chapter covers general information about the physical and chemical properties of the materials, which are PCL, TPU and diisocyanate. Fundamental characters of shape memory polymer is also explained with the test technique and equipment information. The literature review in the chapter 2, makes access to the research easily by cover the current state of knowledge related to the topic. The chapter 3 and 4 are directly related to the experimental part of this research. How the experiment is arranged is explained (chapter 3), and the data from the test with discussion are featured, respectively. Lastly, this research concludes with a conclusion in chapter 5.

1. GENERAL INFORMATION

1.1. Poly(ϵ -caprolactone) (PCL)

PCL is semi-crystalline aliphatic polyester and its structure is shown in Fig.1.1. PCL has a low glass transition temperature (T_g) of -60°C and a melting point (T_m) around from 59 to 64°C depending on the degree of crystallinity and the molecular weight (M_w). PCL is synthesized by the method of ring-opening polymerization which is able to affect the degree of crystallinity and M_w . PCL is biocompatible and degradable by hydrolytic mechanism and microorganisms, however, unlike other polyesters, its velocity of biodegradable is relatively low. Notwithstanding, it shows a rubbery state at room temperature due to its low T_g and T_m , in other words, it is ductile compared to other polyesters. Furthermore, it has good solubility and high miscibility with other polymers. Like these properties make people focus to study PCL as the topic for applying to the biomedical field [28-30].

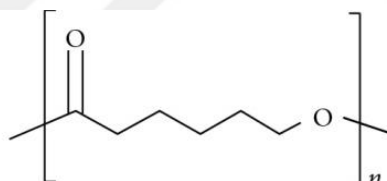


Fig. 1.1. The structure of PCL

PCL is also well studied as the raw material of synthesizing polyurethane. It is frequently applied to the soft segment of polyurethane. PCL crystals serve as switching segments and retain the temporary shape. When the crystals are melted, the permanent shape is restored by the role of hard segments. For this reason, the melting point of PCL can affect the temperature of shape transition in polyurethane. PCL is possible used to the component of shape memory materials. And another way, in the case of cross-linked PCL, it is considered as shape memory polymer by oneself. The cross-linked network of PCL is able to store the energy to offer the driving strength for shape recovery [16].

The mechanical properties of PCL are not superior. Its tensile strength and tensile modulus are relatively low. This point may be the main limitation for the application of PCL, especially the area needed load bearing. This limitation can be tuned by blending with other polymers in diverse strategies [8, 30- 32].

1.2. Thermoplastic Polyurethane (TPU)

TPUs are one of the popular materials being used in biomedical applications. TPUs have a distinct structure which is block copolymers containing “multi-disperse blocks” of hard segment (HS) and soft segment (SS). Three different sorts of raw materials are used to synthesize. Those are diisocyanate, macroglycol (polyol) and chain extender [33]. The components are described as general form:



(M : macroglycol, D: diisocyanate, C: chain extender)

Diisocyanate reacts with chain extender and have a role in shaping HS. Polyester and polyether are generally used as macroglycol and become SS of polyurethane [17, 18]. And, chain extender affects molecular weight and increasing chain length of polyurethane. These incompatible blocks are separated in micro-phase structure because the HS has higher polarity than the SS, and it influence on the mechanical and structural properties.

Polyurethane shows high flexibility, outstanding mechanical characteristics and biocompatibility, moreover it is suitable for applying to shape memory materials. HS serves as net point and memorizes a permanent shape. On the other hand, SS store external force for reversible [17]. Compare to other SMPs, the polyurethane have outstanding shape recoverability more than 400% of recoverable strain and a broad temperature range of shape recovery from 30 to 70°C [34]. The properties of polyurethane are tailored depending on the raw materials used in synthesize and the portion of HS and SS. And, these factors are able to affect shape memory properties [2]. The M_w of polyurethane, especially, have effect upon characteristics like processing and rheological properties [35].

1.3. Diisocyanate

Diisocyanate is the essential precursor for synthesizing polyurethane. There are two types of it. One is aromatic and another is aliphatic. Toluene 2,4-diisocyanate (TDI), 4,4'-methylene diphenyl diisocyanate (MDI), polymeric methylene diphenyl diisocyanate (PMDI), p-phenylene diisocyanate (PDI) and naphthalene-1,5-diisocyanate (NDI) are generally regarded as the important aromatic isocyanates in industrial fields [35]. The diisocyanate structure has a major influence on the properties of shape memory-polyurethane. The aromatic diisocyanate is normally used to synthesize polyurethane. However, the type of diisocyanate is selected depending on the requirements. Aromatic ones have high reactivity and make polyurethane having good thermal and mechanical characteristics but show low oxidation and ultraviolet stabilization. Thence, Aliphatic ones are normally used for the application which is needed a clear color or transparency because it is resistant to turn yellow under exposure of UV [33, 36].

Yang et al. [37] compared the properties between PDI-based polyurethane and MDI-based polyurethane. Shape memory effect and mechanical properties are analyzed. The polyurethane based on PDI has better properties than the one based on MDI because PDI has the planar shape inducing good interaction in hard segments. Even diisocyanates are categorized in the same class, the effects to properties of outcomes are varied. Diisocyanate have a highly reactive part, [-N=C=O] toward proton bearing nucleophilicities in structure. The reaction generally proceeds with addition of hydrogen to the C=N. In this reaction, hydrogen is attached to the nitrogen of diisocyanate (Fig. 1.2).

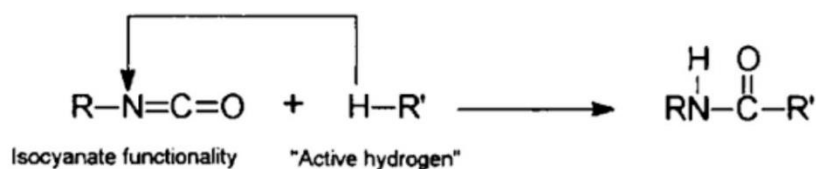


Fig. 1.2. The reaction of active hydrogen and diisocyanates [35]

Other reactions usually break the [C=N] without involving active hydrogens. Reactions generally occurs with [-OH], [-NH], amides, urea and urethane linkages.

The reactions with [-OH] and urethane linkages are considered importantly in the study. Reaction schematics are shown in Fig. 1.3 and Fig. 1.4.



Fig. 1.3. The schematic of reaction with diisocyanate and [-OH][35]



Fig. 1.4. The schematic of reaction with diisocyanate and polyurethane [35]

1.4. Shape Memory Polymer (SMP)

SMPs have gotten a lot of attention for decades as smart polymers. It is a stimuli-responsive material which has ability remembering the original shape after fixing the temporary shape when it gets external stimulus such as light, heat, electric field and so on.

SMP is consisted of switching phase and net point. Switching phase, which is called reversible phase as well, fix the temporary shape with crystallization. On the other hand, net point, which is also called as fixing phase, is in charge of restore the permanent shape [2, 5]. Switching phase is made of a thermoplastic material having phase transition of solid and liquid states, and fixing phase is made of a chemical or physical cross-link network polymer [38]. Fig. 1.5 describes the mechanism of SMP.

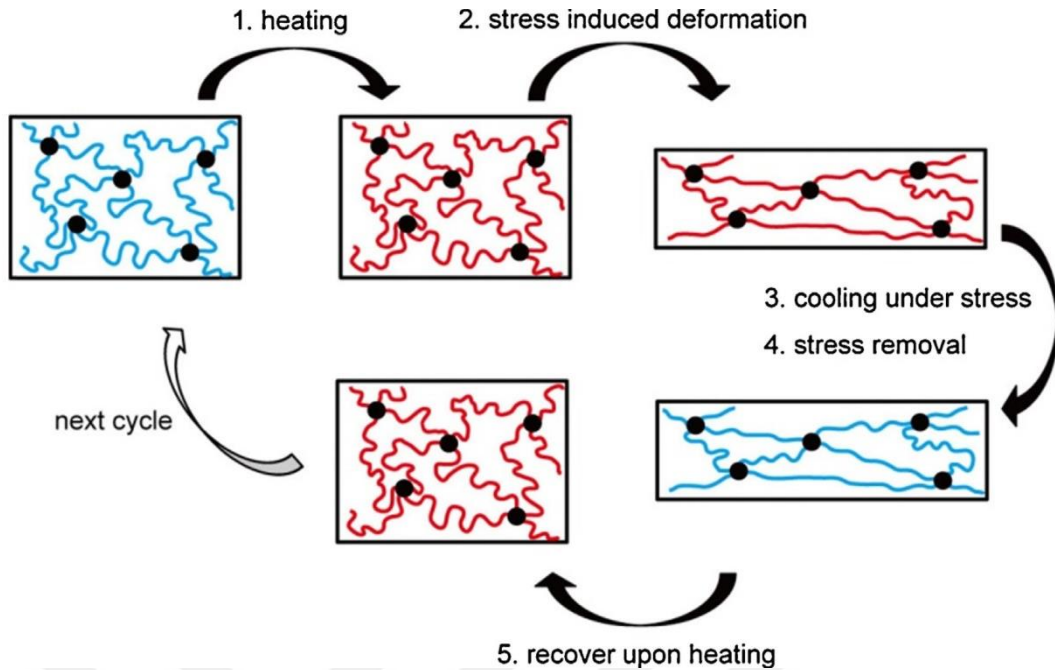


Fig. 1.5. The mechanism of SMP. Black dots indicate net points, blue lines indicate molecular chains below T_{trans} and red lines indicate molecular chains having high mobility above T_{trans} [39]

In the case of SMP induced by heat, shape memory effect can be occurred above the specific T_{trans} depending on the thermal properties of SMP. According to the state of switching segments (SS), SMP can be sub-classified into amorphous SS ($T_{trans}=T_g$) and crystalline SS ($T_{trans}=T_m$) [2].

These facts suggest that thermal properties and mechanical properties thoroughly affect the ability of shape memory. The properties of SMP can be tunable using different composites, synthesis and blending, moreover, the structure of SMP can be structural- designed by modulate the ratio of switching phase and net points. This can be controlled by choosing different polymer and other materials [13].

SMPs have been applied to broad field like aerospace, medicine, smart textiles, electronic devices and so on [40]. Bio-medical applications related with SMP have been studied particularly for a long time.

1.5. Testing Methods and Instruments

1.5.1. Processing

1.5.1.1. Twin-screw compounding

Plastics compounding is generally used for adding functionality and value to polymer systems. Through melt-blended or mixed two or more polymers are with additives, materials get together. Many applications of plastics require enhanced and tailored properties for specific necessity. It helps to meet specific requirements by using compounder. Compounding involves four steps; firstly, ingredients preparation with drying, sizing and heating. Secondly, premixing with dry blending. Thirdly, melt-mixing and lastly, forming.

Extrusion is very important for forming methods in polymer compounding, which has the three basic functions; 1. Melting and forming, 2. Devolatilizing and mixing, 3. Conducting chemical reactions. One of the classification methods of extruder is according to the type of the screw. There are three different type screw extruders – single screw, twin screw and multi screw extruders. Fig. 1.6 displays Twin-screw extruder in diagram form, which is generally used for compounding to prepare polymer blends. The twin screw can operate with the mode of non-intermeshing or intermeshing, counter-rotating or co-rotating. Moreover, the configuration of screws is variously arranged for achieving specific mixing characteristics such as forwarding or reversing to convey materials, kneading blocks and others. Those make possible to design processing specifically for compounding. For example, co-rotating operates at higher speeds under higher shear rate and has more mixing capability than counter-rotating. The aim of the extrusion is producing materials in solids, pellet or powder in the condition of high screw speeds, and used intensive mixing for manufacturing the planned final product [41].

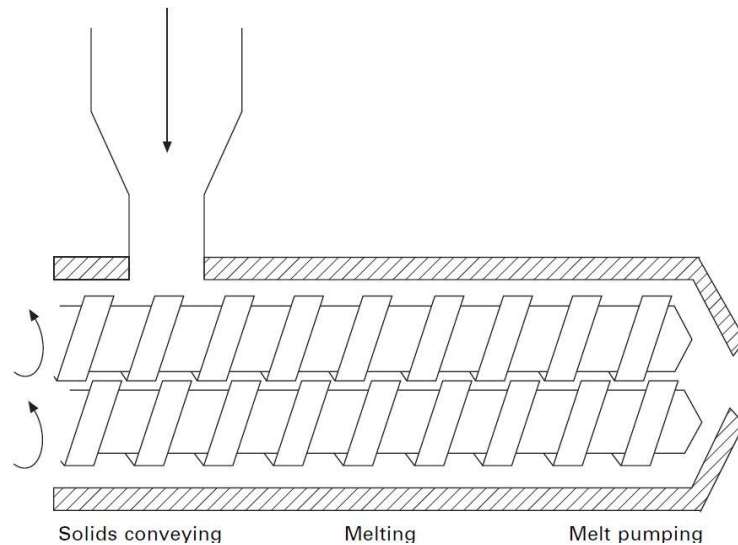


Fig. 1.6. The diagram form of twin-screw extruder [41]

1.5.1.2. Injection molding

Injection molding is most generally used for fabricating accurately equal-sized samples with high production rates. Injection molding process includes three steps – First, melted polymer flows through a piston-injection pistol system. Second, it is injected into a cold mold and packed under high pressure and arranged time. Lastly, it is cooled down to solidification. The polymer can undergo mechanical and thermal influences during this process, and the factors can influence on the final sample. The residual stress and strain, which are occurred in flow and cooling process, makes the sample being shrinkage. The mold temperature and the injection rate can be properly arranged, and cooling of quenching is carefully conducted to prevent this phenomenon [42].

1.5.2. Characterization

1.5.2.1. Tensile test

Tensile test is widely used to observe mechanical properties by measuring behavior of the materials under tension. Through this test, tensile strength, yield point, yield strength, elongation, proportional limit, modulus of elasticity and other mechanical properties are determined. These results are utilized to evaluate developed materials, to ensure quality and to predict physical reaction of material. Especially, stress-strain curve is very important graphical representation of mechanical properties of a

material.

Fig. 1.7 shows the stress-strain curve of a semi-crystalline polymer, which is the most similar model with the materials of this research. At the beginning of giving stress, elastic deformation is occurred. If the loading is removed, the material gets back to its original shape, in other words, it appears complete resilience or recovery. As the amount of stress is increase, the slop of the stress-strain curve (the strain hardening rate) is decreased until the point of ultimate tensile strength, at which necking appears. This point can be considered yield point in plastic. Beyond this point, the amount of stress for increasing additional strain is relatively decreases, and plastic deformation begins. After the neck stretches to the specific ratio, the behavior of the material turns to drawing until the fracture. Drawing process occurs when the breaking load of the microstructure is bigger than the load inducing necking after the necking process makes reinforce the microstructure [43].

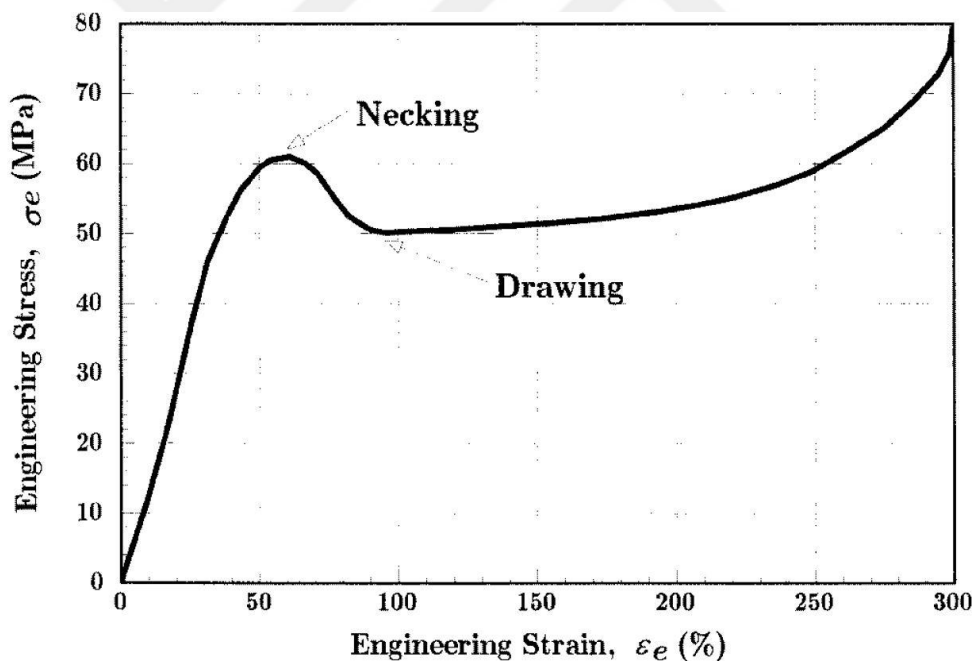


Fig 1.7. The example of the stress-strain curve of a semi-crystalline polymer [43]

The testing machines are commonly universal testers which are proceed under the condition of different tension, compression and bending, and as the outcome, stress-strain curves are acquired. Stress-strain curves are mainly analyzed to see the overall

tensile properties. There are two different type of machine; electromechanical and hydraulic machines. Electromechanical machine is operated by variable speed electric motor. Motion of crosshead give tension or compression to specimen and the speeds are changed with controlling the motor speed. This machine works in a wide range of speeds. Hydraulic machine is operated by acting piston which makes the crosshead move. This machine is cost-effective and it generates higher forces than electromechanical machines [44].

1.5.2.2. Thermal gravimetric analysis (TGA)

TGA is utilized to measure the rate of combustion and the change in the weight of a material in a controlled condition of temperature and time. The outcomes indicate the composition of materials, decomposition kinetics and make to predict thermal and oxidative stability of specimen. Weight loss can be evidence for decomposition occurred from breaking apart chemical bonds, evaporation, reduction or desorption. In the case of weight gain, it can be evidence of oxidation or absorption of materials [45]. The information provided from measurements is used improve a quality and predict a performance of a product, which make possible to better choose the material for an application [46].

The result of TGA can be affected by experimental parameter such as material type, shape and size of pan, mass, form and morphology of sample and ramp rate because TGA analysis is carried as measuring the amount of weight change as function of increasing temperature. The result can be depending on how well transfer the heat to a material. Figure 1.8 shows TGA curves and decomposition curves resulting from different condition of heating rate. The slower the heating speed, the faster the weight decreased and the sooner it was terminated. The peak point in the decomposition graph is most distinct in case of the low speed of heating.

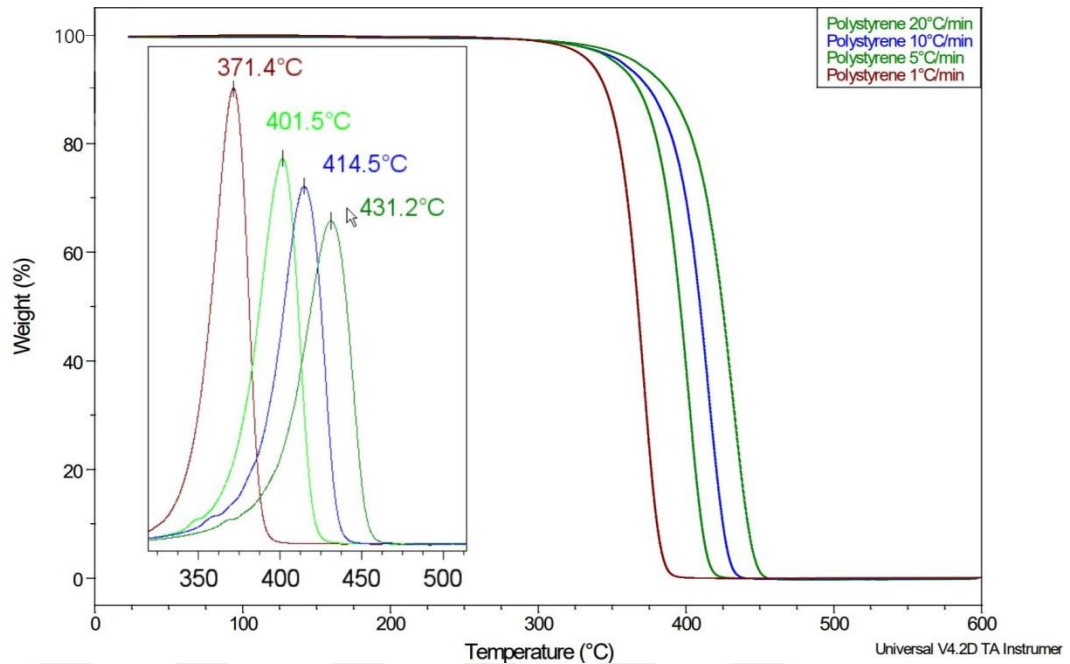


Fig. 1.8. TGA curves and decomposition curves according to the effect of heating rate [45].

1.5.2.3. Differential scanning calorimeter (DSC)

DSC is mainly used for thermal analysis. It measures the gap of heat energy between the sample and the reference by introducing heat energy simultaneously.. Maintaining identical change rate of temperature, different amount of input energy is required because the sample and the reference have different material transitions [47]. DSC records a heat quantity in the state of endothermic and exothermic process. T_m , T_g and crystallization and heat capacity are measured from the output of DSC.

Typical DSC curve of polymer is shown in Fig. 1.9. The representative three transitions are displayed during heating. The first transition point is under T_g . Mechanical properties of material change from elastic to brittle due to changes of chain mobility. The heat capacity is different based on the point of T_g , the slop is observed. Above the T_g , the chain with high mobility has enough energy to undergo crystallization with ordered arrangements, which process is the exothermic process. As the polymer releases heat to surroundings, crystallization is observed. After that, when the heat energy added more, the crystalline regions are melted which is endothermic process required of absorbing heat. The heat flow is increased for

keeping the rate constant of heating, so the curve is observed, and the area of the curve is used for calculating the latent heat. However, all polymers do not undergo three transition points during DSC analysis. The peaks of crystallization and melting are just observed for the polymer having crystal form, which means, in case of purely amorphous, a glass transition is just observed. The crystalline polymer which has also amorphous portion exhibits the three transition states.

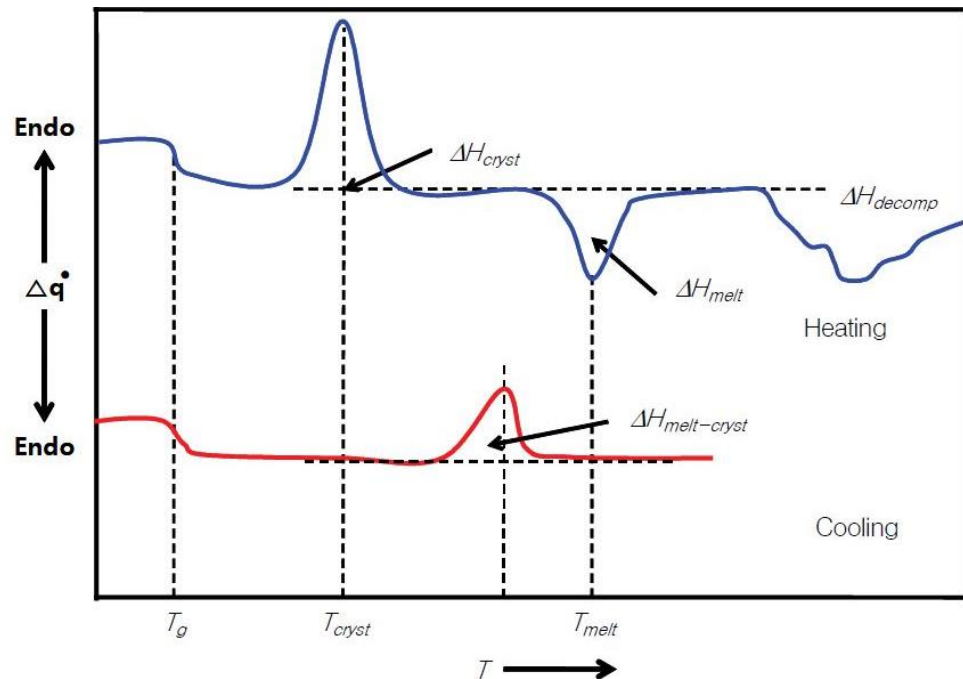


Fig. 1.9. Typical DSC curve of polymer with T_g , T_c and T_m [48]

Except for that, various analyses are possible with the behavior of change on the glass transition such as crosslinking, polymerization, plasticizers, mixtures, copolymers, etc. And, solid state transitions can be also analyzed such as eutectic points, degradation, chemical reactions and so on.

DSC is classified into heat-flux DSC and power-compensated DSC based on the operation mechanism. In the system of heat-flux, the sample is enclosed in a pan and empty pan as reference are put on the thermoelectric disk in a furnace, which transfer to the heat to two pans through thermoelectric disk. Power-compensated DSC, otherwise, two pans are placed separately in furnaces and get heat individually [49]. DSC provides understanding of materials' heat capacity and enthalpy used to

evaluate how the research goes well in view of process operating. In this respect, this technique is the most commonly used for thermal analysis in quality assurance, process control and R&D labs.

1.5.2.4. Rheometer

Rheometer is able to measure rheological properties which are a response of a complex material from an applied stress or strain [50]. Rheology is the study of flow and deformation of material depending on interrelation between deformation, force and time. The deformation relies on the materials condition, [51]. As the outcome, viscoelasticity of fluids and viscosity over a wide range of shear rates is obtained.

Techniques of rheometry are mainly divided into two. One is rotational rheometry and another is capillary rheometry. Rotational rheometer provides the viscosity-shear rate responded from a soft solid. Specimen is put between two plates (it can be other geometries like as cone and plate) and a torque applied to the top plate gives a rotational shear stress to the specimen. The outcome of strain or strain/shear rate is recorded. Rotational rheometer is used for a wide range of samples such as pastes, gels and structured liquids. Shear can be accurately controlled and applied to the very low- shear stress region. It is appropriate to study for stability and yield stress. However, it has mechanical limitations in the case of the high shear region. Capillary rheometry makes specimens extrude by means of a barrel or die under high pressure. The pressure is recorded and the viscosity is calculated. As a result, pressure-flow rate graph is obtained. Since shear rate and temperature can be well controlled, the process proceeds under a required condition. Capillary rheometers are able to apply highly force and it makes possible to study behavior of a material under the condition of much higher shear rates than rotational rheometry. A performance of high shear rate is generally conducted in lots of industrial processes.

1.5.2.5. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is used to get information about specimen including morphology, chemical composition, crystalline structure and crystal orientations. SEM magnifies the surface of specimen using a high-energy focused

beam of electrons. When SEM generates the beam and it heats the specimen, back scattered secondary electrons signal can also be detected. This process is conducted with a chamber a higher vacuum to ensure the beam focused properly and prevent interaction with particles in the air. Collected data based on the diffracted electrons signal provides an image of the surface of specimen in a selected area. The range of selected area is adjusted from roughly 1cm to 5 μ m in width. Magnification range is from 20X to roughly 50,000X for polymers.

SEM has some limitations:

1. Specimen must be solid and fit right into a microscope chamber.
2. Outgassing specimen at low pressure (such as wet samples) is not suitable for examination.
3. Electrically insulating specimen must to be coated with electrically conductive material.

SEM is generally used for applications such as evaluating of reaction interfaces, characterizing structure of specimen, measure the thickness of layered structures, characterizing surface defects, stains and residues on specimen.

1.5.2.6. Shape memory test

Shape memory test is carried into practice to measure the characterization and properties of SMP. There are few parameters to describe the properties such as shape fixity ratio (R_f), shape recovery ratio (R_r), maximum recovery stress (σ_{max}), maximum recoverable strain (ϵ_{max}) and recovery rate [39].

R_f states the percentage how properly fixed after programing the temporary shape. This is also called as shape retention ratio (Equation (1)).

$$R_f = \frac{\theta_{fixed}}{\theta_{max}} \times 100\% \quad (1)$$

R_r states the ability recovering from temporary shape to permanent shape. As SMP has a higher ratio of recovery, It indicates that SMP has the high capacity for recovering (Equation (2)).

$$R_r = \frac{\theta_{\text{fixed}} - \theta_{\text{final}}}{\theta_{\text{fixed}}} \times 100\% \quad (2)$$

These parameters are generally measured the thermal and mechanical response by dynamic mechanical analysis (DMA) [52]. The cyclic test is performed by controlling accurate stress and strain. However, in this paper, Fold-deploy shape memory test is proceed with three steps. Firstly, Samples are heated to specific temperature above T_{trans} , and they are folded to U shape by external physical forces. The angle of folded sample is called as θ_{max} . Secondly, they are cooled down to specific temperature below T_{trans} with the external forces continually. After waiting the samples being cooled down, the external forces are removed, and the angle is recorded as θ_{fixed} . For the last, the samples were heated again, and the angle is recorded as θ_{final} following the temperature under controlled condition for the research [26, 27].

2. LITERATURE REIVEW

In this chapter, the summary and explanation about biodegradable shape memory polymer, the blended SMP based on PCL and/or TPU, are covered relevant to the topic of this research. Current and complete state of knowledge is gathered from available literatures.

Biodegradable SMP is widely studied for decades, and increasingly attracting researcher as a promising topic, which is potentially applied to biomedical field. Biodegradable SMP is generally produced with polyesters [2, 14]. Karger-Kocsis and Keki [53] researched general information with regard to biodegradable polyester SMP. Among polyesters, it has been reported that the SMPs based on PCL are highly likely to be applied to biomedical applications because of the advantage of PCL [5, 6]. When PCL is used as soft phase in SMP, the temperature of recovery is possible to be adjusted around 38 °C, near the temperature of human body by selecting the molecular weight of PCL, or controlling ratio of hard and soft phase. PCL is applied to synthesize polyurethane as the soft phase [54-56]. Ping and coworkers studied SM properties of polyurethane based on PCL. They arranged the samples with different molecular weight of PCL and different composition ratio of hard-soft part. The transition temperature varies from 40 to 60°C. As the M_w increased, so did the recovery temperature. However, the ratio of hard-soft part does not show a distinct effect.

There are various ways to create biodegradable SMP using PCL, and the easiest accessible way is polymer blending. Zhang, et al. [57] prepared novel SMP blend based on SBS and PCL. The samples are arranged with different ratio of PCL from 0 to 100wt%. Two components are immiscible and still remained as immiscible state in the blended sample, which induced shape memory properties. The elastomer part has role of stretching and recovering performance, and the switch part has role of fixing performance. Chen, et al. studied the blends based peroxide and cross linked PCL

with dicumyl peroxide. As peroxide content decreases, it was observed that the degree of fixation decreases. However, the ratio of recovery is almost perfect.

The case of blends of TPU and PCL has been studied. Jing et al. recently studied the blending of TPU and PCL as SMP for applying self-knotting sutures [21]. As adjusting the weight ratios of two materials (TPU; 100, 75, 50, 25 and 0wt%), they found the best ratio having shape memory effect, which is 25% of TPU. It shows high crystallinity in the soft phase (PCL), high ratio of shape fixing (98%) and shape recovery (90%). Ajili, Ebrahimi and Soleimani also investigated shape memory properties of PU and PCL blend [22]. PU copolymer prepared with PCL diol, is melt-blended (in the ratio of 20, 30, 40 and 50wt%) with PCL. The composition is influence on the melting behavior and shape memory properties. The 70(PU)/30(PCL) blends shows shape recovery around body temperature.

Additional additives to blends are also being studied to improve the mechanical properties of the sample. Herein, TPU/PCL blends with other additives are covered. Mosleh and coworkers prepare TPU/PCL blends with the ratio of 70/30, and various content of nano-magnetite powder is added from 0 to 5wt% [58]. Nano-magnetite enhances the crystallinity of soft phase and shape memory behavior. However, the extra amount of nano-magnetite slightly reduces the shape recovery ratio.

Dogan and coworkers add diisocyanate (compatibilizer) to PLA/TPU blends to enhance miscibility [24]. And, Harada et al. [25] also studied the increasing the compatibility of poly(lactic acid)/Poly(butylene succinate) blend by using isocyanate in the reactive processing. Diisocyanates as compatibilizer potentially interacts with $-OH$ of TPU and $-OH/-COOH$ of PCL during compounding.

In the above case, compatibilizer had a positive effect on Bland, and therefore how PDI affect bland is going to be studied as following chapters.

3. EXPERIMENTAL

3.1 Materials

The materials that are used for this research are specified in Table 3.1 down below.

Table 3.1. Used materials, supplier and characters

Materials	Supplier	Characters
Thermoplastic polyurethane (TPU)	Lubrizol, Germany	Shore hardness: 90A Density : 1.25 g/cm ³ Tensile strength : 55 MPa Elongation: 590%
Poly(ϵ -caprolactone) (PCL)	ALDRICH	M_w ~14,000 M_n ~10,000 T_g : - 60°C Melting Temperature: 60°C Tensile Stress: 20.7 – 34.5 MPa Young's Modulus: 0.21 – 0.34 MPa Elongation: 300 – 500 % Degradation (months) \geq 24
1,4-Phenylene diisocyanate (PDI)	Sigma-Aldrich, Germany	Melting temperature: 96°C

3.2. Blends Preparation

Samples are prepared with different ratios of TPU/PCL/PDI blend. TPU content was arranged as 50, 70, 80, 90, 100wt%, respectively. The PDI content was 0, 1, 2, 3wt% (see Table 3.2). These blends were compounded by using a twin-screw compounder (Xplore Microcompounder MC15, The Netherlands) at 200°C. The speed of the screw was 100 rpm and mixing time was 3 min under Argon gas to prevent thermo-oxidative degradation. The molten compound was then transferred to injection molding device (Xplore injection IM 12, The Netherlands). The mold temperature was 25°C and pressure of injection was 8 bars.

Table. 3.2. Blending ratio of the samples

Name of the sample	TPU(%)	PCL(%)	PDI(%)
TPU100	100	0	0
PCL10 PDI0	90	10	0
PCL10 PDI1			1
PCL10 PDI2			2
PCL10 PDI3			3
PCL20 PDI0	80	20	0
PCL20 PDI1			1
PCL20 PDI2			2
PCL20 PDI3			3
PCL30 PDI0	70	30	0
PCL30 PDI1			1
PCL30 PDI2			2
PCL30 PDI3			3
PCL50 PDI0	50	50	0
PCL50 PDI1			1
PCL50 PDI2			2
PCL50 PDI3			3

3.3. Characterization

1. Tensile test

Tensile test was conducted on an Instron (Model 3345) universal testing machine at a room temperature according to ISO 527. At least five samples were analyzed with 5kN load cell and 50mm/min cross-head speed.

2. Thermal gravimetric analysis (TGA)

TGA was conducted on TA Q50 model instrument under nitrogen atmosphere with a 20°C/min flow rate. The range of scanning was 25 to 600°C at heating rate of 20°C/min.

3. Differential scanning calorimeter (DSC)

DSC analysis was done with Mettler Toledo DSC-1 Star system under nitrogen atmosphere. Experiment was conducted from 25°C to 200°C at a scan rate of 10°C/min.

4. Rheological test

Rheological measurements were carried out with a modular compact rheometer (MCR 102, Anton Paar). Samples are tested using parallel measuring plate (D: 25 mm) in the linear viscoelastic region at 200°C. The gap between samples and the plate was 1 mm. Frequency range was from 0.1 to 628 rad/s and 19 points of shear rheology measurement was recorded under the condition of strain 1%.

5. Scanning electron microscopy (SEM)

Morphological properties of the samples were observed by SEM using Quanta 400F field emission model. Observations were made on impact fracture surfaces of the samples. The samples were gold coated before observations to prevent arcing.

6. Shape memory test - Fold-deploy shape memory test

Shape memory properties were evaluated by means of 'fold-deploy shape memory

test' with three steps [26, 27]. Samples were prepared at the size of 2 mm x 10 mm x 80 mm. The general process of the test is shown as the schematic diagram (Fig. 3.1). First, samples were heated to 65°C above its transition temperature, T_{trans} for 2 minutes, and those were folded from the both end-points by external force. The bending angles were down as θ_{max} . Then it was cooled down to 0°C for 2 minutes by applying a constant external force, and then, those are moved to room temperature and waited for 3 minutes without forcing. The shape was slightly recovered and the bending angles of the time were down as θ_{fixed} (Fig. 3.2). Lastly, those are reheated in three different temperatures of water, such as 40°C, 50°C and 65°C for 2 minutes. When the samples completed the recovery of the shape, the bending angles are recorded as θ_{final} (Fig. 3.3). Shape fixity ratio and shape recovery ratio was calculated with results of the test based on the equation below (Equation(1), (2)). Shape fixity ratio is the criterion of the ability of fixation to the temporary shape and shape recovery ratio is also the criterion of the ability of the recovery to the permanent shape.

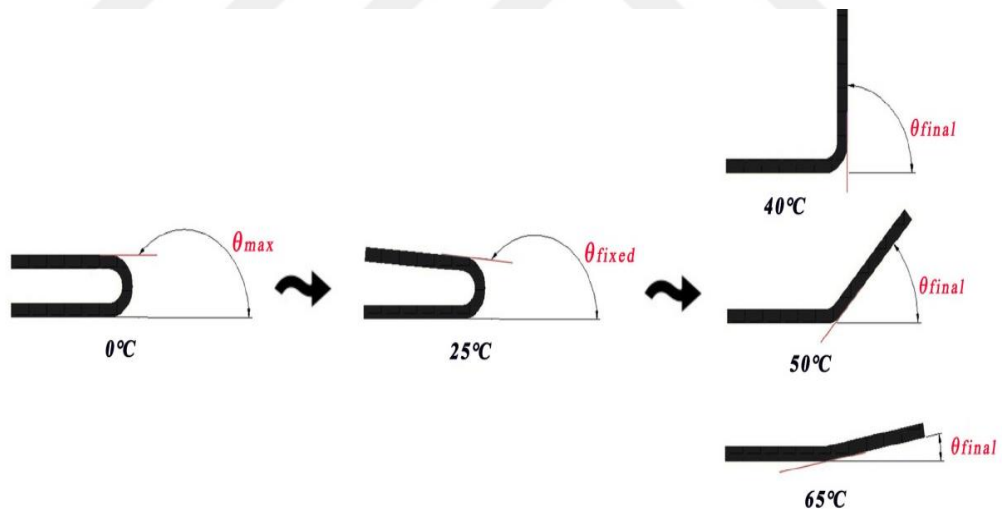


Fig. 3.1. Schematic diagram of the fold- deploy shape memory test

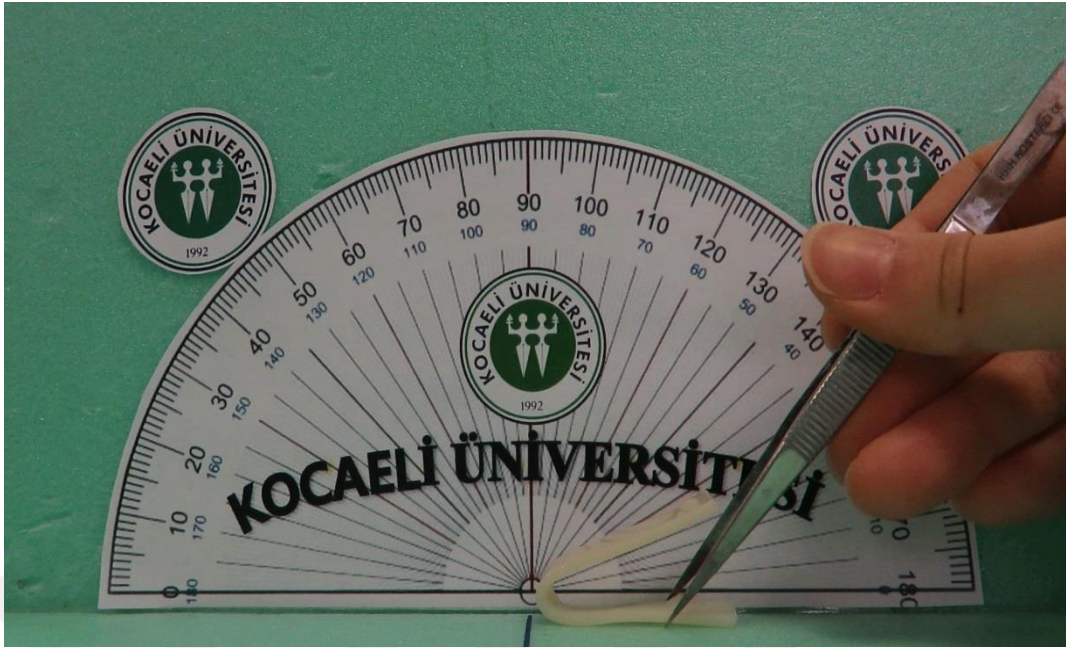


Fig. 3.2. The measuring the angle of fixation (θ_{fixed}) after waiting the samples being cooled down at the room temperature

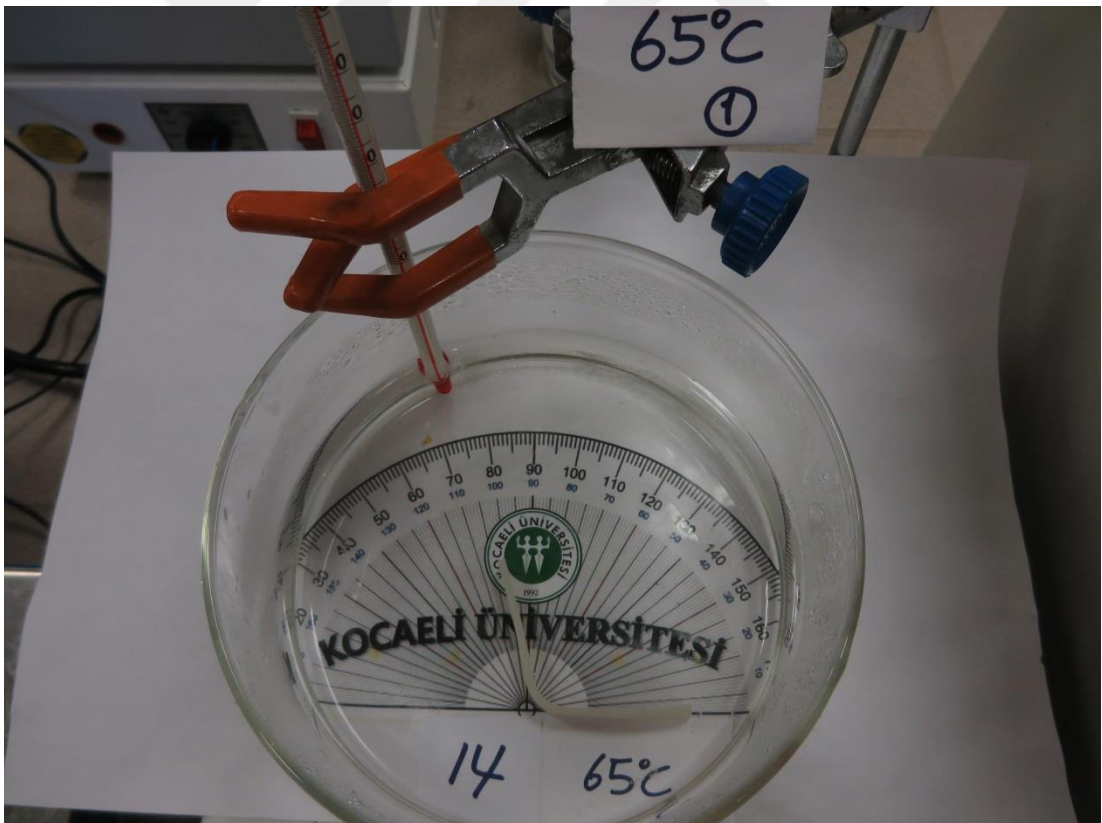


Fig. 3.3. The measuring the angle of fixation (θ_{final}) after waiting the sample being full recovered at the test temperature.

4. RESULTS AND DISCUSSION

4.1. Mechanical Properties

Mechanical properties were investigated by tensile test. Fig.4.4 shows the stress-strain curves of TPU/PCL blends with respect to composition. Pure TPU showed elastomeric behavior with a very low yield point but excessive strain hardening. Both 10 and 20 PCL blends tend to have elastomeric behavior similar to pure TPU. As the content of the PCL increased, young's modulus increases. The decreasing order of modulus is such that $PCL50 > PCL30 > PCL20 > PCL10 > TPU100$. Contrarily, as the content of the PCL increased tensile strength decreases. Unexpected outcome is that PCL/TPU blends record higher elongation than pure TPU, except for the PCL 50 sample. This can be attributed to the compatibility of the PCL with TPU that may result in a plasticization. In addition, the crystallinity of PCL may influence the tensile strength [59, 60]. The modulus and tensile strength may be affected by the structure of crystalline phase with a strong chance.

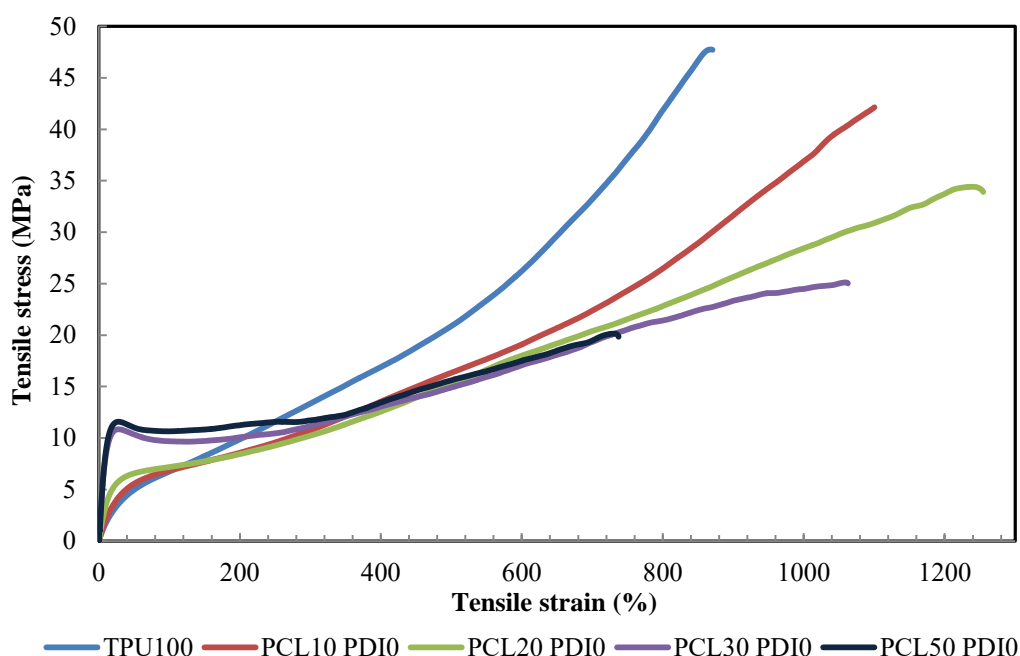


Fig. 4.1. Stress-strain curves of TPU/PCL blends without PDI

The effect of PDI on the mechanical properties of the blends can be observed through Fig. 4.2 and 4.3. In the case of PCL30, As PDI is added to the blends, tensile strength and elongation value is increased, but modulus decreased (Fig. 4.2). The samples including 50% of PCL have shown similar tendency with PCL30. However, the modulus does not show a big distinction between them (Fig. 4.3). PDI has a role to increase tensile strength of the blends and elongation ratio over all. When added more than 2% of PDI, the increase in elongation rather decreased. When PDI is added to the PLA/TPU [24], the elongation ratio at break also increased. This can be explained by the interactions between the PCL and TPU with PDI. As a result of these reactions, PCL-co-TPU linear or branched structures can be formed. The copolymers improve the interfacial adhesion and result in increasing of mechanical properties.

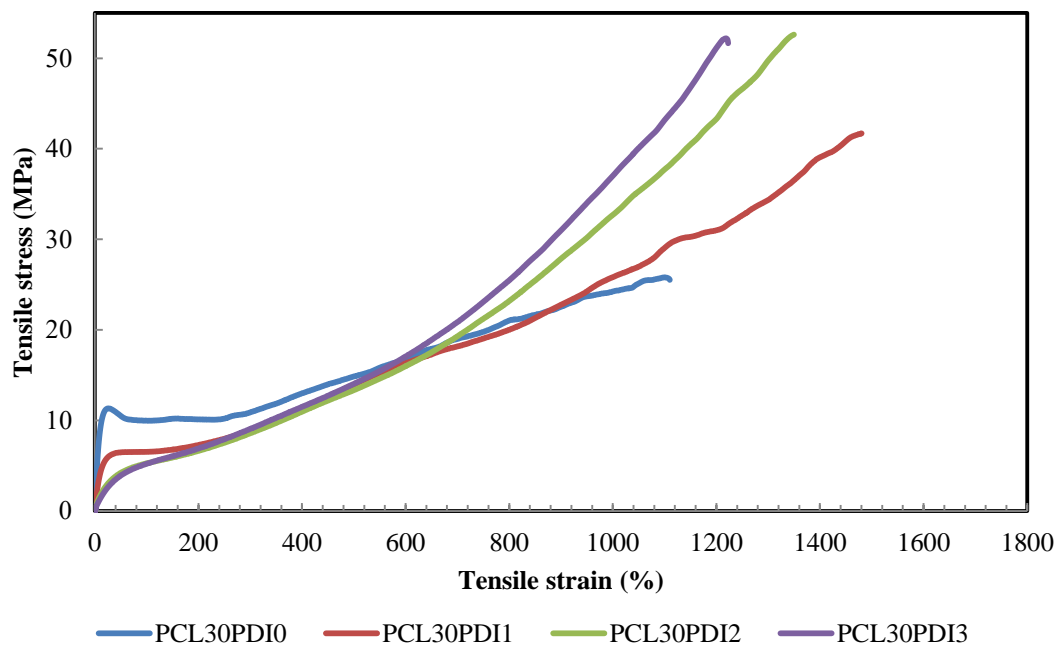


Fig. 4.2. Stress-strain curves of TPU70/PCL30 blends depending on the percent of PDI

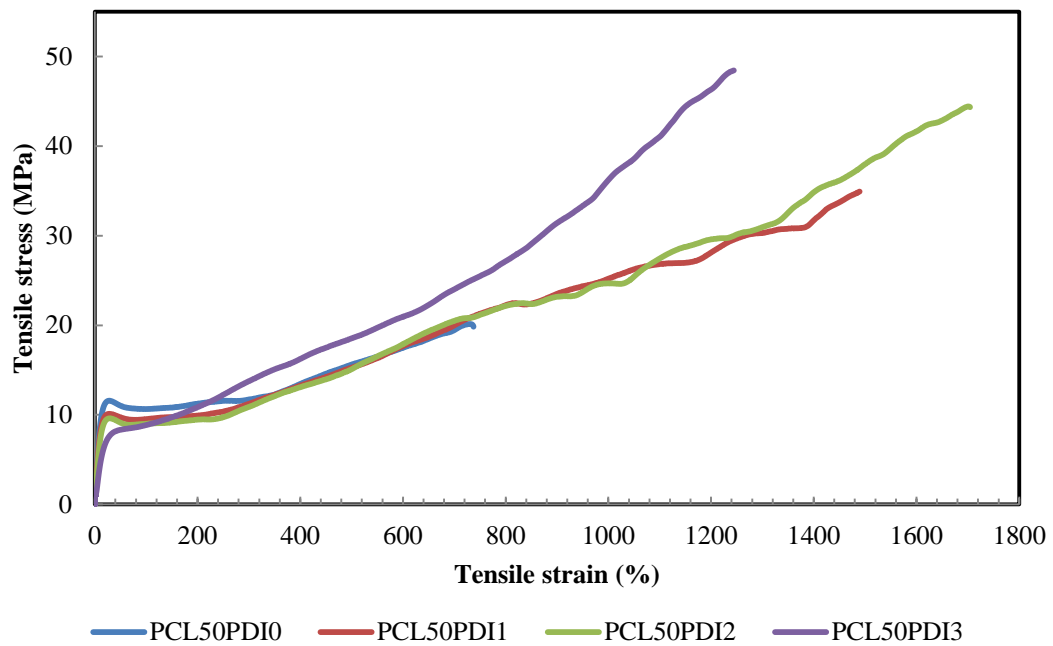


Fig. 4.3. Stress-strain curves of TPU50/PCL50 blends depending on the percent of PDI

The overall results of elongation at break and tensile strength is expressed in Fig 4.4 and 4.5, respectively. The existence of PCL below 20% can make blends having lower elongation at break, but PCL content over than 30% makes it higher. PDI much more affects the tensile strain than PCL. The 30PCL and 50PCL blends tend to get higher in elongation at break with respect to the PDI content. This tendency is strongly expressed in PCL50 type blends. This is possibly due to the formation of softer and branched TPU-co-PCL copolymers, which can possibly enhance the flexibility of the blend. In addition, an increase in hard segment content leads to an increase in yield stress, while an increase in hard segment content also leads to a decrease in strain at the yield point. The accompanying stress depends on crystallinity and lamellar thickness [59].

The influence of PDI on tensile strength is depicted previous paragraph already, PDI can dramatically impact on the blends with high PCL contended samples such as 30 and 50 PCL.

The shape memory properties are highly related with the mechanical properties. A high modulus of glassy states provides materials having a high fixing ratio after programming of the blends. A high modulus of elastic states provides materials

having high recovery ratio. On the other hands, a low stiffness makes materials hard to recover, and results in recovering with a low recovery ratio [2]. According to this, the results of shape memory properties of this study show the tendency in accordance with it.

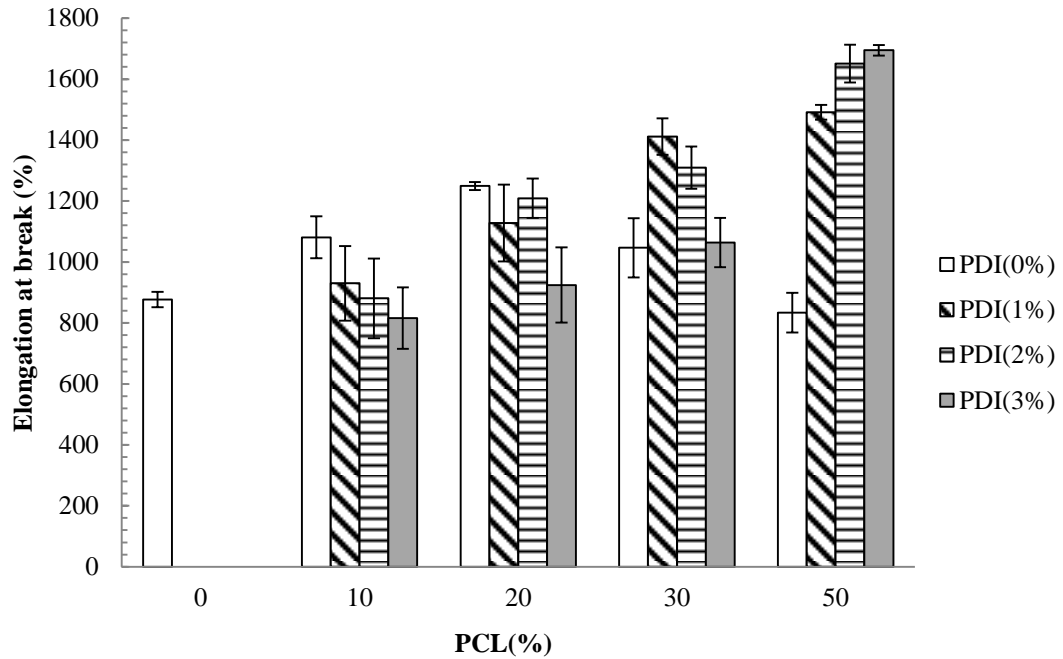


Fig. 4.4. Elongation at break values with respect to PDI content for TPU/PCL blends

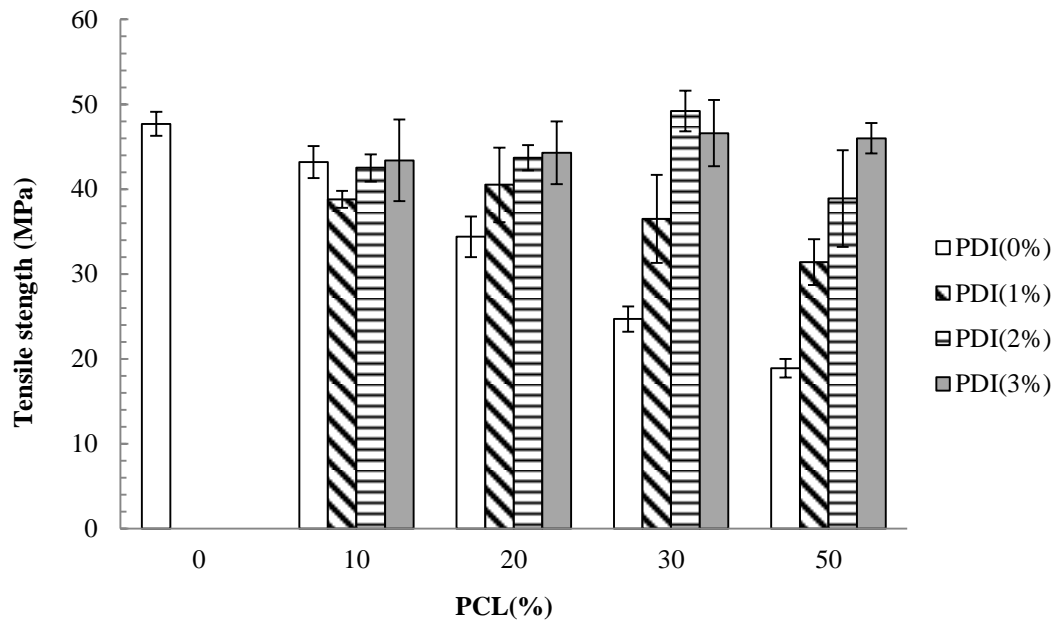


Fig. 4.5. Tensile strength at break with respect to PDI content for TPU/PCL blends

4.2. Thermal Properties

Thermal properties are observed by means of DSC and TGA. The results of DSC are shown in Fig. 4.6-8. Fig. 4.6 provides the description of the thermal responses from pure TPU, PCL and their blends having different compositions. DSC is conducted under the condition of 10°C/min increasing rate from 25 to 200°C. As specified in the thermograms, the melting point gets lower with increasing of PCL contents. Pure PCL indicates T_m of 70.3°C. Samples of PCL50, 30 and 20 indicate 57.5°C, 55.0°C, 52.9°C as T_m , respectively. Pure TPU and 10 percent of PCL contented samples are quiet smooth without peak point throughout the test, which means that their crystallinity is very low and they are mostly amorphous. This tendency is also shown in the study of Ajili and Ebrahimi [61]. In comparison between pure PCL and TPU/PCL blends, T_m decreases around up to 20 degrees Celsius and the region of melting is broader. From the outcome, it was certified that the miscibility between PCL and TPU are evident by showing a decrease in T_c and T_m . In this study, the PCL was affected by the presence of TPU. When two materials have high miscibility, the interaction is occurred and it can slow down the rate of melting. The decreased chain mobility can be another factor to affect the rate of melting as well. In other words, decreasing melting point of blends means that the blend has a degree of miscibility.

T_c of PCL is very important factor, which determines the temperature of shape transition of the blends. The T_c is fixed depending on the ratio of micro-phase separation between hard segment (HS) and soft segment (SS). Except for the degree of separation, M_w of PCL, type of HS and molar ratio of HS and SS can influence on the T_c of PCL [62].

In order to see the effects of PDI on the melting behavior of the blends, 30 PCL and 50 PCL blends were investigated (Figure 4.7 and 4.8). It is seen from 30 PCL blends that the melting point shifted to lower temperature as the PDI content increases. This is possibly due to the formation of TPU-co-PCL structures having limited ability to form perfect crystals. Similar to that a gradual decrease also observed in 50 PCL system. Phenomenon of decreased T_m can be correlated with structural change such as the increased poly-dispersity, or the formation of branching.

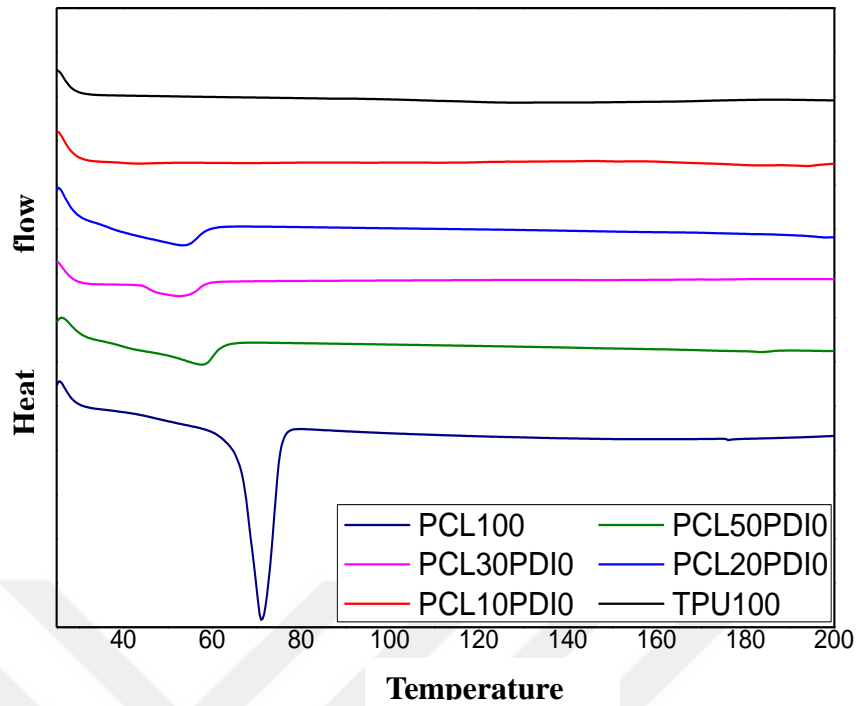


Fig. 4.6. DSC thermogram of samples depending on the PCL/TPU ratio

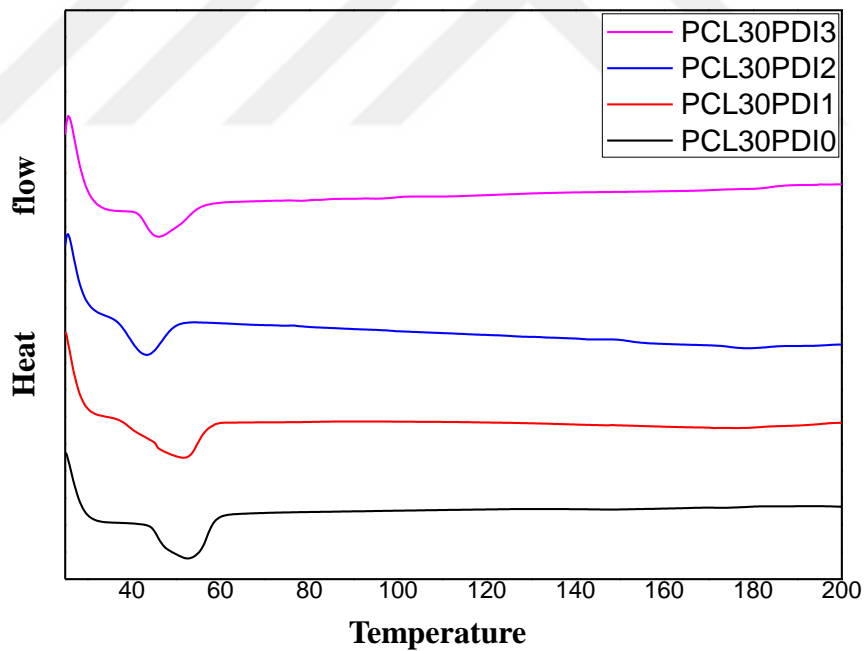


Fig. 4.7. DSC thermogram of PCL30 samples with different ratio of PDI

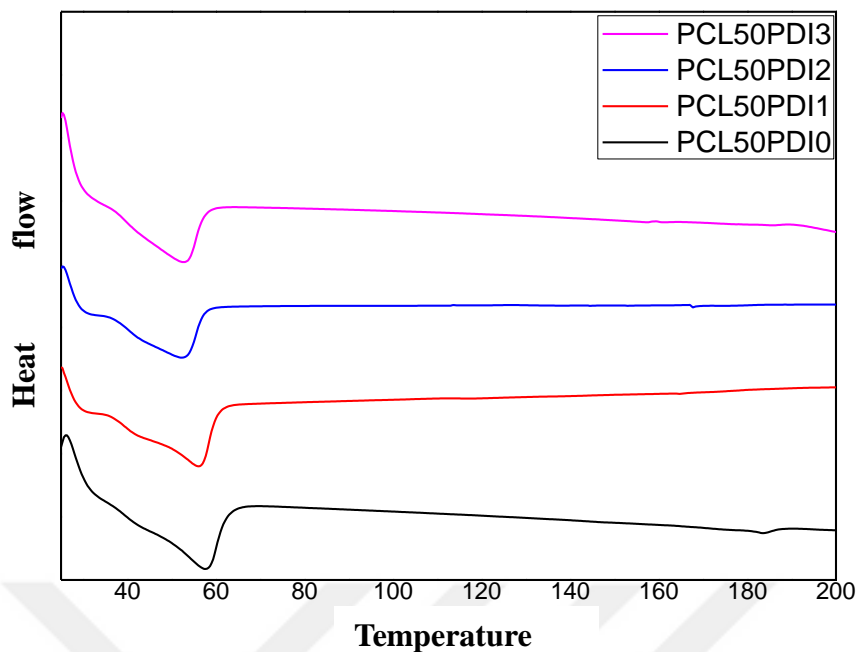


Fig. 4.8. DSC thermogram of PCL50 samples with different ratio of PDI

TGA analysis is conducted to study thermal stability of blends. The change in mass is evaluated up to 600°C upon heating. The TGA curves of blends with different ratio of TPU/PCL are showed in (Fig. 4.9).

The existence of PCL makes the samples thermally stable. PCL50 sample yields the highest stability. The stability of materials can be also evaluated with the highest decomposition temperature. Temperatures at the highest degradation peak of the samples are represented in Table 4.1. It is also seen that PCL50 samples have highest temperatures compare to other samples. TPU starts to be degraded at lower temperatures relative to PCL. Carbon dioxide was found to be the most abundant product during the first step of degradation in nitrogen for both polymers, indicating the scission of the urethane bond. For the second degradation stage in nitrogen a much more complex mixture of products was identified, most probably originating from the polyol-segment [63]. On the other hand, PCL degrades relatively at higher stages. The first degradation process implies a statistical rupture of the polyester chains via ester pyrolysis reaction. The produced gases are H₂O, CO₂, and 5-hexenoic acid. The second step leads to the formation of caprolactone (cyclic monomer) as result of an unzipping depolymerization process [64].

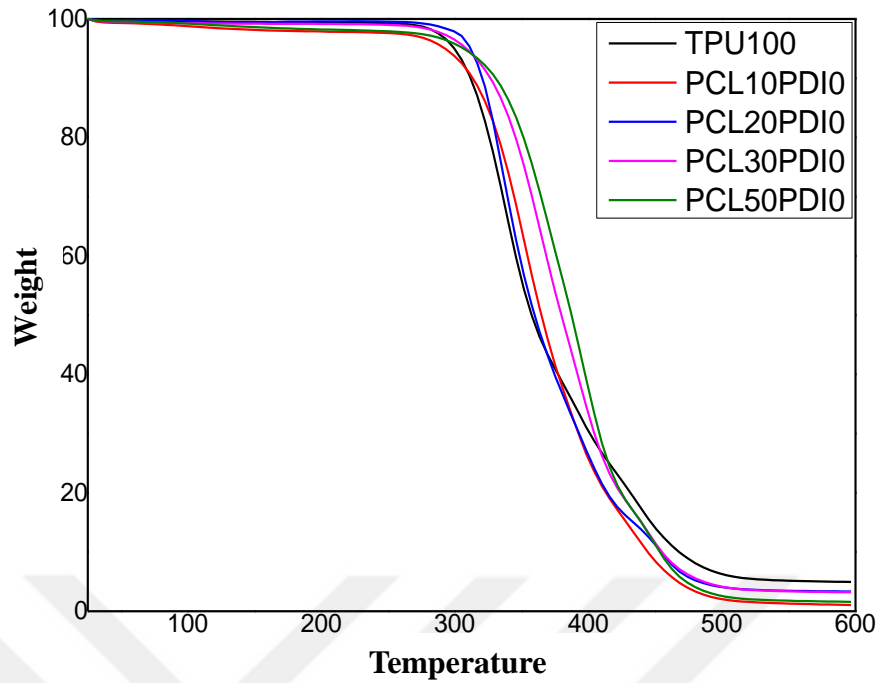


Fig. 4.9. TGA thermogram of samples depending on the PCL/TPU ratio

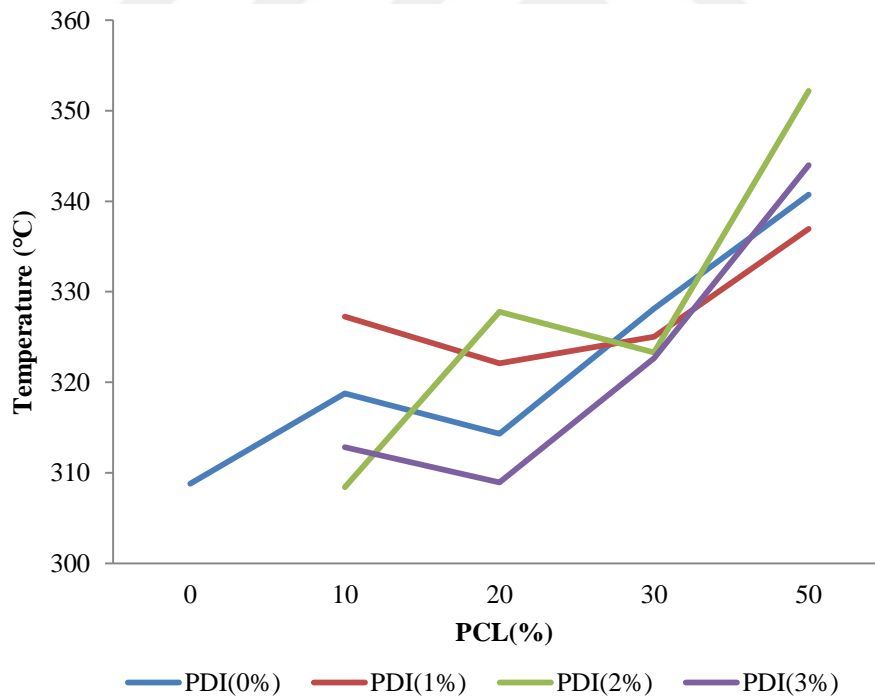


Fig. 4.10. The onset point of decomposition of the samples

Table 4.1. The temperature at the highest degradation peak of the samples

	PDI0	PDI1	PDI2	PDI3
TPU100	338.3	-	-	-
PCL10	352.1	356.9	338.7	353.8
PCL20	353.8	357.6	361.4	331.6
PCL30	365.5	363.1	361.8	361.4
PCL50	396.2	394.9	397.0	396.2

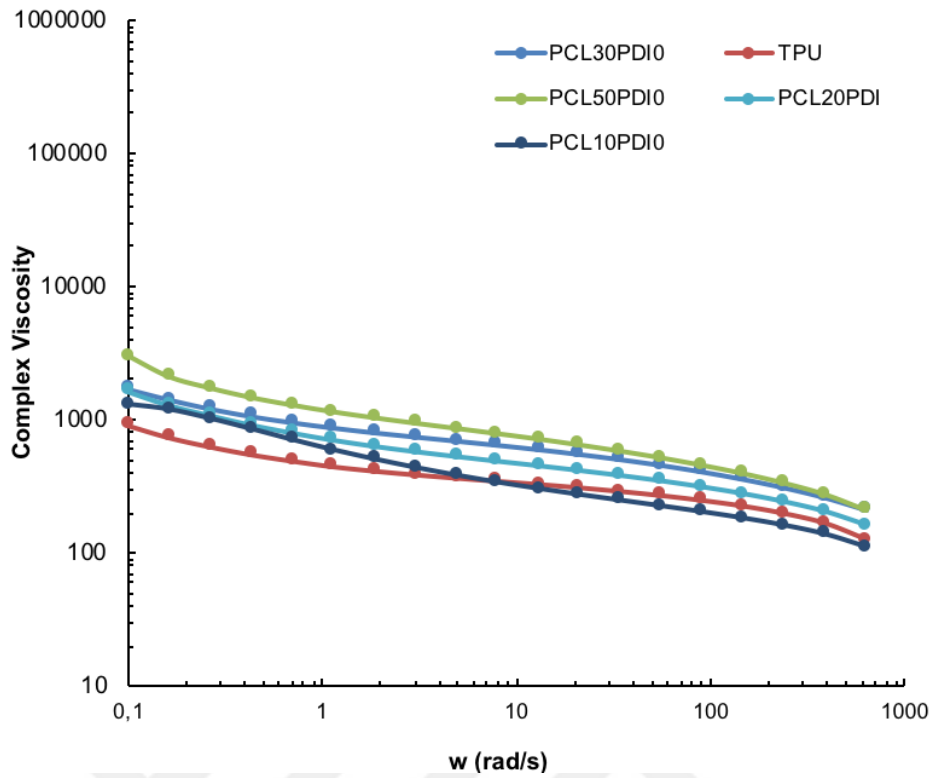
Table 4.2. The chart of onset and endset temperature

PCL(%)	PDI(%)	Onset(°C)	Endset(°C)
0	0	308.8	394.2
10	0	318.8	410.1
	1	327.3	439.8
	2	308.4	404.3
	3	312.8	382.5
20	0	314.3	395.1
	1	322.1	432.5
	2	327.8	439.1
	3	308.9	405.3
30	0	328.1	425.3
	1	325.0	425.3
	2	323.3	430.7
	3	322.7	429.1
50	0	340.7	434.4
	1	336.9	433.2
	2	352.2	428.5
	3	344.0	429.0

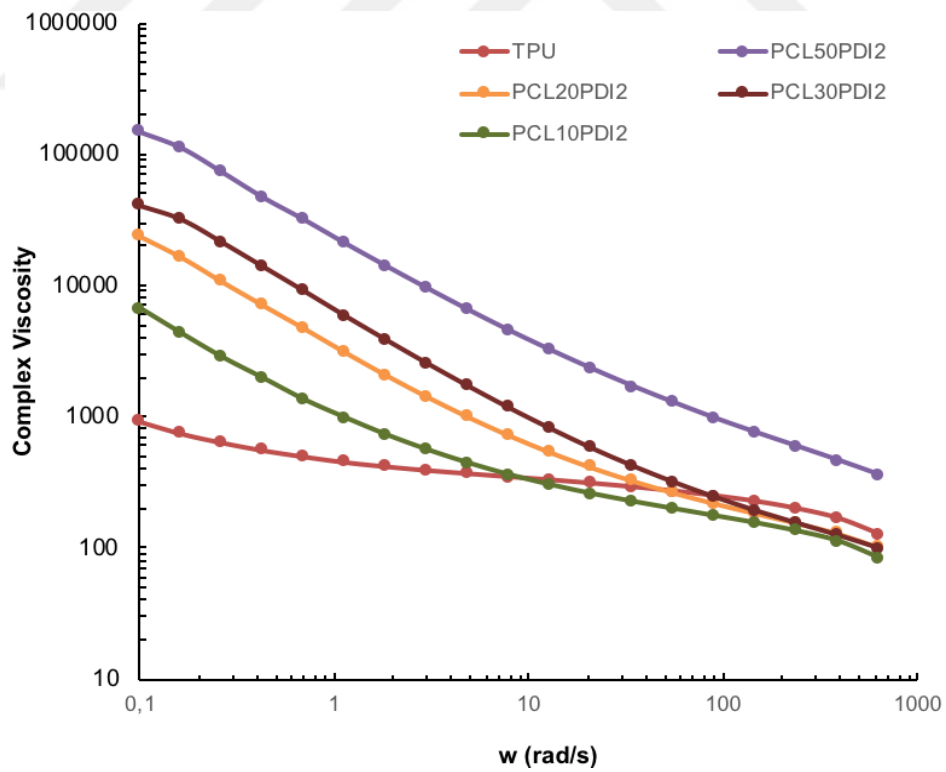
While shape recovery is occurred, the temperature should not over the onset temperature of decomposition. TGA analysis determines the critical point during the process of decomposition [34]. The onset and end-set temperatures are represented in Table 4.2, and the tendency of onset temperature depending on the composition of blends, can be seen in Fig. 4.10. The range of onset temperature is over 300°C in this study. Generally, it shows the tendency of increasing on the onset temperatures as increasing of PCL ratio. The effect of PDI ratio on the decomposition temperatures is not significant.

4.3. Rheological Properties

Fig. 4.11 represents the variation of complex viscosity with respect to angular frequency for PCL/TPU blends with/without PDI. It is seen from Figure 4.11 – (a) that the neat TPU depicts the lowest complex viscosity with a linear behavior in the frequency range. All the blends exhibited linear behavior at low frequency plateau, however due to shear-thinning, all incompatibilized blends depict a slight decrease in the melt viscosity at high frequency region. The increasing content of PCL in TPU resulted in an increase in the complex viscosity of the blends through-out the whole frequency range. This is due to formation of H-bonding between TPU chains and PCL chains. The formation of this new interaction restricted the flow of the TPU chains. Incorporation of 2 wt % PDI to the incompatibilized PCL/TPU blends caused pronounced effect on both the magnitude and the frequency dependence of the complex viscosity. It is observed that the addition of PDI remarkably increases the complex viscosity of the polymer blends. A maximum increment of one order of magnitude is reached at the lowest frequencies. Additionally, shear thinning becomes more prominent in the compatibilized blends suggesting dramatic changes in the polymer blend relaxation time. This may be caused by both increment of molecular weight and possible formation of branched structure [25].



(a)



(b)

Fig. 4.11. The variation of complex viscosity with respect to angular frequency (a) PCL/TPU blends without PDI, (b) PCL TPU blends with PDI

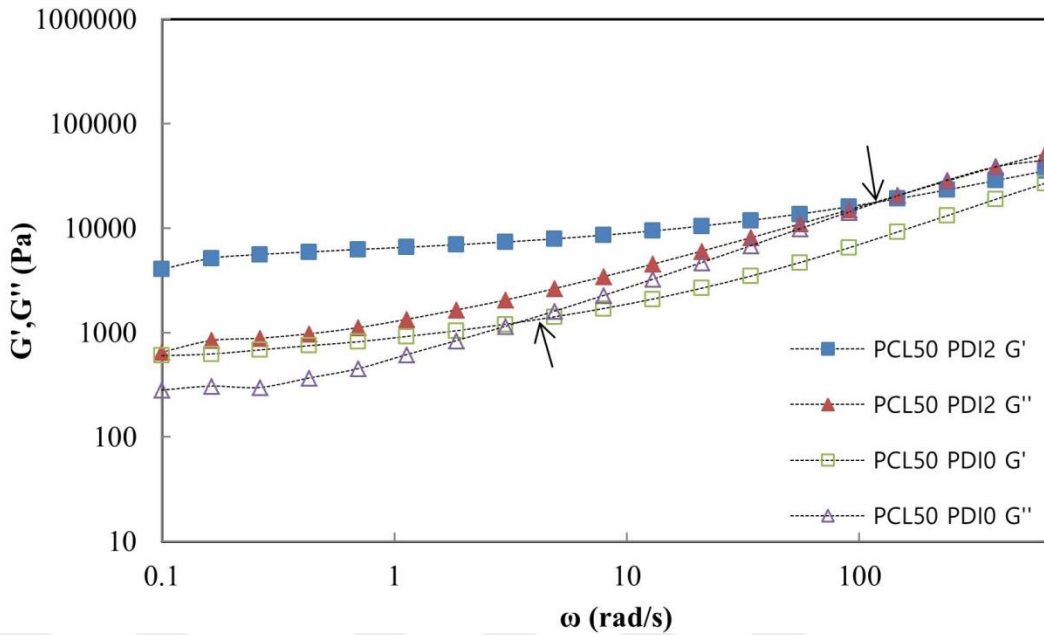


Fig. 4.12. Storage (G') and loss modulus(G'') to frequency of the PCL 50 samples (with 2% of PDI and without PDI)

Figure 4.12 shows storage and loss modulus to frequency for PCL 50 samples with and without PDI. The sample with PDI shows higher storage and loss modulus in comparison with the sample without PDI at lower and intermediate frequency. It causes that the copolymer forms make stable the interface as reducing the interfacial tension, and as follows, interfacial viscosity and adhesion are enhanced [24]. The noticeable point in this result is that both two samples exhibit the G'/G'' cross-over point. The relaxation of the sample without PDI stopped earlier than the one with PDI, which reasons seem to the increase in molecular weight as forming extension reactions and branched structure.

The research of Dogan et al [24] suggested similar effect of PDI in the blends of TPU and PLA in contrast with this research. PDI acts as a compatilizer in the blend. The value of complex viscosity is remarkably increased, and the behavior of the blends clearly becomes to shear thinning by the role of PDI. They analyzed that the increase of complex viscosity with adding PDI results from both chain extension (branched structure) and increase in molecular weight. PDI functions as extender and makes connect TPU to PLA and results in forming linear and branch structures. The storage and loss modulus are also increased, and crossing point is appeared with adding PDI. They have supposed that the reasons of these outcomes are from both an increase in

molecular weight and a formation of branch chain resulting from the react with PDI. The crossover point of G' and G'' is occurred by the reason of relaxation in the branched structure and increase of poly-dispersity index.

4.4. Morphological Properties

It is well known that the mechanical properties of blends are strongly dependent on their morphology and the control of the morphology is of vital importance for the final properties of the product [65]. SEM images on cryo-fractured surfaces of the samples are shown in Fig. 4.13-15. As a general saying, all results displayed smooth surfaces. This indicates that TPU and PCL show good miscibility and tend to form homogeneous mixtures [21]. Despite the behavior of TPU/PCL system is ductile at room temperature, the surfaces represent brittle structure with large deep cracks because of the cryo-fracturing.

The representative blends of PCL20 and PCL50 did not exhibit any phase separation at micrometer level. In larger magnifications (Fig. 4.14 and 4.15), a fibrillar structure formation was observed in the fracture surface. The density of this fibrillar formation got higher as the PCL and PDI content increased. The phenomena can be associated with the increasing molecular weight and branching with increasing PCL and PDI content, which results in the formation of more viscous dispersed phase that may form fibrils.

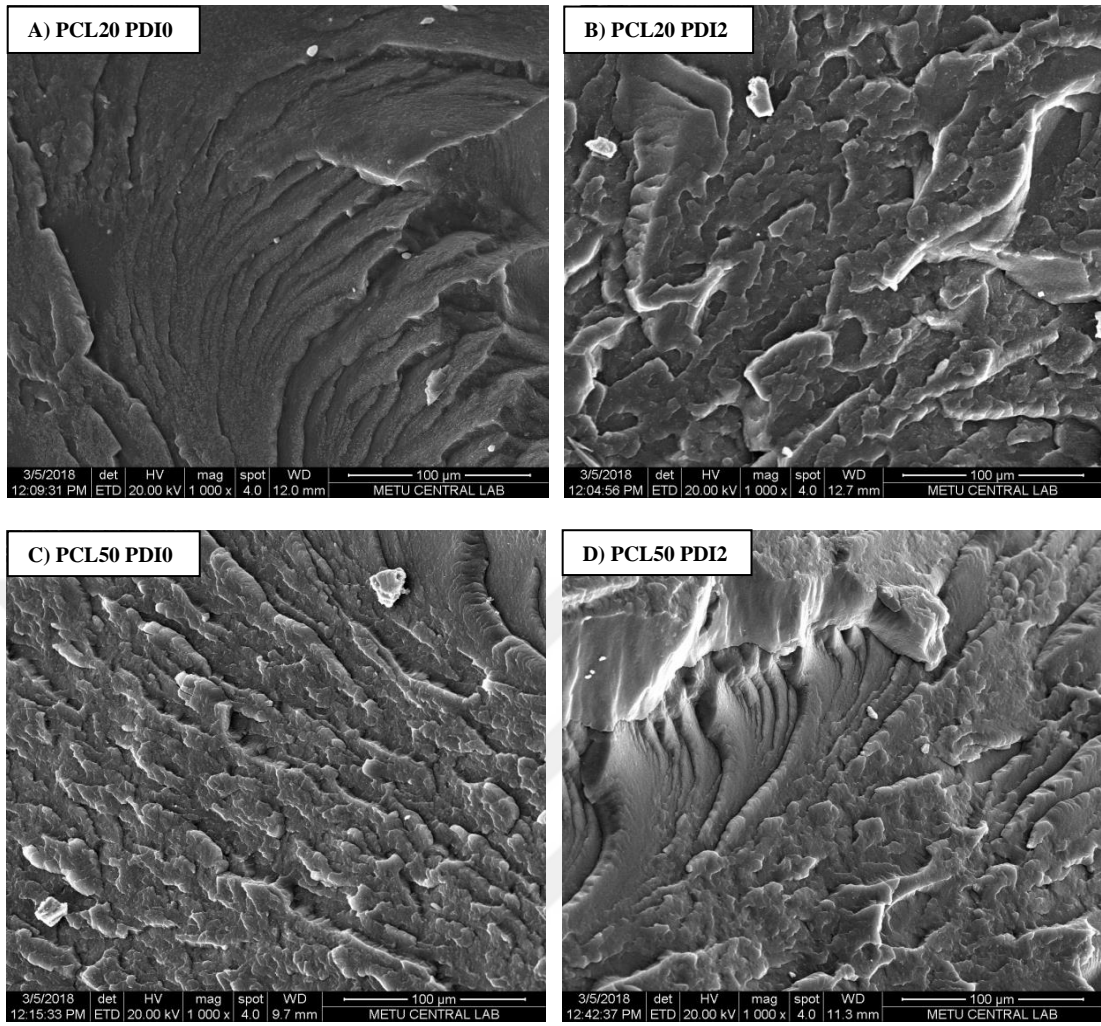


Fig. 4.13. SEM results on the cryo-fractured surfaces of samples (x1000)

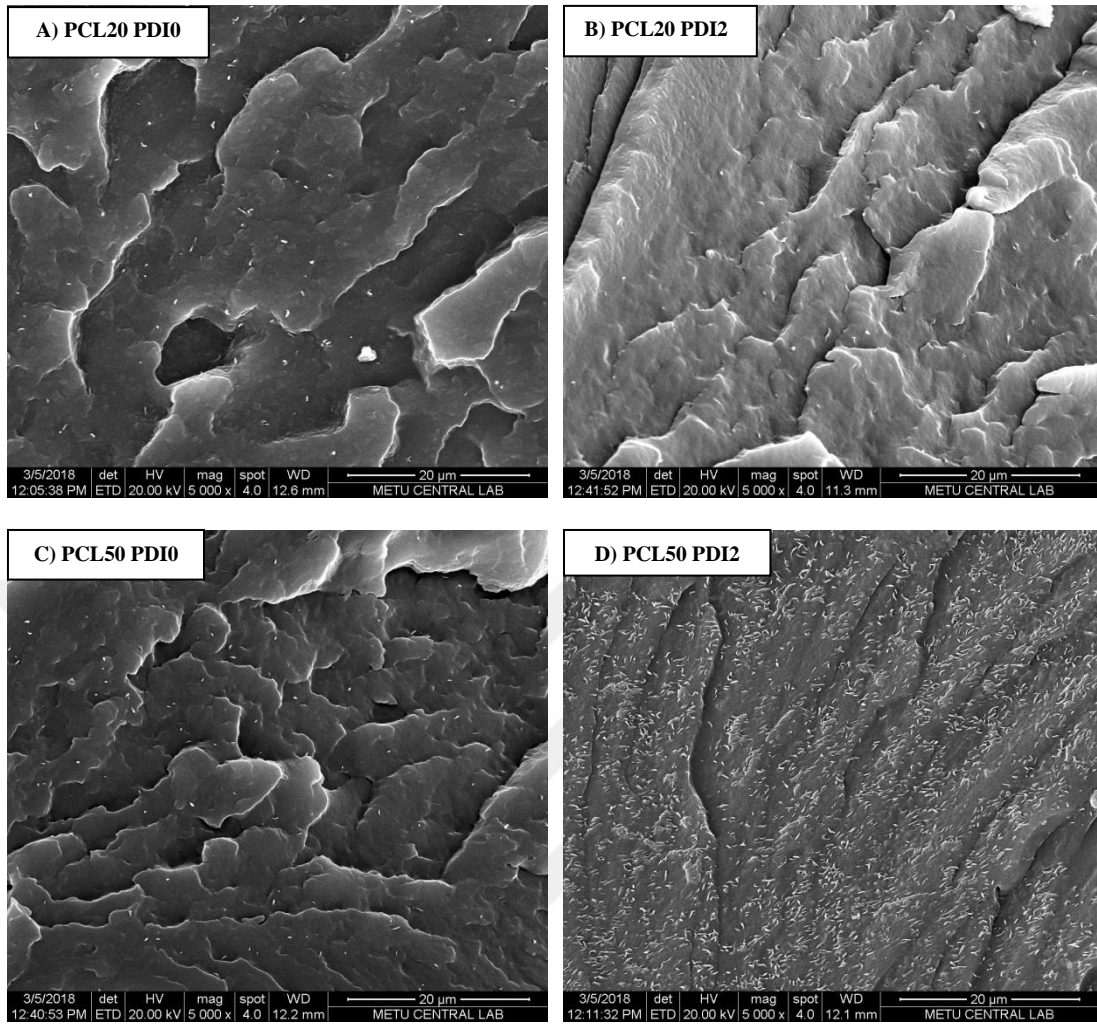


Fig. 4.14. SEM results on the cryo-fractured surfaces of samples (x5000)

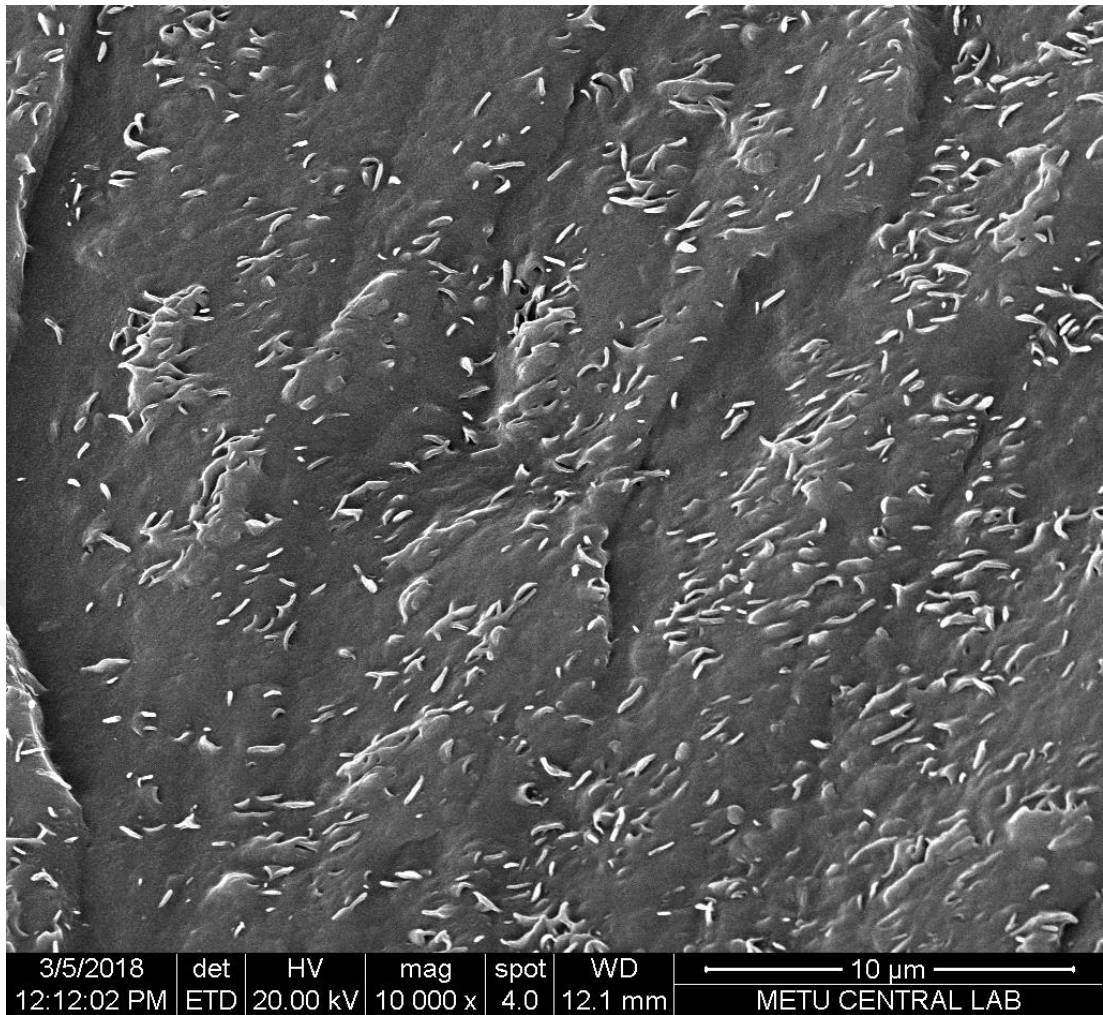


Fig. 4.15. Magnified SEM images on the cryo-fractured surfaces of PCL50PDI2 (x10000)

4.5. Shape Memory Properties

Shape memory properties are evaluated with ‘fold-deploy shape memory test’ (Fig 4.16). Based on the data from the test, shape fixity ratio (R_f) and shape recovery ratio (R_r) are calculated, and those are drawn the bar graph of R_f (Figure 4.17) and R_r (Figure 4.18) under the different condition of temperature, respectively.

In the PCL/TPU blends, the elastic TPU functions as the permanent phase contributing the performance of shape recovery, and the semi-crystalline PCL functions as reversible phase (switch segments) contributing the performance of shape fixing because it is influenced by the external heat

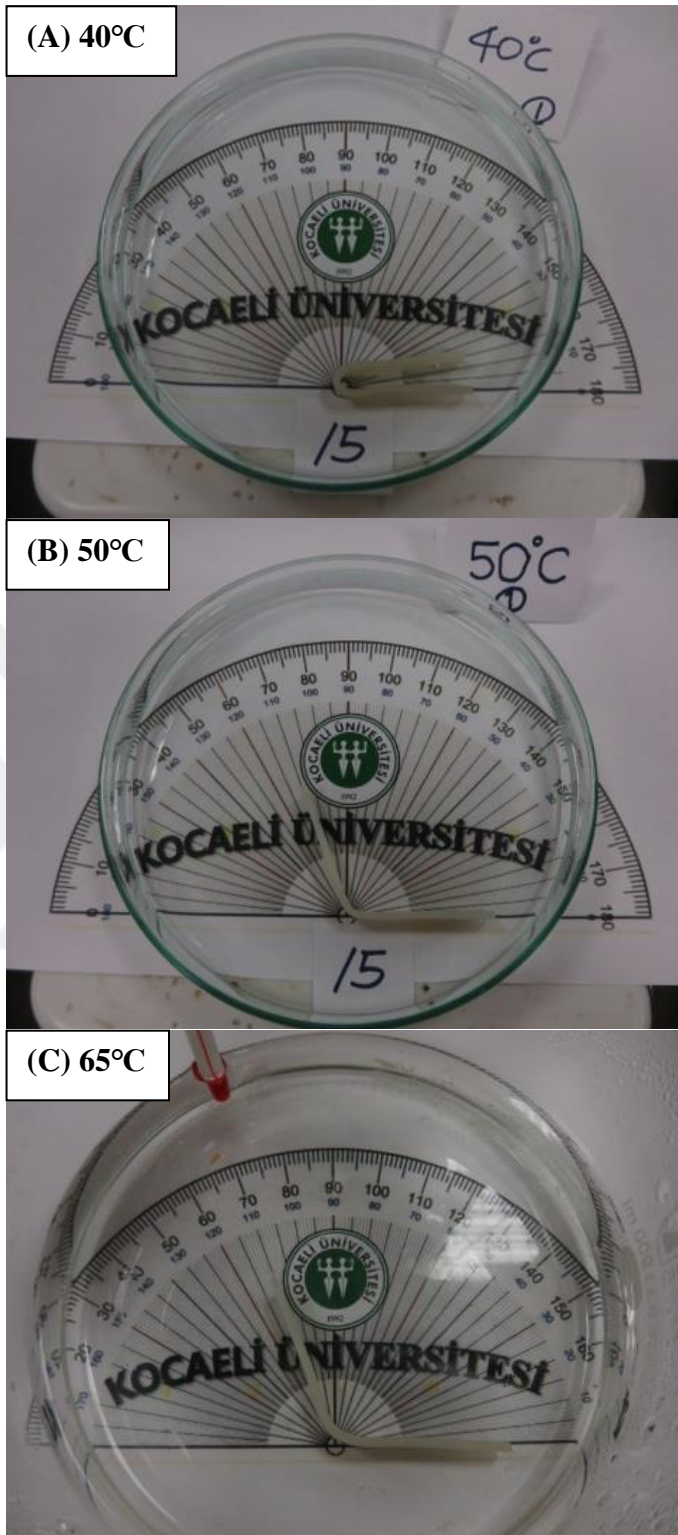


Fig. 4.16. The pictures on the shape memory test of the PCL50 PDI2 sample with different condition of the temperature ((A)is under 40°C (B)is under 50°C, and (C) is under 65°C)

4.5.1. Shape fixity ratio

As the ratio of PCL in the blend is increased, the ratio of shape fixity is increased (Fig. 4.17). These results indicate that PCL affected the fixing performance and determined the ratio of shape fixity with the crystalline structure. PCL crystals have a role of thermal switches to fix a temporary shape [16, 62].

The blends with PDI showed relatively low R_f ratio compared with the blends without PDI. The blends with 30 percent of PCL especially showed the considerable distinction between the samples with and without existence of PDI. PDI (polyisocyanates) is very reactive. Its functional groups are able to react with many other functional groups. In this study, It is expected that diisocyanates from PDI reacted with hydroxyl groups of PCL and TPU, and as the outcome of reaction, it connected with urethane bonds [36]. The reaction is shown schematically in Fig. 1.3 as well. Urethane bonds make impact on the ratio of HS [66, 67], and guess hinder the highly micro-separation between HS and SS. However, the blends included 50 percent of PCL are totally fixed at room temperature, regardless of the PDI-existence.

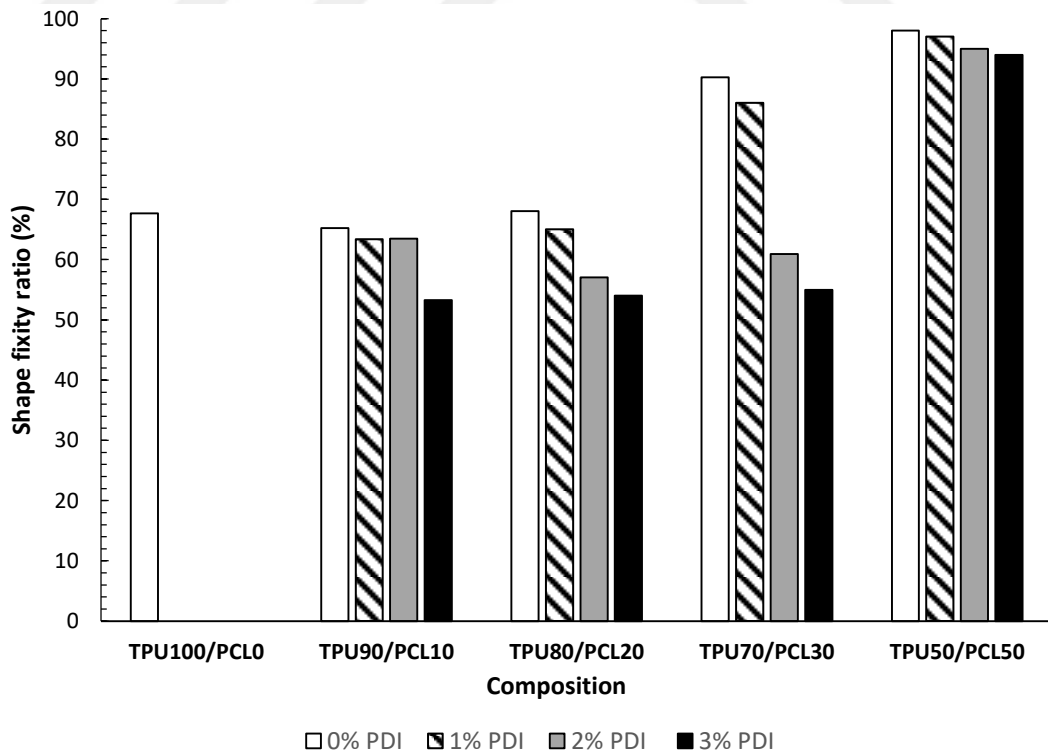


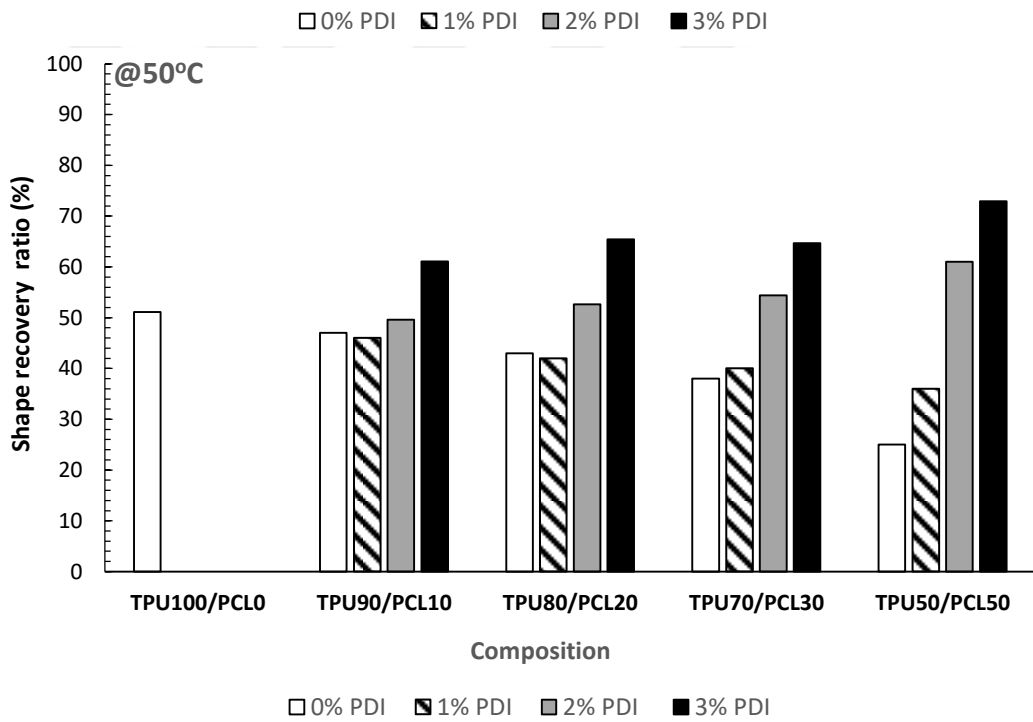
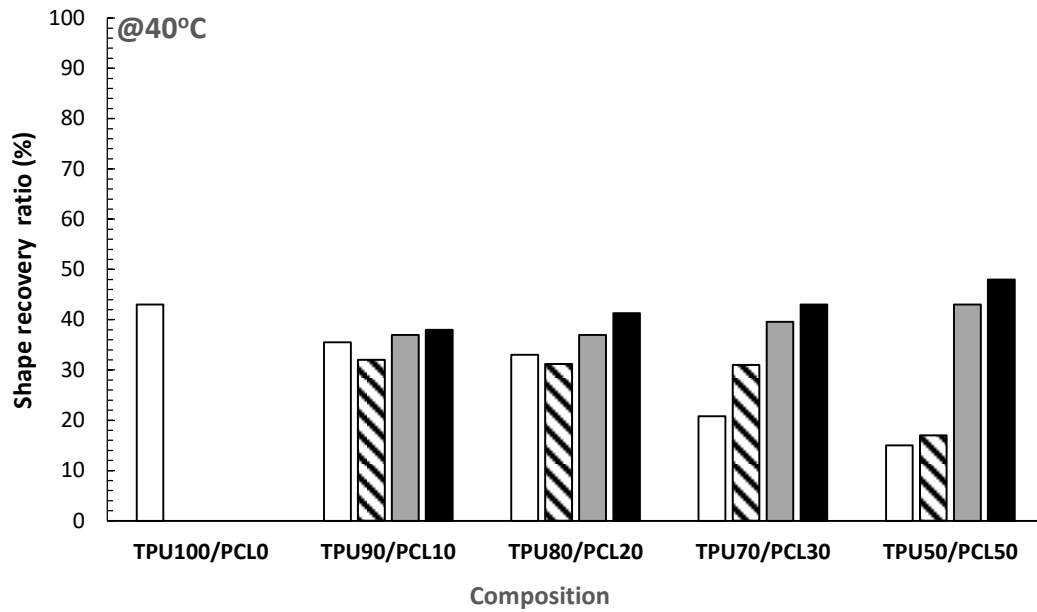
Fig. 4.17. Shape fixity ratio of the samples

4.5.2. Shape recovery ratio

Shape memory test was performed in three different condition of temperature to observe recovery properties and compare the reactivity between below and above the T_{trans} . The comparisons are shown in Fig. 4.18. As expected, the R_r of the response to 40°C was relatively low. Shape recovery significantly occurs only in the range of transition temperature and the recovery ratio is generally proportionate to the increased temperature in the range [16]. Especially PCL 50 samples almost did not react except the sample with 2 and 3% of PDI. In the condition of 65°C near T_m , samples are comparatively restored with high recovery ratio within the range from 70 to 80. This tendency indicates that high temperature help deformation much easily because rubbery states of samples make the orientation more feasible [2]. However, the PCL 50 samples stood out conspicuously as being restored with low recovery ratio. If chain flexibility is increased due to high PCL content, the ability to store force for recovering original shape would be decreased [68].

When the interactions among HS are broken due to the excess stress, shape memory properties become poor and permanent shape cannot be repaired. As the samples have high ratio of PCL, it showed the tendency to have a fracture during the test. Add to this, the balance between HS and SS is very important for high performance of shape memory effects. Most of all, the HS have a role of the net points which control the original shape and R_r [62]. The reason of the low R_r about PCL 50 samples is presumed that the HS is quiet low to go into action property for recovery of shape. Viewed in this light, PDI guess affects the HS ratio. Among the PCL 50 samples showed relatively low R_r , PCL 50 PDI 3 showed high R_r .

PCL 30 PDI 3 sample had the highest shape recovery ratio, even under the condition of 40°C. On the basis of shape fixity and shape recovery ratios so far, the most ideal ratio is PCL 50 with PDI 3.



r

Fig. 4.18. Shape recovery ratio of the samples (under the condition of 40, 50 and 65°C)

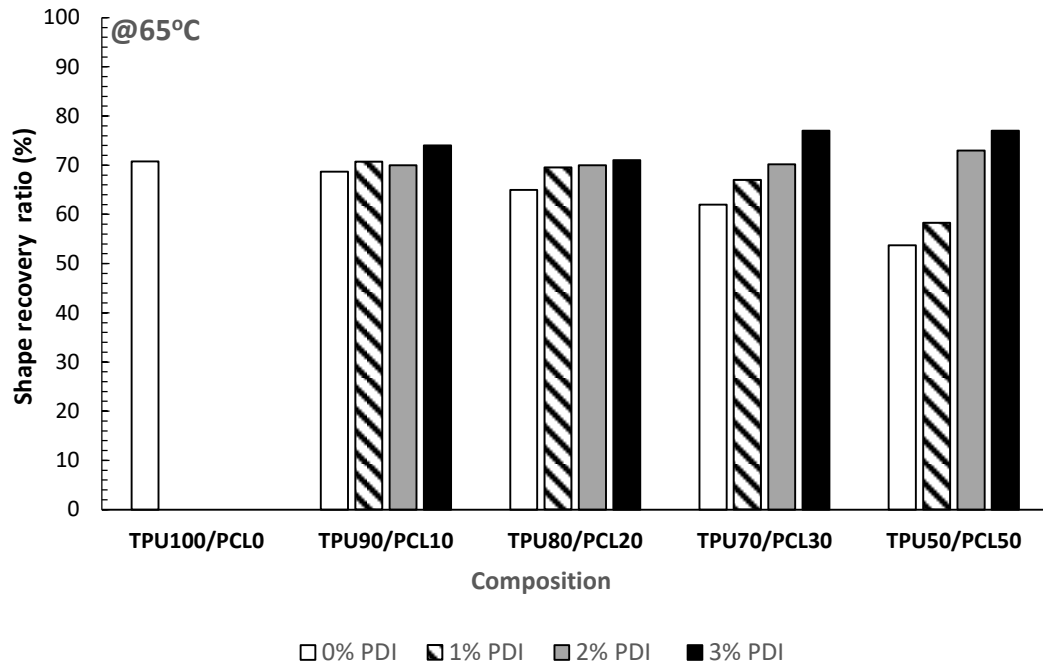


Fig. 4.18. (Continuation) Shape recovery ratio of the samples (under the condition of 40, 50 and 65°C)

Overall, samples in this study did not have over 80 percent of shape recovery ratios. Comparison with the similar concept of studies, the figure is comparatively low. The cause might be the thickness of samples which was approximately 2mm. The size or thickness can affect to shape recovery properties. Small size samples are expected to have an advantage of high ratio of shape recovery because it can be the main parameter to reduce the temperature gradient during the process of shape recovery [16].

4.5.3. Effect of programming temperature to shape memory properties

The performance of shape memory might be possibly tailored by regulating the parameters such as temperature and strength during programming [16]. To evaluate the effect of programming temperature, the test is observed by setting the different condition of temperature, which is 55 and 65°C. Fig. 4.19 shows the shape retention ratio under each condition of pre-deformation. There are not shown the stark differences between the two, but 65°C-condition is superior to fix the temporary shape in general. This is particularly obvious for PCL 50 samples.

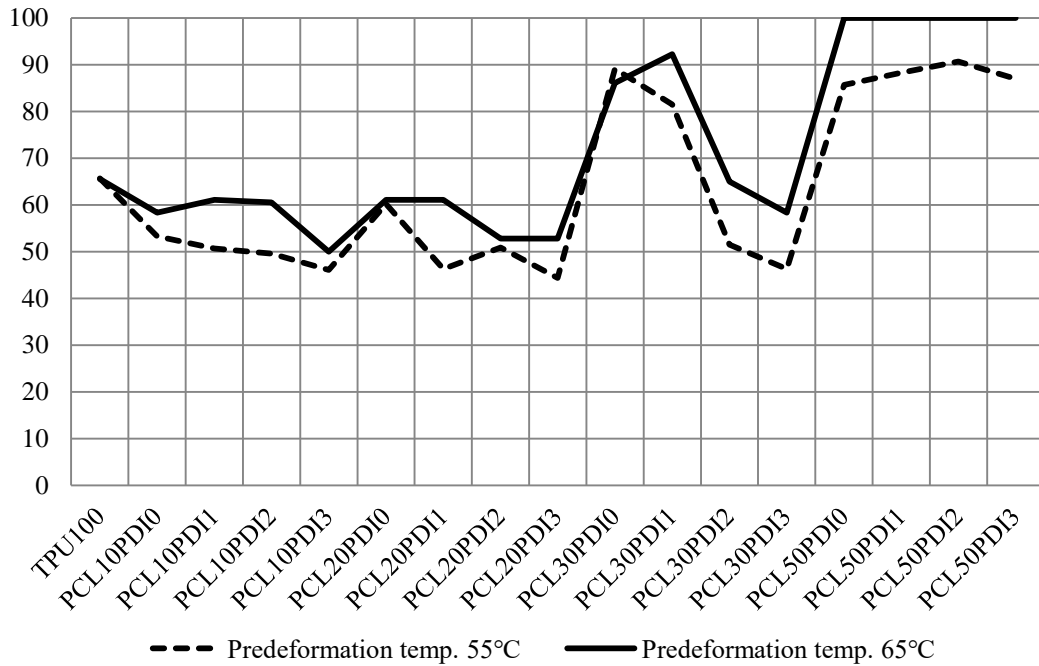


Fig. 4.19. Shape retention ratio depending on different pre-deformation temperature.

The samples which are pre-deformed each under 55 and 65°C is observed to see the ability of shape recovery at 55°C (Fig. 4.20.). 65°C-preformed samples clearly indicate low shape recovery ratio by comparison with the 55°C-preformed samples. This tendency is also specified by other studies [69-71]. As the programming temperature increases, the highest recovery stress occurs under higher temperature around the programming temperature [16] In other words, 65°C-preformed samples have lower recovery stress than 55°C-preformed samples at 55°C. Sun, L. and the coworkers [70] studied optimization of the SME depending on different programming temperature of SMP. They chose four different temperatures within the scope of the overall glass transition temperature for programming the SMP, and found that the majority of the shape restoration occurred near the temperature of programming SMP except for the lowest temperature in the four conditions. The SMP programmed in the lowest temperature is gradually restored the original shape and full recovery is over at the end point of the glass transition temperature.

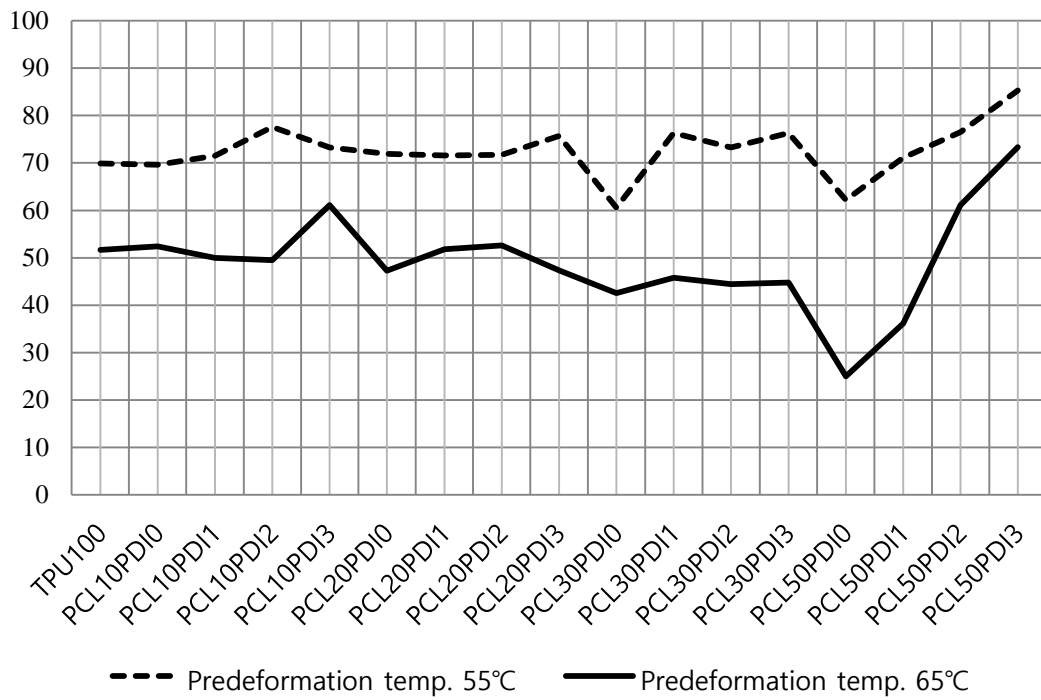


Fig. 4.20. Shape recovery ratio at 55°C with different pre-deformation temperature.

5. CONCLUSIONS AND SUGGESTION

In this study, the shape memory properties of the blends are mainly evaluated with different ratio of TPU and PCL (Pure TPU, PCL 10, 20, 30 and 50 wt%). On top of that, diisocyanate is added to observe the role in TPU/PCL blends. To examine the shape memory properties thoroughly, thermal properties, mechanical properties and morphology properties are additionally investigated.

Semi-crystalline PCL affect the mechanical properties. The modulus and tensile strength at yield point is increased by increase in the content of PCL. The tensile strain at break is diminished. PDI provides blends with high ratio of elongation and tensile strength at break. Increasing mechanical properties are explained by improvement of interfacial adhesion with the role of PDI.

DSC and TGA are conducted to analyze thermal properties of the blends. The transition temperature for shape memory transition is observed by DSC. As the contents of PCL and PDI are increased, transition temperature is getting higher showing specific melting point at the result thermogram of DSC. It is interpreted that the content of PCL affects the ratio of the crystallinity. The stability is observed by TGA. The peak temperature of the highest degradation is moved to higher as increasing of PCL and PDI which indicates the high crystallinity makes the blends stable.

Rheometer is used to observe the flow and deformation of the samples depending on the interrelation between deformation and force, which depends on the condition of samples. As increasing of PCL content in the blends, the complex viscosity is increased due to the formation of H-bonding between PCL and TPU chains. The formed interactions become the cause of restriction on the flow of the sample. The addition of PDI remarkably increases the complex viscosity and stands out the behavior of shear thinning, which results from both increase in molecular weight, and formation of branched structure.

SEM is used to examine the surface of the blends. When the blends have high ratio of PCL, the micro phase is shown rougher than the samples with relatively low contented of PCL. And, the reaction between PDI and TPU/PCL blends provides the fibers on the surface.

The shape memory test is done with 'fold-deploy shape memory test' under different condition of temperature, 40, 50 and 65°C. Programming of shape memory in different temperature, also proceed to see the effect of the programming temperature to shape memory properties. PCL provides high shape fixity ratio. However, 50 percent of PCL did not recover which has the lowest shape recovery ratio without PDI. PDI slightly disturb the shape fixing, but in the case with PCL50, it could not affected to shape fixing of the blends. PDI forms the urethane linkage with PCL/TPU, and impacts on HS, resulting in high recovery ratio.

It is concluded that the content of PCL highly affects the mechanical, thermal, morphological and shape memory properties. PDI is expected to role as the compatilizer to improve miscibility, but the effect is not obvious like the case of the PLA/TPU blends

REFERENCES

- [1] Meng H., Li G., A review of stimuli-responsive shape memory polymer composites, *Polymer*, 2013, **54**, 1-23.
- [2] Ratina D., Karger-Kocsis J., Recent advances in shape memory polymers and composites: a review, *J Mater Sci*, 2008, **43**, 254-269.
- [3] Xie T., Recent advances in polymer shape memory, *Polymer*, 2001, **52**, 4985-5000.
- [4] Behl M. and Lendlein A., Actively moving polymers, *Soft matter*, 2007, **3**, 58-67.
- [5] Hager M. D., Bode S., Weber C and Schubert U. S., Shape memory polymers: Past, present and future developments, *Progress in Polymer Science*, 2005, **49-50**, 3-33.
- [6] Lendlein A., Kelch S., Shape-Memory Polymers, *Angew. Chem. Int. Ed.*, 2002, **41**, 2034-2057.
- [7] Liu C., Qin H., Mather P.T., Review of progress in shape-memory polymers, *J. Mater. Chem.*, 2007, **17**, 1543–1558.
- [8] Small W., Singhal P., Wilson T. S. and Maitland D. J., Biomedical applications of thermally activated shape memory polymers, *J. Mater. Chem.*, 2010, **20**, 3356–3366.
- [9] Hearon K., et al., A processable Shape Memory Polymer System for Biomedical Applications, *Adv. Healthcare Mater.*, 2015, **4**, 1386–1398.
- [10] Zhu G., Liang G., Xu Q. and Yu Q., Shape-Memory Effects of Radiation Crosslinked Poly(ϵ -caprolactone), *J. Appl. Polym. Sci.*, 2003, **90**, 1589–1595.
- [11] Zhang X., Tan B. H., Li Z., Biodegradable polyester shape memory polymers: Recent advances in design, material properties and applications, *Materials Science & Engineering C*, DOI: 10.1016/j.msec.2017.11.008.
- [12] Wang K., Strandman S., A mini review: Shape memory polymers for biomedical applications, *Front. Chem. Sci. Eng.*, 2017 **11**(2), 143–153.
- [13] Hu J., Zhu Y., Huang H. and Lu J., Recent advances in shape-memory polymers: structure, mechanism, functionality, modeling and applications, *Progress in Polymer Science*, 2012, **37**, 1720-1763.
- [14] Karger-Kocsis J. and Keki S., Biodegradable polyester-based shape memory polymers: Concepts of (supra)molecular architecturing, *eXPRESS Polymer*

Letters, 2014, **8**, 397-412.

- [15] Lendlein A. and Langer R., Biodegradable, Elastic Shape-Memory Polymers for potential Biomedical Applications, *Science*, 2002, **296**, 1673-1676.
- [16] Salvekar A. V., et al., Shape/temperature memory phenomena in un-crosslinked poly- ϵ -caprolactone (PCL), *European Polymer Journal*, 2015, **72**, 282-295.
- [17] Xue L. and Greisler H.P., Biomaterials in the development and future of vascular grafts, *J Vasc Surg*, 2003, **37**, 472-80.
- [18] Santerre JP, Woodhouse K., Laroche G. and Labow RS, Understanding the biodegradation of polyurethanes: From classical implants to tissue engineering materials, *Biomaterials*, 2005, **26**, 7457-7470.
- [19] Mi HY., Jing X., Napiwocki BN, Hagerty BS, Biocompatible, degradable thermoplastic polyurethane based on polycaprolactone-block-polytetrahydrofuran-block-polycaprolactone copolymers for soft tissue engineering, *J. Mater. Chem.*, 2017, **5**, 4137–4151.
- [20] Qi X., et al., Enhanced shape memory property of polylactide/thermoplastic poly(ether)urethane composites via carbon black self-networking induced co-continuous structure, *Composites Sci. and Tech.*, 2017, **139**, 8-16.
- [21] Jing X., Mi HY, Huang HX and Turng LS, Shape memory thermoplastic polyurethane(TPU)/poly(ϵ -caprolactone)(PCL) blends as self-knotting sutures, *Journal of the mechanical behavior of biomedical materials*, 2016, **64**, 94-103.
- [22] Ajili S. H., Ebrahimi N. G., Soleimani M., Polyurethane/polycaprolactane blend with shape memory effect as a proposed material for cardiovascular implants, *Acta Biomaterialia*, 2009, **5** 1519–1530.
- [23] Ajili S. H., Ebrahimi N. G., Ansari M., Rheological study of segmented polyurethane and polycaprolactone blends, *Rheol Acta*, 2008, **47**, 81-87.
- [24] Dogan S. K., Reyes E. A., Rastogi S. and Ozkoc G., Reactive compatibilization of PLA/TPU blends with a Diisocyanate, *J. APPL. POLYM. SCI.*, 2004, **131**, 40251.
- [25] Harada M., Ohya T., Lida K. and Hayashi H., Increased Impact Strength of Biodegradable PLA/Poly(butylene succinate) Blend Composites by using Isocyanate as a Reactive Processing Agent, *J. APPL. POLYM. SCI.*, 2007, **106**, 1813-1820.
- [26] Liu Y., Han C., Tan H. and Du X., Thermal, mechanical and shape memory properties of shape memory epoxy resin, *Materials Science and Engineering A*, 2010, **527**, 2510-2514.
- [27] Guo J., Wang Z., Tong L. and Liang W., Effect of short carbon fibres and

- nanoparticles on mechanical, thermal and shape memory properties of SMP hybrid nanocomposites, *Composites Part B*, 2016, **90**, 152-159.
- [28] Engelberg I. and Kohn J., Physico-mechanical properties of degradable polymers used in medical applications: a comparative study, *Biomaterials*, 1991, **12**, 292-304.
- [29] Labet M. and Thielemans W., Synthesis of polycaprolactone, *Chem. Soc. Rev.*, 2009, **38**, 3484-3504.
- [30] Woodruff M.A. and Hutmacher D.W., The return of a forgotten polymer-PCL in the 21st century, *Progress in Polymer Science*, 2010, **35**, 1217-1256.
- [31] Semba T., Kitagawa K., Ishiaku U. S. and Hamada H., The effect of crosslinking of the mechanical properties of PLA/PCL blends, *J. APPL. POLYM. SCI.*, 2006, **101**, 1816-1825.
- [32] Kweon HY, et al., A novel degradable PCL networks for tissue engineering, *Biomaterials*, 2003, **24**, 801-808.
- [33] Thakur S. and Hu J., Polyurethane: A Shape Memory Polymer (SMP), Editor: Yilmaz F., *Aspects of Polyurethanes*, 1st ed., Intechopen, London, 2017.
- [34] Leng J., Lan X., Liu Y. and Du S., Shape-memory polymers and their composites: Stimulus methods and applications, *Progress in Materials Science*, 2011, **56**, 1077-1135.
- [35] Szycher M., *Szycher's Handbook of Polyurethanes*, 1st ed., CRC Press, Boca Raton, 1999.
- [36] Thomas F. G. and Michael R. K., Plant Oil-Based Polyurethanes, Editors: Madbouly S. M., Zhang C, Kessler M. R., *Bio-based plant oil polymers and composites*, 1st ed., William Andrew, Pennsylvania 37-42, 2015.
- [37] Yang JH, Chun BC, Chung YC and Cho JH, Comparison of thermal/mechanical properties and shape memory effect of polyurethane block-copolymers with planar or bent shape of hard segment, *Polymer*, 2003, **44**, 3251-3258.
- [38] Kurahashi E., Sugimoto H., Nakanishi E and Nagata K., Shape memory properties of polyurethane/poly (oxyethylene) blends, *Soft matter*, 2012, **8**, 496.
- [39] Zhao Q., Qi H. J., Xie T., Recent progress in shape memory polymer: New behavior, enabling materials, and mechanistic understanding, *Progress in Polymer Science*, 2015, **49-50**, 79-120.
- [40] Mu T., et al., Shape memory polymers for composites, *Composites Science and Technology*, 2018, **160**, 169-198.
- [41] Silviya E K., Varma S. and Unnikrishana G., Compounding and mixing of

polymers, *advances in polymer processing*, 2009, **4**, 71-105.

- [42] Isayev A.I. and Crouthamel D.L., Residual Stress Development in the Injection Molding of Polymers, *Polymer-Plastics Technology and Engineering*, 1984, **22**, 177-232.
- [43] Roylance D., Stress-Strain Curves, Saylor Academy, <https://www.saylor.org/site/wp-content/uploads/2012/09/ME1022.2.4.pdf> (Date of visit: 10 April 2018).
- [44] Davis J. R., *Tensile testing*, 2nd ed., Introduction to Tensile Testing, ASM international, Ohio, 2004.
- [45] Dean D., Thermal Gravimetric Analysis, University of Alabama (UAB), https://www.uab.edu/engineering/home/images/downloads/TGA_UAB_TA_MAy_absolute_final_2014.pdf (Date of visit: 12 April 2018).
- [46] Sichina W.J., Characterization of polymer using TGA, Perkin Elmer instruments, https://www.perkinelmer.com/CMSResources/Images/44-132088APP_CharacterizationofPolymersUsingTGA.pdf (Date of visit: 12 April 2018)
- [47] Durowoju IB., Bhandal KS, Hu J. and Carpick B., Differential Scanning Calorimetry - A Method for Assessing the Thermal Stability and Conformation of Protein Antigen, *J Vis Exp.*, 2017, **121**, 55262.
- [48] Kim Y.S., Jung H.M., Thermo polymer, *polymer Science and Technology*, 2011, **22**, 370-374.
- [49] Gill P., Moghadam T. T. and Ranjbar B., Differential Scanning Calorimetry Techniques: Applications in Biology and Nanoscience, *J Biomol Tech.*, 2010, **21**, 167-193.
- [50] Grillet A.M., Wyatt N.B. and Gloe L.M., Polymer gel rheology and adhesion, *Intech*, 2012, **3**, 59-80.
- [51] Goodwin J. W. and Hughes R. W., *Rheology for Chemists: An Introduction*, 2nd ed., Royal Society of Chemistry, Cambridge, 2008.
- [52] Chen T., Characterization of Shape-Memory Polymers by DMA, *TA instruments*, TA374, 1-8, 2009.
- [53] Balk M., Behl M., Wischke C. and Zotzmann J., Recent advances in degradable lactide-based shape-memory polymers, *Advanced Drug Delivery Reviews*, 2016, **107**, 136–152.
- [54] Hu J., et al., Cross-linked polyurethanes with shape memory properties, *Polymer International*, 2005, **54**, 854-859.
- [55] Ping P., Wang W., Chen X. and Jing X., Poly(ϵ -caprolactone) Polyurethane and Its Shape-Memory Property, *Biomacromolecules*, 2005, **6**, 587–592.

- [56] Wang W., Ping P., Chen X. and Jing X., Biodegradable Polyurethane Based on Random Copolymer of L-Lactide and ϵ -caprolactone and Its Shape-Memory Property, *Biomacromolecules*, 2005, **6**, 587–592.
- [57] Zhang H., Wnag H., Zhong W. and Du Q., A novel type of shape memory polymer blend and the shape memory mechanism, *Polymer*, 2009, **50**, 1596–1601.
- [58] Mosleh Y., Ebrahimi NG, Mahdavian A. and Ashjari M., TPU/PCL/nanomagnetite ternary shape memory composites: studies on their thermal, dynamic-mechanical, rheological and electrical properties, *Iran Polym J.*, 2014, **23**, 137-145.
- [59] Heijkants R.G., et al., Uncatalyzed synthesis, thermal and mechanical properties of polyurethanes based on poly(ϵ -caprolactone) and 1,4-butane diisocyanate with uniform hard segment, *Biomaterials*, 2005, **26**, 4219-4228.
- [60] Niesten M.C.E.J. and Gaymans R.J., Tensile and elastic properties of segmented copolyetheresteramides with uniform aramid units, *Polymer*, 2001, **42**, 6199-6207.
- [61] Ajili S.H. and Ebrahimi N.G., Miscibility of TPU(PCL diol)/PCL Blend and its effect on PCL Crystallinity, *Macromol. Symp.*, 2007, **249-250**, 623-627.
- [62] Kalajahi A. E., Rezaei M., Abbasi F. and Sadeghi GMM., The Effect of Chain Extender Type on the Physical, Mechanical, and Shape Memory Properties of Poly(ϵ -Caprolactone)-based Polyurethane-ureas, *Poly.-Plastics Tech. and Engineering* 56, 2017, **18**, 1977-1985.
- [63] Herreraa M., Matuscheka G., Kettrup A., Thermal degradation of thermoplastic polyurethane elastomers (TPU) based on MDI, *Polymer Degradation and Stability*, 2002, **78**, 323–331.
- [64] Persenaire O., Alexandre M., Degee P. and Dubois P., Mechanisms and kinetics of thermal degradation of Poly(ϵ -caprolactone), *Biomacromolecules* 2001, **2**, 288-294.
- [65] Feng F. And Ye L., Morphologies and Mechanical Properties of Polylactide/Thermoplastic Polyurethane Elastomer Blends, *J. APPL. POLYM. SCI.*, 2011, **119**, 2778-2783.
- [66] Tatai L., et al., Thermoplastic biodegradable polyurethanes: The effect of chain extender structure on properties and *in-vitro* degradation, *Biomaterials*, 2007, **28**, 5407-5417.
- [67] Guelcher S. A., Biodegradable Polyurethanes: Synthesis and Applications in Regenerative Medicine, *Tissue engineering: Part B*, 2008, **14**, 3-17.
- [68] Mya KY., et al., Star-shaped POSS-polycaprolactone polyurethanes and their shape memory performance, *Chem.*, 2011, **21**, 4827–4836.

- [69] Sun L. and Huang W.M, Mechanisms of the multi-shape memory effect and temperature memory effect in shape memory polymers, *Soft Matter*, 2010, **6**, 4403-4406.
- [70] Sun L. et al., Optimization of the Shape Memory Effect in Shape Memory Polymers, *Polymer Science Part A: Polymer Chem.*, 2011, **49**, 3574-3581.
- [71] Xie T., Tunable polymer multi-shape memory effect, *Nature*, 2010, **464**, 267-270.



ACADEMIC ACHIEVEMENT

- [1] **Lee, NY.,** Özkoç, G., Shape Memory Property of Poly(ϵ -caprolactone)(PCL)/thermoplastic Polyurethane(TPU) Blends in the Presence of a Diisocyanate Compatibilizer, *3. International Congress on Engineering Architecture and Design*, Kocaeli, 04-05 May 2018.



PROFILE

Nayeon Lee was born in Seoul, South Korea in 1989. She went through primary, middle and high school in Seongnam, South Korea and went into Hanyang University in 2010. In university, she majored in Chemistry and minored in Bio-nano engineering. In 2015, she graduated and decided to study for master course in Turkey. Following Turkish Preparation course at school of foreign languages, she has been going through master's course of Polymer science and technology in Kocaeli University since 2016.

