

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**EFFECT OF SOFT SEGMENT LENGTH ON FOAM STRUCTURE OF
EXPANDED THERMOPLASTIC POLYURETHANE (ETPU) BEAD FOAMS**



M.Sc. THESIS

Bige BATI

Graduate School of Science Engineering and Technology

Polymer Science and Technology Graduate Programme

DECEMBER 2018

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**YUMUŞAK SEGMENT UZUNLUĞUNUN GENLEŞTİRİLMİŞ
TERMOPLASTİK POLİÜRETAN (ETPU) TANECİK KÖPÜK YAPISINA
ETKİSİ**

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To my mother,



FOREWORD

First and foremost, it is a genuine pleasure to express my deep sense of thanks and gratitude to my thesis advisor Asst.Prof. M. Reza NOFAR. He consistently allowed this thesis project to be my own work, but steered me in the right the direction whenever he thought I needed it. I would also like to greatly aknowlage Huntsman Polyurethanes (Belgium) who fully sponsered this project and provided this appportunity for us to work on such an innovative research project. I would also like to highly appreciate and aknowlege the contributions made by the scientist from Huntsman Polyurethanes, specifically Ms. Conny NIJS, Dr. Rene KLEIN, and Mr. Giovanni TOMEI.

I express my gratitude to Assoc. Prof. Ali DURMUŞ from Istanbul University, Prof. Gürbüz GÜNEŞ, Prof. Servet TİMUR, Prof. Mustafa ÜRGEN, Prof Kürşat KAZMANLI from Istanbul Technical University, and Gizem AKAY from Anton Paar, for providing their laboratory spaces and equipments. Also I want to thank Research Assistant Erkan KAÇAR and Begüm ALANALP for their help in running characterization experiments.

My thanks also go to the past and present members of Nofar group for all their contribution to this thesis. In particular, Emine Büşra KÜÇÜK who was my workmate in this project, Emre DEMİRTAŞ who helped us to get many results, and Elif ÖZPERK for her positive energy and motivation. It has really been a great pleasure with all of them.

It is my privilege to thank Şimal AYKAÇ and Gülbahar BOZAN for their worthy friendships and unrequited help all the time in the university. Also, I wish to express my special thanks to Ece ENGİZEK and Esra OSMANOĞULLARI, my dearest friends for many years.

A special thanks to the most thoughtful person in the world, Berkay NERSE for his full support, motivation and love.

Most importantly, I owe a dept of gratitude to my mother, Nuran TİRİŞ, my sister Ümran BATI, and my father, Ali BATI for their endless love, unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them.

December 2018

Bige BATI
(Chemist)



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ABBREVIATIONS

ABS	: Acrylonitrile Butadiene Styrene
CBA	: Chemical Blowing Agent
CFC	: Chlorofluorocarbon
CNT	: Classical Nucleation Theory
DSC	: Differential Scanning Calorimeter
DFT	: Density-functional Theory
ETPU	: Expanded Thermoplastic Polyurethane
EPE	: Expanded Polyethylene
EPLA	: Expanded Polylactide
EPP	: Expanded Polypropylene
EPS	: Expanded Polystyrene
FIM	: Foam Injection Molding
FTIR	: Fourier Transform Infrared Spectroscopy
GC	: Gas Chromatography
GMS	: Glycerol Monostrate
HCFC	: Hydrochlorofluorocarbon
HDI	: 1,6-Hexamethylene Diisocyanate
H12 MDI	: Bis(4-isocyanatocyclohexyl)methane
HS	: Hard Segment
IPDI	: Isophorone Diisocyanate
MDI	: Methylene Diphenyl Diisocyanate
MFI	: Melt Flow Index
NMR	: Nuclear Magnetic Resonance
PBA	: Physical Blowing Agent
TGA	: Thermogravimetric Analysis
TPU	: Thermoplastic Polyurethane
TSE	: Twin-screw Extruders
SCFT	: Self Consistent Field Theory
SEM	: Scanning Electron Microscope
SS	: Soft Segment

SSE : Single-screw Extruders
VOC : Volatile Organic Compounds



SYMBOLS

C	: Concentration
D	: Diffusivity
D₀	: Diffusivity Coefficient Constant
E_D	: Activation Energy for Diffusion of Gas
J	: Nucleation Rate
M_{air}	: Weight of Sample in Atmospheric Conditions
M_{water}	: Weight of Sample in Pure Water
N	: Number of Cell in Foam
P_{bub}	: Pressure Inside the Bubble
P_{sys}	: Pressure of the System
R	: Universal Gas Constant
r	: Radius of the Bubble
r_c	: Critical Radius
R	: Relative Density
T	: Temperature
T_g	: Glass Transition Temperature
T_m	: Crystal Melting Temperature
W_{hom}	: Homogenous Nucleation Energy Barrier
W_{het}	: Heterogenous Nucleation Energy Barrier
ρ_{foam}	: Foam Density
ρ_{polymer}	: Polymer Density
ρ_{water}	: Water Density
γ	: Surface Tension
ΔG	: Gibbs Free Energy



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EFFECT OF SOFT SEGMENT LENGTH ON FOAM STRUCTURE OF EXPANDED THERMOPLASTIC POLYURETHANE (ETPU) BEAD FOAMS

SUMMARY

Since the second world war, many types of polymers and their products have been produced. This is because of their broad range of properties compared to other materials such as metals and composites, including toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals. The most prominent features of polymers are, however, their low density, ease of manufacturing, and hence cost-effective.

Thermoplastic polyurethane (TPU) is a thermoplastic based elastomer, which means it is meltable and processable when heated, formable and shapable when cooled, and capable of being reprocessed multiple times. TPU is well-known for its many features including; high abrasion resistance; flexibility over a wide range of temperatures; high tensile strength; good resistance to weathering; good resistance to oil, grease, solvents and chemicals. These properties make TPU extremely useful for hundreds of applications such as automotive instrument, caster wheels, power tools, sporting goods, medical devices, drive belts, footwear, and a variety of extruded film, sheet and profile applications.

TPU is a block copolymer including alternating sequences of hard and soft segments formed by the reaction of diisocyanates with short-chain diols and diisocyanates with long-chain diols. By varying the ratio, structure and/or molecular weight of the reaction compounds could be changed, and different TPU with varying properties can hence be produced. This allows to tailor the desired final properties of the material. For instance, a greater ratio of soft segments to hard segments will result in a softer TPU, while the reverse will result in a more rigid TPU.

The polyol chain of TPU can be either polyether based or polyester based. Polyester TPUs are compatible with polar plastics, offer a good balance of physical properties and are perfect for use in polyblends. Polyether TPUs are slightly lower in specific gravity than polyester. They offer low temperature flexibility and good abrasion and tear resilience. They provide excellent hydrolysis resistance – making them suitable for applications where water is a consideration. TPUs can also be subdivided into aromatic and aliphatic isocyanates. TPUs with aromatic isocyanates like Methylenediphenyl diisocyanate (MDI) can be used in applications that require flexibility, strength and toughness. TPUs with aliphatic isocyanates like-Methylenedicyclohexyl diisocyanate (H12 MDI), hexamethylene diisocyanate (HDI), and isophorone diisocyanate IPDI are commonly used in projects where optical clarity, adhesion and surface protection are required.

Polymeric foams are made up of a polymer matrix with either closed bubbles (cells) or interconnected tunnels, which are known as either closed-cell or open-cell structures. Open-cell foams are mostly flexible, while closed-cell foams are generally

more rigid. The gas that is used in the foam is known as blowing agent, which can be either chemical or physical. Physical blowing agents are gases which do not react chemically in the foaming process, while chemical blowing agents take part in a reaction or decompose, giving off chemicals in the process. Polymer foams can be divided into either thermoplastics or thermosets, which are further divided into rigid or flexible foams. The thermoplastics are usually breakable and able to recycle, while thermosets are harder to recycle because they are usually heavily crosslinked.

The first polymer foam was foamed polystyrene in the 1930's. During second World War polyurethane was invented. After the war, the flexible polyurethane foam was produced and used for furniture and automotive industry. In the following years, polymer foams were more widely used as new technologies developed, such as injection molding and several extrusion techniques. Recently, bead foaming technologies are developed including several methods, for instance foam extrusion with underwater pelletizer, suspension polymerization with blowing agent, and batch foaming process.

Batch foaming is noncontinuous process that is qualified to study the foaming behavior of polymers and also exist for industrial applications. In this process, polymer is firstly saturated with physical blowing agent in a high pressure cell. Later, foaming is initiated by either a pressure drop or increase in temperature which results in a thermodynamic disequilibrium. In pressure drop method, pressure drop rate effect on the cell nucleation can be investigated, while increase in temperature method suits to evaluate the processing window of the polymer. The reason why polymer foams are widely used is that they have a lot of advantageous such as low density, cheaper, tailored properties which could influence the final functional properties such as insulation properties. Bead foams have an extra advantages compare to foam extrusion and foam injection molding, which is its ability to form low density three dimensional complex geometry foam products.

This thesis focus on foaming behavior of expanded thermoplastic polyurethane (ETPU) through batch foaming process. TPUs samples that have different molecular weights and different polyol types are examined. The effect of process conditions; saturation pressure, time and temperature on foam morphology; also, the effect of pressure drop rate on cell nucleation are investigated.

At first, to investigate the onset of degradation and thermal decomposition behavior, TPU samples were analyzed by thermal gravimetric analysis (TGA). To know the materials better, the rheological properties of the TPUs were also measured using a rheometer under oscillatory shear loads and using melt flow indexer. Later, the effect of molecular weight and polyol types of TPU on the crystallization behavior was explored with non-isothermal melt analysis in differential scanning calorimetry (DSC). The next step was isothermal crystallization analysis in DSC, which simulates foaming process without blowing agent, to understand how isothermal annealing in DSC can modify the crystals and influence the cell nucleation.

After the thermal analysis, samples were foamed at different temperatures under 2000psi for 30min to find the optimum process temperature. When optimum temperatures were determined for all samples, they were also foamed at 1000psi and 1500psi for 30 min to monitor the saturation pressure effect on TPU's foaming behavior, also at 2000psi for 15min and 60 min to investigate the saturation time effect. Furthermore, to understand how the hard segment crystals were modified by

isothermal annealing under CO₂, all process conditions were repeated with extremely slow pressure drop rate that would not cause foaming for all samples.

The foamed TPU samples were characterized in two aspects. Firstly, the density of foamed samples and their expansion ratio were measured in pure water and calculated using archimedes equation. On the other hand, the morphology of cellular structure in foamed samples were observed using scanning electron microscope (SEM). After the observation of cellular morphology; cell distributions and cell dimensions were examined and the cell density of each of samples was calculated. Thermal analysis performed for foamed samples by DSC to monitor the foaming effect on further modification of hard segment crystals.





YUMUŞAK SEGMENT UZUNLUĞUNUN GENLEŞTİRİLMİŞ TERMOPLASTİK POLİÜRETAN (ETPU) TANECİK KÖPÜK YAPISINA ETKİSİ

ÖZET

İkinci dünya savaşından bu yana, birçok çeşit polimer ve polimer ürünleri geliştirilmiştir. Bunun nedeni, metaller ve kompozitler gibi diğer malzemelere kıyasla, polimerlerin viskoelastisite, camsı yapı ve yarı kristal oluşturma eğilimi gibi geniş yelpazedeki özellikleridir. Ancak polimerlerin en göze çarpan özellikleri, düşük yoğunlukları, imalat kolaylığı ve dolayısıyla düşük maliyetli olmalarıdır.

Termoplastik poliüretan, termoplastik esaslı bir elastomerdir. Isıtıldığında yumuşayan, soğutulduğunda sertleşebilen ve bu özellikleri ile ekstrüzyon, enjeksiyon gibi ısı-ışıl işlem proseslerinde rahatça işlenebilen bir özelliğe sahiptir. TPU yüksek aşınma direnci, geniş bir sıcaklık aralığında esneklik, yüksek bir uzama kuvveti, hava koşullarına karşı iyi direnç, yağ ve kimyasallara karşı direnç gibi birçok ayırt edici özellik gösterir. Bu özellikler, TPU'yu otomotiv gösterge panelleri, döküm tekerleri, elektrikli el aletleri, spor malzemeleri, tıbbi cihazlar, tahrik kayışları, ayakkabılar, şişme salları ve çeşitli ekstrüde film, levha ve profil uygulamaları gibi yüzlerce uygulama için son derece yararlı kılmaktadır.

TPU, NCO fonksiyonel grubuna sahip diizosiyanatlar, OH fonksiyonel grubuna sahip dioller ve zincir uzatıcıları olarak işlev gören kısa zincirli diollerin oluşturduğu kopolimerlerdir. Diizosiyanatlar ve kısa zincirli dioller sert, dioller ise yumuşak segmentleri oluşturur. Reaksiyon bileşiklerinin oranını, yapısını veya molekül ağırlığını değiştirerek, farklı özellikte TPU'lar üretilebilir. Bu varyasyonlar malzemenin istenen nihai özelliklerinin yaratılmasına izin verir. Örneğin, yumuşak segmentlerin sert segmentlere oranla daha çok olması, daha yumuşak bir TPU ile sonuçlanacak, tersi ise daha sert bir TPU ile sonuçlanacaktır.

TPU'nun polioller zinciri polieter bazlı ya da poliester bazlı olabilir. Poliester TPU'lar polar plastiklerle uyumludur, iyi bir fiziksel özellik dengesi sunar ve harman polimerle kullanım için mükemmeldir. Polieter TPU'lar ise poliesterden özgül ağırlıkta biraz daha düşüktür. Düşük sıcaklık esnekliği ve iyi sürtünme ve yırtılmaya karşı dayanıklılık sunarlar. Mükemmel hidroliz direncini sağlarlar; bu da suyun dikkate alındığı uygulamalar için çok önemlidir. TPU'lar ayrıca aromatik ve alifatik izosiyanatlar olarakta sınıflandırılabilir. Metilen difenil diizosiyanat (MDI) gibi aromatik izosiyanatlı TPU'lar esneklik, dayanıklılık ve tokluk gerektiren uygulamalarda kullanılabilir. Metilen disikloheksil diizosiyanat (H12MDI), heksametilen diizosiyanat (HDI) ve izoforon diizosiyanat (IPDI) gibi alifatik izosiyanatlara sahip TPU'lar optik netlik, yapışma ve yüzey korumasının gerekli olduğu projelerde yaygın olarak kullanılmaktadır.

Polimer köpükler, kabarcıklar (hücreler) içeren bir polimer matrisinden oluşur. Bu hücreler hava tünelleriyle bağlantılı ise açık hücreli, değilse kapalı hücreli köpük

olarak adlandırılır. Açık hücreli köpükler genellikle esnektir, kapalı hücreli köpükler ise genellikle daha serttir. Köpükte kullanılan gaz, kimyasal veya fiziksel olabilen köpürtme ajanı olarak bilinir. Fiziksel köpürtme ajanları, köpürme işleminde kimyasal olarak reaksiyona girmeyen gazlardır, kimyasal köpürtme ajanları ise reaksiyona girer ve işlem sırasında kimyasallar açığa çıkarır. Polimer köpükler, ayrıca sert veya esnek köpüklere ayrılan termoplastik veya termosetlere ayrılabilir. Termoplastikler genellikle kırılabilir bağlara sahiptir ve geri dönüşümü mümkündür, termosetler ise çokca çapraz bağa sahiptirler ve geri dönüşümü daha zordur.

İlk polimer köpük 1930'larda üretilmiş olan köpürtülmüş polistirendir. İkinci Dünya Savaşı sırasında ilk poliüretan üretilmiştir. Savaştan sonra, esnek poliüretan köpük mobilya ve otomotiv endüstrisi için üretilmiş ve kullanılmıştır. Sonraki yıllarda polimer köpükler, enjeksiyon köpürtme ve çeşitli ekstrüzyon teknikleri gibi yeni teknolojiler ile üretilerek daha yaygın olarak kullanılmaya başlamıştır. Son yıllarda, tanecik köpürtme teknolojileri, örneğin sualtı peletleme ile köpük ekstrüzyonu, köpürtme ajanı ile süspansiyon polimerizasyonu ve otoklav köpürme işlemi gibi çeşitli yöntemler geliştirilmiştir.

Otoklav prosesi genellikle polimerlerin köpürme davranışını incelemek için kullanılır fakat bazı endüstriyel uygulamalar için de mevcut olan bir işlemdir. Bu işlemde polimer yüksek basınçlı bir kapalı bir sistemde ilk olarak fiziksel köpürtme ajanı ile (genellikle CO₂ ya da N₂) doyurulur. Daha sonra köpürme, bir termodinamik dengesizlikle tetiklenmelidir. Bunun için iki yöntem bulunmaktadır; ani basınç düşüşü yöntemi (basınç metodu) ya da ani sıcaklık artışı yöntemi (sıcaklık metodu). Ani basınç düşüşü yönteminde, basınç düşüş oranının kabarcık nükleasyonu üzerindeki etkisi incelenebilir, ani sıcaklık artışı yöntemi ise polimerin işlem aralığını araştırmak için kullanılabilir. Polimer köpüklerin çok yaygın kullanılmasının nedeni, oldukça hafif ve düşük maliyetli ürünler olmalarının yanı sıra, düşük yoğunluk ve yalıtım özellikleri gibi birçok avantajlı özelliğe sahip olmalarıdır. Tanecik köpükler ise diğer köpük teknolojilerine kıyasla üç boyutlu kompleks ürünler oluşturabilir.

Bu tez, geliştirilmiş termoplastik poliüretanın (ETPU) tanecik köpürme işlemiyle köpürme davranışına odaklanmaktadır. Farklı molekül ağırlığına ve farklı poliol tiplerine sahip TPU'lar incelenmiştir. Proses koşullarının (doyma basıncı, sıcaklığı ve zamanı) köpük morfolojisine etkisi ve basınç düşüş oranının kabarcık nükleasyonuna etkisi araştırılmıştır.

İlk olarak, bozulma başlangıcı ve termal ayrışma davranışını araştırmak için TPU örnekleri termal gravimetrik analiz (TGA) ile analiz edilmiştir. Malzemenin eriyik davranışını daha iyi anlamak için, malzemenin reolojik özellikleri salınımlı reometre ve eriyik akış indeksi ölçüm cihazlarıyla ölçülmüştür. Daha sonra, moleküler ağırlığın ve TPU'nun poliol tiplerinin kristalizasyon davranışı üzerindeki etkisi, diferansiyel taramalı kalorimetrisinde (DSC) non-izotermal eriyik analizi ile araştırılmıştır. Ayrıca köpürtme prosesinin de bir adımı olan izotermal tavlamanın kristalleri nasıl modifiye edebileceği ve kabarcık nükleasyonunu nasıl etkileyebileceğini anlamak amacıyla, DSC'de izotermal erime analizi yapılmıştır.

Termal analizlerden sonra numunelerin optimum işlem sıcaklıklarını bulmak için 30 dakika boyunca 2000 psi basınç altında farklı sıcaklıklarda köpürtme deneyleri yapılmıştır. Tüm numuneler için optimum sıcaklıklar belirlendiğinde, doyma basıncının köpük yapısı üzerindeki etkisinin görülmesi için, 30 dakika boyunca 1000psi ve 1500psi basınç altında da optimum sıcaklıklarıyla köpürtme işlemi yapılmıştır. Daha sonra doyma zamanının etkisinin görülmesi için 15 dakika ve 60

dakika boyunca 2000 psi basınç altında optimum sıcaklıklarında da tekrarlanmıştır. Dahası, kristallerin CO₂ altında izotermal tavlama ile nasıl modifiye edildiğini anlamak amacıyla, tüm numuneler için köpürtmeye sebep vermeyecek yavaşlıkta bir basınç düşüşü ile tüm işlem koşulları tekrarlanmıştır.

Köpürtülmüş termoplastik poliüretan örnekleri farklı açılardan karakterize edilmiştir. İlk olarak, köpürtülmüş numunelerin yoğunlukları suda ölçülmüş ve arşimet denklemi kullanılarak hesaplanmıştır. Daha sona genleşme katsayıları yoğunluklarından yola çıkarak hesaplanmıştır. Diğer yandan, köpürtülmüş numunelerin hücresel yapıların morfolojisi, taramalı elektron mikroskobu (SEM) kullanılarak gözlenmiştir. Taramalı elektron mikroskobunda hücresel yapı tayini yapıldıktan sonra ise tüm numunler için hücrelerin polimer matrixi içerisindeki dağılımları ve hücre boyutları incelenmiş ve her bir numunenin hücre yoğunlukları hesaplanmıştır. Son olarak köpükleşmenin sert segment kristallerine olan etkisini gözlemlemek için, köpürtülmüş numunelerin DSC ile termal analizleri de yapılmıştır.





1. INTRODUCTION

Thermoplastic polyurethanes (TPUs) are formed by polyaddition reaction of polyols, short chain diols as chain extender and diisocyanates, which create two separated phase of hard segment and soft segment. The combination of diisocyanate with short-chain diol produces the hard segment (rigid) that forms crystalline structures acting as physical cross-links [1]. This gives plastic belongings to the polymer such as processing temperatures, continuous use temperature, tensile strength, tear strength, chemical and fluid resistance, adhesion to inks, adhesives and over-molding substrates. Soft segment (flexible) of TPU is created by the reaction of diisocyanate with long chain diol, and give TPU its elastomeric character such as hardness and flexibility, compression set and tensile set [2].

Polyols that produce soft segment are formed with a series of backbones and hydroxyl functionalities that provide processing and property requirements. The most industrially superior polyol backbones are ether and ester based. The polyester based TPUs generally show high characteristic features such as higher mechanical properties and higher heat resistance comparing to polyether based TPUs [2]. Polyether based TPUs have good hydrolytic stability and temperature flexibility, moreover, if polyether polyol is based on tetrahydrofuran, TPUs show higher mechanical properties as polyester based TPUs [3].

Polyols are often used as mixtures of molecules that are similar in nature but with different molecular weights, which defines the final properties of the polymer. Polyols used to make rigid polyurethanes have molecular weight in hundreds, while used to make flexible polyurethanes have molecular weights up to ten thousand or more [4].

A number of interesting properties resulting from rigid and flexible complex structure lead to the use of TPU in many applications in industry, especially in the form of foams [1]. TPU can be foamed by typical technologies such as foam extrusion, and foam injection molding. On the other hand, low density three dimensional complex geometries can be produce by bead foaming technology. In contrast to foam extrusion

and foam injection molding, bead foams are required to be molded and sintered in an steam chest molding machine [5]. Batch foaming process is one of the most common way to produce bead foams, with uniform and controlled morphologies, especially for lab scale studies, which involves a closed system such as an autoclave. The process is a one step manufacturing; first, polymer sample is saturated with a physical blowing agent such as CO₂ or hydrocarbons (i.e., butane or pentane) under certain temperatures and pressures for a certain time. Later, thermodynamic instability either by depressurization or by dipping in heated oil bath is introduced into saturated polymer sample. The modifications to the processing conditions, such as pressure drop rate (depressurization method), saturation pressure, temperature and time, alongside the polyol type and length affects the overall cell morphology in terms of cell size, cell density and foam density [6].

In this work, different types of TPUs that are different in soft segment length and their polyol backbone are foamed by depressurization batch foaming process. For a better understanding on how process conditions affects overall cell morphology and final foam product, all TPU samples were foamed with specific saturation time, temperature, pressure, and pressure drop rate. Thermal analysis was performed in differential scanning calorimetry (DSC) before and after foaming to observe crystal modifications and their relationship with foam morphology and property. Foamed samples were characterized using scanning electron microscope (SEM) to observe their cellular morphology and their cell densities. Densities of the foams were also seperately calculated.

ETPU bead foams with fine cell structure were obtained. By comparing TPUs having different Mw of polyol, how the length of soft segment can affect foam morphology was detaily studied. Process parameters on foam morphology and HS crystal structure were also investigated. Foaming process, which needs isothermal temperature and gas, simulated by annealing the samples at autoclave under high pressure CO₂ without inducing foaming (releasing the pressure very slowly) and its effect on crystalline structure of samples were examined using DSC.

2. LITERATURE REVIEW

2.1 Overview of Polymeric Foams

Polymeric foams include porous structures perceived as gaseous voids surrounded by a polymer matrix. The difference in nature between gas and solid makes polymeric foams unique materials that have special properties for several applications, such as specific tensile strength, light weight, toughness and sound insulation properties [7].

2.1.1 Classification of polymeric foams

Polymeric foams can be viewed from different practical perspectives, such as products, technology and components. Products can be categorized by their morphology as cell structure, cell size, and foam density; for instance, open cell versus closed cell, microcellular versus cellular, high density versus low density.

2.1.1.1 Cell structure classification

Depending on cell structure, polymeric foams are often categorized as either "open-cell" or "closed-cell". There are several differences between the two types, leading to advantages and disadvantages for both, depending on the desired application requirements.

In open cell foam, the surfaces of the bubbles are broken and air fills all of the spaces in the material; therefore, they have softer and spongier appearance. Open cell foam is incredibly affective as a sound barrier in normal noise frequency ranges and provide better absorptive capability. Open cell foam has lower densities than close cell foam which provides economical yield. However, the R-value of open cell foam is lower, thus heat resistance level is lower [8].

The closed cell foam structure is produced with composing gas bubbles in polymer matrix and after that matrix is stiffened because trap the gas bubbles [9]. The advantages of closed-cell foam compared to open-cell foam include its strength, higher R-value, and its greater resistance to the leakage of air or water vapor.

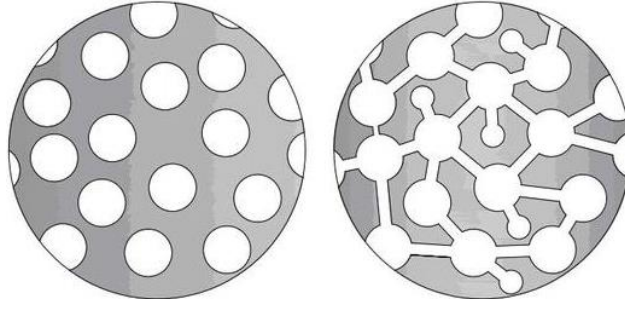


Figure 2.1: Open cell foam and Closed cell foam [8].

2.1.1.2 Cell size classification

Depending on cell sizes, polymeric foams can be classified as macrocellular foams ($> 100 \mu\text{m}$), microcellular foams ($1\text{-}100 \mu\text{m}$), ultra-microcellular foams ($0.1\text{-}1 \mu\text{m}$) and nano-cellular foams ($<0.1\mu\text{m}$) [10]. Cell size has effect on mechanical properties on material and depending on their mechanical properties polymeric foams have been used in different areas of applications. Microcellular materials have superior thermal, mechanical properties such as toughness, strength-to-weight ratio, high impact strength, also electrical and acoustic insulation properties [11]. On the other side nano-cellular polymer foams have many promising applications, for example to passively enhance the energy efficiency of buildings. The smaller the diameter, the lower the thermal conductivity and the better the insulating effect [12].

2.1.1.3 Cell density classification

Cell density is usually expressed as kg.m^{-3} . A more fundamental measure is relative density, R , which is defined in equation (2.1)

$$R = \frac{\rho_{foam}}{\rho_{polymer}} \quad (2.1)$$

Where ρ_{foam} is the foam density and $\rho_{polymer}$ is the original polymer density. Relative density may also be regarded as the volume fraction of polymer in a foam in the case of there is no other phases. Low density foams have $R < 0.1$, while structural foam injection moldings have R in the range between $0.4\text{-}0.8$ [13]. Foam density has impact on mechanical properties of foam. For instance, low density foams have good sound isolation and impact absorption. They can be preferred packaging materials because of lower good lower energy insulation [14]. On the other hand, high density foams used in building materials, furnishing, and transportation products.

2.1.2 Blowing agents

Blowing agents or foaming agents are used for generating gaseous phase in the polymeric foams. Since the particle size of the blowing agent and their uniform dispersion in the polymer matrix impact the cell distribution and the ratio of open cells to closed cells [15], the type of blowing agent is very important. There are some properties required for blowing agents, such as, high stability during storage, good affinity with the polymer, maximum production of gases at the polymer foaming temperature, nontoxic and noncorrosive, and low cost.

2.1.2.1 Physical blowing agents

Physical blowing agents (PBAs) do not participate in chemical reaction, liquids can be evaporated or gas is solved in a polymer matrix under high pressure could be desorbed by decompression. Subsequent pressure release or temperature increase results in a super-saturation state, and gas starts to form nuclei and expand [16].

Typical physical foaming agents are volatile chemicals such as chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC); however, their use has been greatly reduced globally due to their ozone-depleting potentials [17]. Volatile organic compounds (VOCs), such as hydrocarbons and alcohols, can also be used as PBAs, but they are flammable, detrimental to health, and react with ultraviolet light and nitrogen oxides to form tropospheric ozone. Therefore, there is an increasing pressure to also regulate the uses of them. Other choices of PBAs include hydrocarbons (HFC), inert gases such as N_2 , Ar and He, also CO_2 , and water. However, these are less soluble and more diffusive in polymer melts than their less environmental-friendly counterparts [18].

2.1.2.2 Chemical blowing agents

Chemical blowing agents are usually reactive species that generate gas by thermic decomposition through a chemical reaction with other constituents in polymer matrix [19].

According to the enthalpy of the process, there are two major types of CBAs; endothermic and exothermic. Endothermic foaming agents are substances that absorb energy for the decomposition. They are mostly inorganic chemicals like carbonates, hydrogen phosphates, tartrates and organic acid derivatives. The economically most

important endothermic foaming agents are sodium bicarbonate and citric acid derivatives which generate CO_2 upon decomposition. Exothermic foaming agents are mostly organic substances that, on reaching a certain temperature, decompose and release gas and energy. The released heat increases the temperature and reaction becomes even faster. That is why once started the reaction can no longer be influenced. Materials mainly foaming agents used as exothermic are Azodicarbonamide and hydrazide derivatives which generate N_2 upon decomposition [20].

Advantages of using CBAs are that they do not require any modification of existing equipment, and it is easier to form an even distribution of gas in the polymer matrix. However, they are more expensive than PBAs [16].

2.1.3 Foaming mechanism

Properties of polymer foams are originated by contained gas and polymer matrix as foam morphology. That is way, the mechanism of polymeric foams will be affected by alternatives of polymers, blowing agents and the controls of the cell structures. There are several methods to obtain polymeric foams, known as foam extrusion and injection foam molding. The cellular structure in plastics could be formed mechanically, chemically, or physically. Usually, there are four major steps in every foaming processes: (i) Formation of polymer/gas solution; (ii) Cell nucleation; (iii) Cell growth; and (iv) Cell Stabilization.

2.1.3.1 Formation of polymer/gas solution

Polymer foams contain generally two phases: solid phase and gaseous phase. Gaseous phase is dispersed matrix phase as voids or cells. To obtain gaseous cells, foaming agents, volatile liquids, and inert gases can be used. Because homogeneity of the polymer/gas solution has great influence the last cell morphology and mechanical properties, firstly, single-phase polymer/blowing agent solution should be produced. Moreover, gas solubility gives information about kinetic of foaming mechanism, cell nucleation, and also it has effect on physical properties of a polymer melt such as swollen volume, isothermal compressibility, and thermal expansion coefficient.

To be sure of the polymer/gas solution is uniform, the amount of blowing agent added to the mixture should be above the solubility limit of the process temperature and pressure. How much foaming agent is able to be solved in polymer/gas solution at

various temperature and pressure is very significant factor [5]. For this reason, existence of large gaps can be avoided during the foam producing process. There are plenty of methods for measuring the gas solubility and diffusivity in polymer at high temperatures and high-pressures such as the pressure decay method, the electro-balance method and magnetic suspension balance [21]. However, due to volume swelling of polymer melts, Equation of State approach was proposed for calculation gas solubility and PVT behavior of polymer melt [22]. Also, Flory Huggins, The Flory EOS, Simha–Somcynsky EOS and Sanchez–Lacombe EOS are the most popular approaches that used for polymeric system [23,24].

In addition to the system pressure requirement, it is also necessary to enhance the diffusion of gas in a polymer to meet the processing time requirements in a continuous process such as extrusion foaming. Arrhenius equation helps to calculate the diffusivity which expresses the speed of gas enter or leave out of polymer [25];

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \quad (2.2)$$

In this formula;

D = diffusivity

D₀ = diffusivity coefficient constant,

E_D = Activation energy for diffusion of gas

R = univarsal gas constant

T = system temperature

Since the diffusivity increases with temperature, the rate of gas diffusion is enhanced by an elevated temperature in typical extrusion foaming processes. To obtain ideal foaming conditions, gas solubility should be higher. Moreover, it provides forming greater cell nucleation and growth.

2.1.3.2 Cell nucleation

Cell nucleation is any process that leads to the formation of small bubbles in the polymer or polymer composite matrix from metastable polymer melt. Considering a polymer melt has been completely saturated with a blowing agent, the already saturated system becomes supersaturated as the gas solubility reduces by either heating or a pressure drop which is needed to break free energy barrier in polymer melts. Hence, small clusters of gas molecules become very small bubbles as energetically

stable pockets [16]. Generally, nucleation has been clarified by the classical nucleation theory (CNT). According to CNT, physically metastable state which corresponds supersaturated vapor phase will transform stable liquid phase. Chemical potential of liquid phase is lower than supersaturated vapor phase which is thermodynamically favorable for transformation of liquid to vapor. The system should have maximum free energy to overcome free energy barrier in spite of transformation. Overcoming energy barrier causes formation of small parts of the nucleus. If fluctuations are large enough, nucleus reach critical size and eventually nucleus grow spontaneously (Figure 2.2).

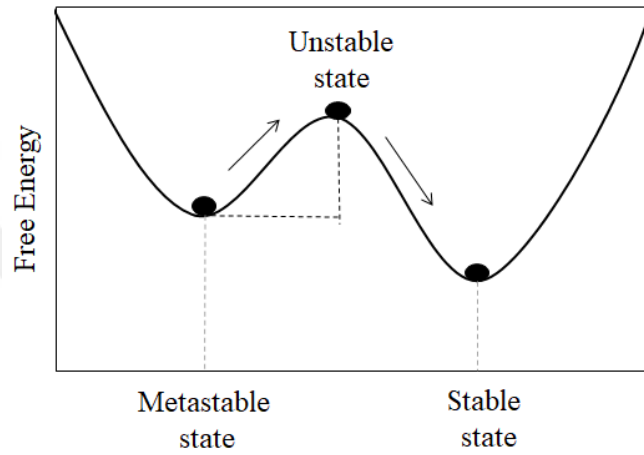


Figure 2.2: An illustration of Cell Nucleation Theory.

However, this theory is valid the reverse case in polymeric foam applications. To understand of nucleation in polymers some theoretical techniques were developed such as statistical mechanical density-functional theory (DFT), and self-consistent field theory (SCFT) [26].

In the Classical Nucleation Theory (CNT), nucleation presumably occurs in the new phase in the form of nucleus with a critical size and it is separated from the old phase by a dividing surface and thus the molecules of the old and new phases are separated [27]. CNT proves that the bubble will form smaller than critical size in the case of the energy given to the system is lower than maximum. Bubbles can grow spontaneously while bubbles are smaller than critical size precipitates into system. Critical size can be found from the following equation,

$$r_c = \frac{2\gamma}{P_{bub}P_{sys}} \quad (2.3)$$

where r_c is critical radius, γ is interfacial tension between liquid phase and cluster, P_{bub} is pressure inside the bubble and P_{sys} is pressure of the system. And the free energy given as;

$$\Delta G = 4\pi R^2\gamma + \frac{4\pi}{3}r^3(P_{bub} - P_{sys}) \quad (2.4)$$

where ΔG is Gibbs free energy and r is radius of the bubble [28]. If the nucleus is assumed to be spherical then equations can be written as;

$$r^* = \frac{2\gamma}{\Delta P} \quad (2.5)$$

$$\Delta G^* = \frac{16\pi\gamma^3}{\Delta P^2} \quad (2.6)$$

In this theory, generally two types of nucleation exist in polymeric foam applications which are homogenous and heterogeneous [27]. Homogeneous nucleation takes place in the initial single phase mixture and heterogeneous nucleation also occurs in the presence of a second phase such as additives. The second phase plays the role of nucleation sites and reduces the nucleation energy while increasing the rate of nucleation [27]. The nucleation rate, J , is given by:

$$J = J_0 e^{-W/k_B T} \quad (2.7)$$

W derives from equation by Gibbs energy. According to classical nucleation theory, homogeneous (W_{hom}), heterogeneous (W_{het}) energy barriers also are associated with the surface tension;

$$W_{hom} = \frac{16\pi\gamma^3}{3(\Delta P)^2} \quad (2.8)$$

$$W_{het} = \frac{16\pi\gamma^3 F}{3(\Delta P)^2} \quad (2.9)$$

Where γ is the surface tension between metastable polymer-gas mixture and nucleus site and according to equation surface tension is related with nucleus size. ΔP is the pressure difference of nucleating phase and metastable phase or it can be described

with difference inside and outside of the bubble. This explanation is for only bubble is very large [29-30]. Moreover, inner pressure of bubbles cannot estimate. $\Delta P/\Delta t$ is pressure drop which causes nucleation.

Homogenous cell nucleation

Classical nucleation theory has been used to define this type of nucleation behavior in which molecules are randomly nucleated inside of the polymer melt. Additives are not used into the solution. Besides, Han et al. [32], Lee et al. [33], and Leung et al. [34] calculated higher nucleation rates than those calculated by CNT.

Heterogenous cell nucleation

Addition of a second insoluble phase (solid particles) to the solution leads to a heterogeneous nucleation. The interfacial tension is reduced and the nucleus develops in the interface with the addition of the second phase known as the nucleation agent or nucleation site [35]. Heterogeneous nucleation becomes supersaturated due to the nucleating agents or impurities in composition of bubble. Number of nucleated cells can be controlled by varying the amount of nucleating agent. Heterogeneous nucleation decreases the free energy because of the phase boundaries between the impurities or nucleating agents and polymer melt, rather than homogeneous nucleation. Crystals in polymer matrix could also behave as cell nucleating agent and hence the crystal morphology and structure is extremely important to manufacture foams without using any additives.

2.1.3.3 Cell growth

After nucleated cells are formed, they can proceed to grow due to gas diffusion from the polymer matrix. Since the inside cells have higher pressure than outside pressure, nucleated cells want to decrease the drop of pressure difference between the inside and outside by gas diffusion [35]. Various parameters like viscosity, diffusion, number of nucleated cells, and gas concentration has great influence on cell growth. Further, cell growth mechanism can be controlled by process temperature since it affects diffusion and viscosity. For instance, gas diffusion and melt viscosity of polymer matrix improves when the temperature rises, which will cause to remain in cell growth rate. However, coalescence can occur if the growth rate is too fast [36]. Since the shape and structure of the cells have a great effect on the properties of the foam, the fundamentals of cell growth are important. Hence, it is necessary to be able to predict and control

the cell size during foam growth. There are two well-known cell growth models to study the dynamics of bubble growth during foaming process: Patel model (1980), also known as single bubble growth model and Amon and Denson cell model (1994).

Single bubble growth model

In 1980, Patel developed a simplified model for bubble growth in a viscous Newtonian fluid in which he considered an isolated stationary spherical gas bubble growing in a stagnant liquid of infinite extent because of diffusion from the liquid to the gas phase. [37] This model assumes that all physical properties of the liquid and the gas are constant, the system is isothermal and there is thermodynamic equilibrium, and the bubble is completely homogeneous and has a spherical symmetry [38]. Although this model gave several insights into the bubble growth phenomenon, its practical application in industry was severely limited, in real life a swarm of bubbles grows simultaneously, and they are expanding in close proximity to one another with a limited supply of gas. Hence, the application of the single bubble growth model in polymer foaming industry was very limited [39].

Cell model

Previous model defines the foaming system as a single spherical bubble growing in a large pool of polymer melt with enormous amount of gas available for growth. However, actually happening is a large amount of gas bubbles grow in close proximity to each other in a polymer-gas solution. The concept of a cell model was first introduced by Amon and Denson [40] in 1984. The study involved the growth of a group of gas bubbles divided by a thin film of polymer and dissolved gas into spherical microscopic unit cells of equal and constant mass during the injection molding process [39]. Cell model depends on the following assumption; there is a thermodynamic equilibrium at all times at the gas-liquid interface according to Henry law, the liquid in the polymer shell is incompressible, material properties of the polymer are independent of the blowing agent concentration, coalescence is negligible, and the number of bubbles per unit volume is assumed to be constant throughout the growth process [38]. These more realistic assumptions let the cell model to yield a final radius while other single bubble growth models show infinite growth of bubble radius with time [39]. This fundamental improvement caused more interest in this area of research and several studies have emerged since then.

2.1.3.4 Cell stabilization

Cell growth is associated with spherical bubbles [41]. When the bubbles expand in polymer matrix depending on the gas amount, their walls become thinner and fragile, thus they may rupture. This depends on the gas amount in the mixture and melt strength of the polymer matrix. When the wall between bubbles ruptures, the neighboring bubbles may combine together and form one larger bubble, which will assume non-spherical shape [41]. This is called as “cell coalescence”. It is also possible that gas molecules from smaller gas bubbles may diffuse to bigger ones through tunnels formed from wall rupture caused by the lower internal pressure in the larger cell, and finally results in disappearance of smaller gas bubbles. This is called as “cell coarsening” (cell ripening). If the amount of blowing agent is large, the bubble wall ruptures can become so severe that a great amount of gas may escape, which causes to “cell collapse”.

All these phenomena are significant mechanism of reduction of the final bubble density of foamed samples; therefore, they are not desirable because they affect the density as well as mechanical properties. The bubble stability depends on gas diffusivity, surface tension and viscosity since the cell coalescence, coarsening and collapse are affected by these parameters [42].

2.1.4 Properties of polymeric foams

2.1.4.1 Mechanical properties

Foam structure directly affects the mechanical properties of foam. For instance, the gases cannot stay together in open cell structure, which cause to foams to be stressed more than close cell structure. Moreover, air flow properties are affected by the cell size since they are dependent on strain rate [43]. On the other hand, air flow effect can be neglected in most cases in closed cell foams [44]. If cell sizes of foam are smaller, they have better energy absorption. Further, amount of closed cell structure increases, if cell size of foam lower. Foams that have open cell structure show lack of mechanical properties, however, they have better sound absorption.

2.1.4.2 Thermal conductivity

Thermal conductivity remains low for polymeric foams due to the lack of amount of solid structure. The gas in polymer responsible the most of heat transfer. Light gases provides better thermal conductivity; therefore, heavy gases are favorable as foaming

agents. However, their costs and impact on environment makes them almost impossible for the use [43]. Usually, CO₂ are used as foaming agents since the gas phase of foam is replaced by air which has only a higher thermal conductivity than heavy gases.

2.1.4.3 Flammability

Foams that are produced from volatile liquids as blowing agents are easily combustible. Since the flexible polyurethane foams are permeable to air due to their open-cell structure, they may burn easily when they exposed to a flame. Using flame retardants such as chlorinated phosphate esters, chlorinated paraffin, melamine powders and graphite can be used for increasing the safety of the industrial products [43].

2.1.5 Applications of polymeric foams

Polymer foams with the lowest density and greatest flexibility among porous materials are widely used in industry for a wide range of applications. Since they have many advantages, such as light weight, great specific strength, good sound attenuation and thermal insulation, and having a high energy absorption capacity, they can be widely used in many areas, including agriculture, aircraft and automotive industry, buildings and packaging, and daily necessities [45].

Polymer foam properties and applications mainly depend on the physical and chemical properties of the matrix and the cell structure, which is principally characterized by the cell density, shape, size, and the open- vs. closed-cell ratio. All these structural parameters have a great influence on the macroscopic properties of these foams.

2.2 Foam Manufacturing Technologies

2.2.1 Foam extrusion

Extrusion is the most common method of polymeric foam manufacturing. The type of extrusion process can be change according to morphology of foam and blowing agent which is used. Since the processing techniques and materials vary, there is no standard device and process method. For instance, both single-screw extruders (SSEs) and twin-screw extruders (TSEs) are used in foam extrusion for a variety of foamed products. The advantages of using SSEs are; they cost less than TSEs, and they are simpler to

understand and continue than TSE [46]. TSEs are generally preferred because of their performance over SSEs such as more useful solids feeding, better mixing of nucleating agents and polymer systems, better cooling and temperature control capability and so on [46].

Basically the foam extrusion process involves the following five distinctive steps: melting, mixing, cell nucleation, cell growth and solidifying of the polymer liquid. Firstly, the polymer and the blowing agent are mixed together and are melted by heating at high pressure in an extruder. The gas bubbles which are generated by the blowing agent are dissolved in the polymer melt under the pressure of inner part of the extruder.

When this mixture of gas bubbles and polymer melt is exposed to the atmosphere through the die of the extruder, it gets the super-saturation form, the pressure of the polymer melt are lowered, thus the dissolved gas forms the nucleus. The diffusion of dissolved gas in the polymer melt and the momentum transfer extend the nucleus. The decrease in temperature of the polymer melt due to cooling at the surface of the mold causes the viscosity of the polymer melt to increase.

Finally, the polymer melt near the surface is solidified because the gas bubbles near the surface cannot grow, and polymer melt in the central part is foamed [29]. In the foam extrusion process, growth of the gas bubbles is affected by the parameters of the concentration of the dissolved gas in the polymer melt, the distribution of the pressure, and the diffusivity of the gas, besides the mass, momentum, and the energy transfer between the polymer melt and the gas bubbles [29].

2.2.2 Foam injection molding

Foam injection molding technology (FIM), is a classical injection molding production process that an inert gas such as N_2 or CO_2 interpenetrate the polymer melt, and the foamable composition consisting of a single phase polymer/gas solution is injected into the mold cavity to produce foamed parts. Comparing to other methods, FIM has several advantages like capability of manufacturing lightweight and lightdensity products using less material and energy at rapidly manufacture rates with improved viscosity and temperature. Recent studies show that foams produced by FIM technology have improved mechanical and physical properties [35]. Notwithstanding, FIM technology lack of producing complex geometry products for foams.

FIM technology can be classified in two type, which are low-pressure and high-pressure foam injection molding. Low pressure FIM which its cavity pressure between 0.5 to 10 MPa are able to reach by the small shot size and also lower tonnage in the molding machine. Low pressure FIM is preferred when producing of thick-walled products on account of filling most of the cavity volume in the mold. Low pressure FIM reduces cost and stress, and it also improves dimension stability. However, high pressure FIM is distinguished with quick filling of the mold cavity, the split of the core foaming and solid skin layer formation, and the core foaming owing to cooling polymer shrinkage. Process requires more cost and material since the volume expansion from foaming is minimum.

2.2.3 Bead Foaming

Foam extrusion and foam injection molding are the two main continuous process in foam industry. However, there is another technology, i.e., bead foaming, which has both the foam expansion of extrusion foaming and the part geometry complexity of injection foam molding. Therefore, it is a very encouraging option for foaming technologies. In contrast to foam extrusion and injection molding, bead foaming is a production method that beads would be molded and hence low density foam with three dimensional complex geometries can be formed [47].

One of the most popular bead foams is expandable polystyrene (EPS) bead foams which are offenly used in cooler and cushioning materials. Also expanded polypropylene (EPP) bead foams having special properties such as high dimensional stability and superior elasticity are widely used in automotive industry and high-end packing materials. Apart from EPS and EPP, thanks to its biodegradability, expanded polylacticacid (EPLA) bead foams are recently drawing interest [48].

There are three methods to produce bead foams: suspension polymerization with blowing agent, extrusion foaming with underwater pelletizer, and autoclave (batch) foaming process.

2.2.3.1 Suspension polymerization with blowing agent

Suspension polymerization consists polymerisation where the monomer is suspended as droplets in water, and the addition of blowing agent, which diffuse into the droplets during the final stage of polymerization [49]. After polymerization, polymer beads are

sieved which is sorting the beads through meshes to get several fractions of uniform bead size. At ambient temperatures, the polymer shell is stiff; however, when beads are exposed to heat above the glass-transition temperature of the shell polymer and the boiling temperature of trapped blowing agent, polymer shell softens and the hydrocarbon increases the internal pressure, which causes microspheres to expand [50]. After cooling, the blowing agent is entrapped in polymer bead and the volume of bead is retained. This process is known as pre-expansion, which can be performed either by steam or hot air. Pre-expanded beads are usually aged for at least 24 hours before molding, which allows air to cool and make them harder. After aging, the beads are fed into a mold of desired shape and beads are expanded once more by injected low pressure steam between them. Amorphous polymers can be synthesized by suspension polymerization. Expandable polystyrene is the most commonly produced polymer by suspension polymerization. Main disadvantage of suspension polymerization is clearly not all polymers can be synthesized by this method; moreover, using hydrocarbon (pentane etc) as blowing agent is harmful for ozone layer.

2.2.3.2 Foam extrusion with underwater pelletizer

Foam extrusion with underwater pelletizer is a method mostly used in industry to produce expandable or expanded beads. This method provides bead foams by first introducing polymer and blowing agent into an extruder, then polymer/gas melt discharging through a hole-plate into a water-stream and cutting chamber [51]. During cooling step, blowing agent traps in polymer since the water steam pressure is higher than vapour pressure blowing agent. Later this dissolved gas evaporates and results in expanded beads at lower pressures [52]. One advantage of this method is that pellet size and weight can be varied since the extrusion rate and the speed of the cutter can be controlled. Another advantage is properties of final product can be changed easily since processing and performance additives can be added during extrusion process [53]. However, speed of the cutter and temperature/pressure of the water can affect the required process temperature which is a challenge since it may cause unusable products [54].

2.2.3.3 Autoclave foaming

Autoclave foaming is a discontinuous foaming process which includes a closed system such as an autoclave. It involves two steps; the saturation of polymer sample with a

physical blowing agent such as CO₂ or N₂ under a specific temperature and pressure for a certain time, and expansion of supersaturated polymer sample by thermodynamic instability. Thermodynamic instability can be introduced to the sample either by depressurization or increase of temperature. Depressurization method includes release of pressure to induce foaming after sample saturation. Pressure drop-rate is very important factor as it affects the overall cell morphology [55]. Increase of temperature method involves the removal of saturated sample from the autoclave and dipping into pre-heated oil bath.

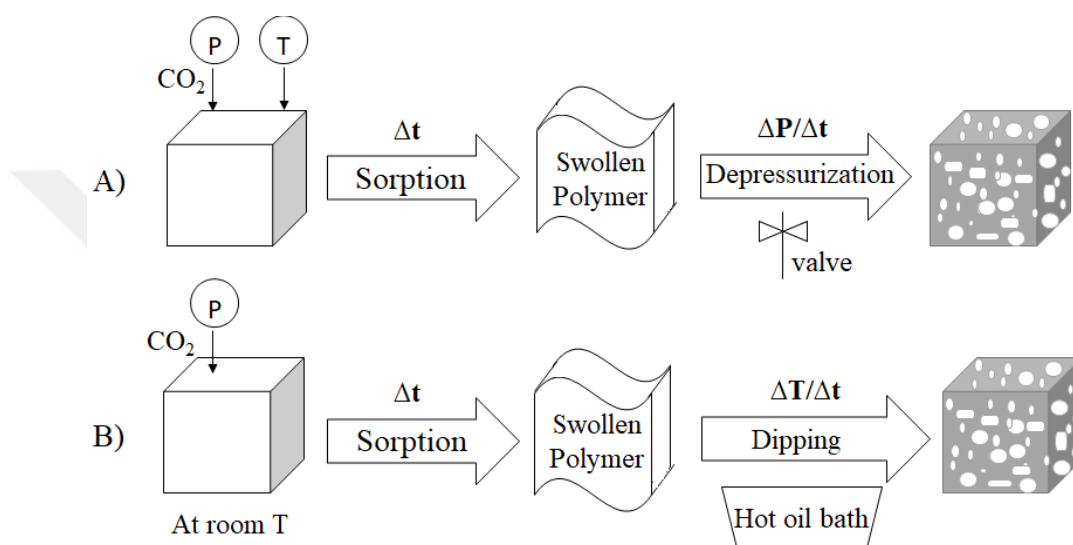


Figure2.3: Schematic of batch process A) Pressure induced method, B) Temperature induced method.

Autoclave foaming process shows a good reproducibility due to the exact process controlling; however, suffers from the intrinsic problem of low production rate. Therefore, it is best suited for lab-scale studies and understanding foam mechanisms such as cell morphology of foam, cell nucleation and growth, sorption kinetics, and influence of process conditions on foam.

2.2.3.4 Sintering with steam-chest moulding

After bead foaming process, foamed beads are molded in steam-chest moulding machine to produce complex parts. High temperature steam softens the surface of the beads and cause interbead bonding development involved the diffusion of polymer chains across interbead regions [56]. Interbead bonding increases with the moulding pressure and time, which is necessary to provide favourable mechanical properties. However, if the moulding time is too long, their cell structure might collapse [56].

The sintering process includes a series of operations. Firstly, the mold is filled by beads. Then, beads are molten with hot steam which penetrates and condenses in beads. When depressurized, steam inside the cells begins to gasify and expand the foams. During water cooling, dimensional stability is ensured by solidification of interfaces of the beads. Last step is ejection of the molded part from steam chest moulding machine.

2.3 Thermoplastic Polyurethane (TPU)

Thermoplastic polyurethane (TPU) is a multi-phase block copolymer that is created when three basic raw materials are combined together; a polyol (long chain diol), a chain extender (short chain diol), and a diisocyanate. TPU includes of thermodynamically incompatible hard and soft segments (Figure 3.1).

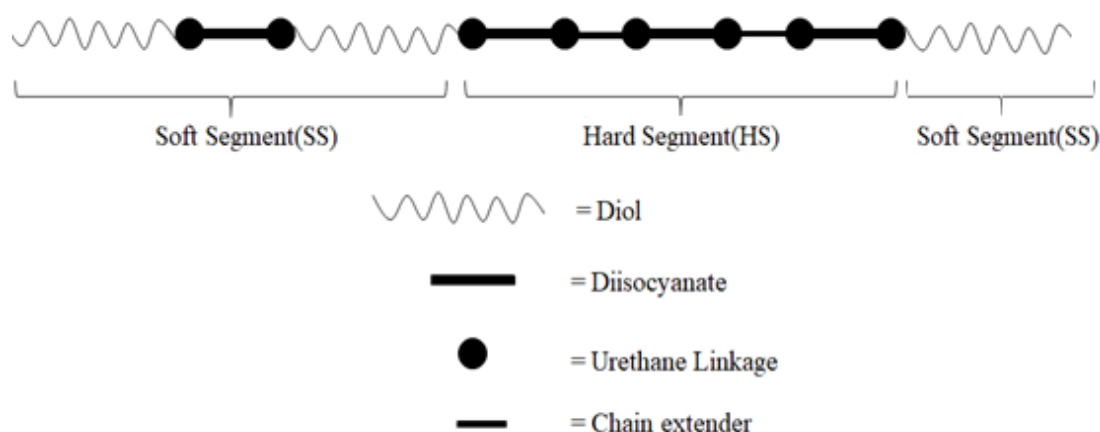


Figure 2.4: Molecular structure of a thermoplastic polyurethane.

Soft segment which is based on the type of polyol can either be a polyether or polyester. The polyester-based TPUs have the characteristic features such as higher mechanical properties and higher heat resistance, and higher resistance to mineral oils compering to polyether-based TPUs. However, the polyether-based TPUs have the characteristic features such as best-low temperature flexibility, acid-base resistance, and hydrolysis resistance [57]. Also, hard segment which is based on the type of isocyanate can either be aromatic or aliphatic group aromatic isocyanates like 4,4'-methylenediphenlydiisocyanate (MDI) give flexibility, strength and toughness, while aliphatic isocyanates like dicyclohexylmethane 4,4'-diisocyanate (H12MDI) and hexamethlyene diisocynate (HDI) give light stable and optical clarity properties [58].

2.3.1 TPU synthesis

2.3.1.1 One shot method

In one-shot technique, polyols, isocyanates, chain extenders and additives are mixed together and reacted all at once. Therefore, isocyanates are free to react with any other compound, especially with chain extenders since they are more reactive than high molecular weight polyols. The one-shot method yields a narrower distribution of hard segment lengths. One-shot process is frequently applied in industry to reduce the cost. This cause to the formation of hard segment in random length. There is no control over hard segment chain length and, as a result, the hard block domain sizes are highly dispersed as well, which reduces physical properties [59]. Even though, one shot method is not quite as good in terms of physical properties, do have important advantage that they are easier to work with because high molecular weight, high viscosity pre-polymers are avoided. As a result, one-shot process is frequently applied in industry to reduce the cost.

2.3.1.2 Pre-polymer method

The pre-polymer method includes a different sequence of reactions. First step is a diisocyanate is reacted with a high molecular weight diol to obtain an NCO-terminated prepolymer of low NCO group concentration. Second step, called as chain extension, links the high molecular weight pre-polymer chains together. Since a pre-polymer is synthesized prior to forming the final polymer, this method also called as two-shot technique. Creating the pre-polymer leads to most of the diisocyanate molecules bond to the end of a long polyol chain. Upon chain extension, the remaining NCO groups are reacted, forming uniform hard segments of one chain extender and two isocyanate units, which causes hard block domains to be relatively small and numerous. This molecular regularity results in better material properties [59].

2.3.2 Crystal structure and morphology of TPU

TPU final properties are mostly affected by its morphology. Especially, the soft and hard domain size and amount, the nature of domain interface, also mixing of hard segments into the soft segment phase greatly change most of physical properties such as elasticity and energy capacity [60]. Typical polyurethane is extensively hydrogen bonded, the donor being N-H group of urethane or urea linkage in the hard segment.

The proton acceptor may be either carbonyl group in the urethane or urea hard segment, or the carbonyl of ester or ether in the soft segment (Figure 2.5)

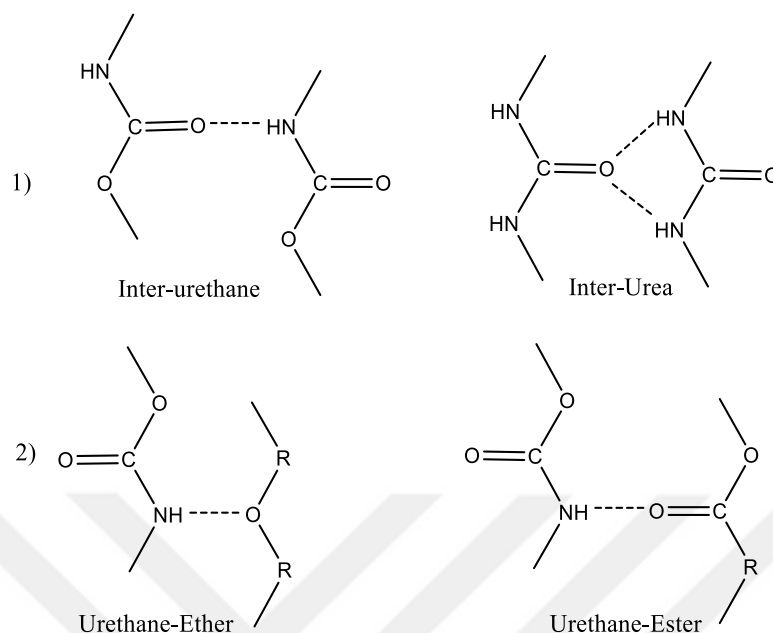


Figure 2.5: Hydrogen bonding in polyurethanes; (1) between HS-HS and (2) between HS-SS.

The primary force for microphase separation is believed to be the strong intermolecular interaction (hydrogen bonding) between urethane units. The relatively non-polar polyol soft segments and short polar isocyanate/chain extender hard segments of the polymer backbone are incompatible and tend to aggregate into their own microdomains, called hard domains (hard block) and soft domains (soft block), respectively (Figure 2.6).

Hydrogen bonding in hard domains forms not a chemical but a physical cross-link, which makes TPU thermally reversible. This means like all thermoplastic elastomers, TPU is elastic and melt-processable.

2.3.3 Thermal behavior of TPU

As it was mentioned before, TPUs consist of hard and soft segments which induce phase separation due to thermodynamic incompatibility between the segments. Phase separation causes a microdomain structure. Since TPUs have different hard segment morphology, more than one endotherms in TPU exist. Differential scanning calorimetry (DSC) is used for investigating the endothermic behavior of TPU. The endothermic peak at low temperature represents the short range order crystalline

which is obtained by annealing. On the other hand, long range order crystalline of hard segment is disordered at higher endothermic peak [61].

Analyzing the thermal behavior of the TPU is essential for the processing and designing. The investigation of thermal decomposition leads to determine optimum process condition. By thermal gravimetric analysis (TGA), thermal stability of TPU can be observed. Generally, with increasing temperature trapped volatile materials inside the TPU are released at the beginning. Further temperature, de-polymerization takes place and induces weight loss. Finally, thermal break down of the chains occurs and complex char, decomposition products form [62]. Beside the TGA analysis, FTIR, GC and NMR are also used for investigate decomposition route. DTG is another method which is used for understanding onset decomposition temperature of TPU. Thermal stability is basically associated with hard and soft segment and chain extender structure. Composition and length of HS/SS, branching and molecular weight have an impact on thermal behavior of TPU [63].

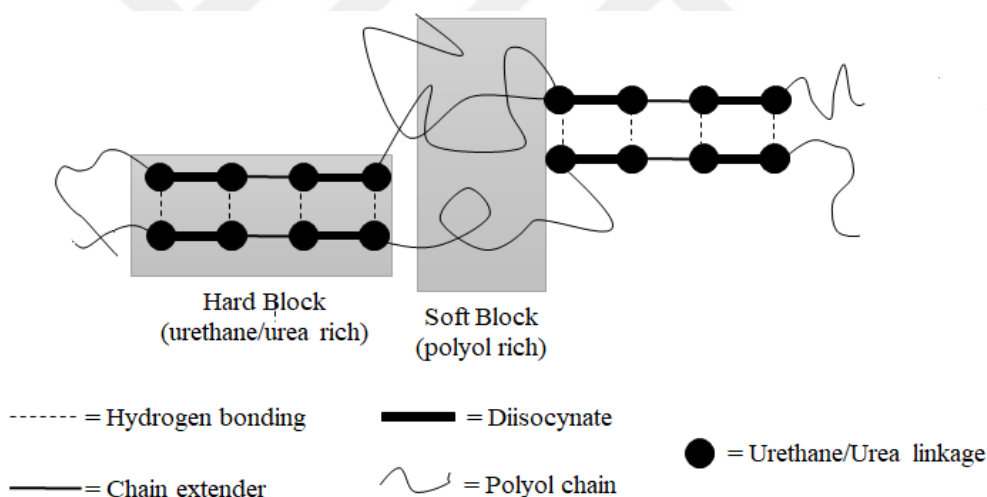


Figure 2.6: Molecular morphology of a typical TPU: Hard and Soft domains.

Moreover, the phase separation in TPU depends on hydrogen bonding between two phases. If hydrogen bonds exist only within the hard segment domains, phase separation occurs to a greater extent. However, if they can be formed between the soft and hard segments, interphase hydrogen bonding improves the phase mixing [64]. Generally, phase separation is not complete and the microstructure of TPU is not pure, includes of mixed hard segment and soft segment chains [5]. The intersegmental mixing within the phases affects both morphology and mechanical properties. For instance, inclusion of hard segments within the soft microphase increases the glass

transition temperature and decreases the elastic properties of TPU. On the other hand, inclusion of soft segments within the hard microphase, decreases the glass transition temperature [65].

Also the plasticity and viscosity of the material arise because this intermolecular interaction based on hydrogen bonding between hard segments. Hard segments are organized molecular parts and they stay together due to hydrogen bonding between them. Crystalline properties increases proportion of hard segments increase in TPU. The residual hard segments which exist in soft domains dissolve in the soft domains at elevated temperature. Heating above the melting temperature of the hard segment cause to a homogenous viscous melt and following cooling result in separation of soft segments and hard segments. Phase separation is dependent on the cooling rate and annealing conditions, since the mobility of the polymer chains decreases with lowering temperature. Thus, domain structure or crystallite morphology can be changed by different phase separation [65].

2.4 Expanded TPU (ETPU)

Expanded TPU bead foams (ETPU) is widely used in furniture, automotive, sportswear, and packaging applications, since shows many properties such as light-weight, high flexible, great cushioning effect and fast energy restoration in compression [66]. Foaming of TPU has advantages of reducing its hardness without adding any plasticizers, which relatively reduces its high cost. Softer TPUs which have low concentration of hard segment and low melting point shows better flowability in lower processing conditions (i.e. temperature, pressure). The softness of the beads also makes adhesive-bonding of the ETPU beads more effective during sintering step [67].

Production of ETPU can be achieved by both extrusion with underwater pelletizer and batch process with high pressure chamber. In batch process, TPU pellets first are placed into high pressure cell, saturated with blowing agent under a certain pressure, and heated up to near its softening temperature. The impregnation with foaming agent near its softening point leads to present HS crystal region in TPU rearrange. In the end of saturation time, high pressure chamber is depressurized to induce foaming. This final step result in formation of new HS crystallites in microstructure, which applies as heterogeneous bubble nucleating agents and forms ETPU bead foams [68].

ETPU bead foams are mostly preferred for their good sintering behavior even at lower vapor pressures. Molded ETPU product shows small deformation, low shrinkage, and good appealing appearance [69].

2.4.1 Foaming behavior of ETPU

As it was mentioned before HS crystallites in TPU have a role as nucleating agent; therefore, they have a critical effect on overall foam morphology, expansion ratio and foam density. During foaming process existing crystallites arrange themselves under the effect of process temperature and pressure. Hence, these parameters need to be chosen as to TPUs HS crystallites. For instance, low amount of HS crystallites provides higher elastic properties, thus higher expansion could be observed. For TPUs that have higher amount of HS crystallites, higher temperatures needed for impregnation of blowing agent and sufficient expansion. However, it should be considered that HS crystallites should not be completely melted for their role as nucleating agent. TPUs that have more SS parts are more flexible and shows higher entanglement, thus blowing agent can easily impregnate which leads to easier expansion [5].

2.4.2 Thermal behavior of ETPU

Foaming causes biaxial stretching, which enhance the amount and/or degree of perfection of HS crystallites of TPU. Hence, ETPU bead foams could possess higher melting temperature and/or wider melting peak comparing to its non-foam material. Furthermore, foaming with water leads to increase the melting temperature of ETPU because of increasing the total heat of fusion (ΔH_T) (J/g). Remaining the annealing temperature also increases the melting temperature of ETPU foam since the overall crystallinity is effected [5].

2.4.3 Developments of ETPU bead foam

Recently, researchers have started to explore the foaming behavior of ETPU bead foams. Since the influence of polymer crystallines can induce cell nucleation during foaming process [71], there has be growing interest in the role of the HS crystalline domains of TPU on foaming.

Hossieny et al. [72] indicated that dissolved butane gas acts as a plasticizer and improves phase separation of HS chains leading HS crystalline domains to enlarge. As

a result, cell nucleation is evolved by these large HS domains. Researches compared T_g values of two different TPU samples after annealing at various temperatures without gas and with butane gas (Figure 2.7).

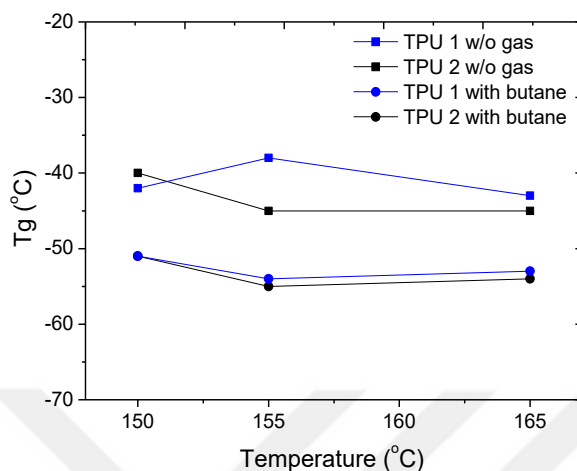


Figure 2.7: T_g values of annealed TPUs with and without gas [72].

They indicated that T_g values lowered, since butane gas distanced the intermolecular distance and mobility of chains. As a result, rearrangement of chains caused to evolve phase separation between hard and soft segments and resulted in growing HS crystallinity of melting peaks of TPUs, meaning an increase in heat of fusion (ΔH_{T_m}). Moreover, heat of fusion (ΔH_{T_m}) increased even more by remaining the butane pressure, since butane improved further the HS chain mobility.

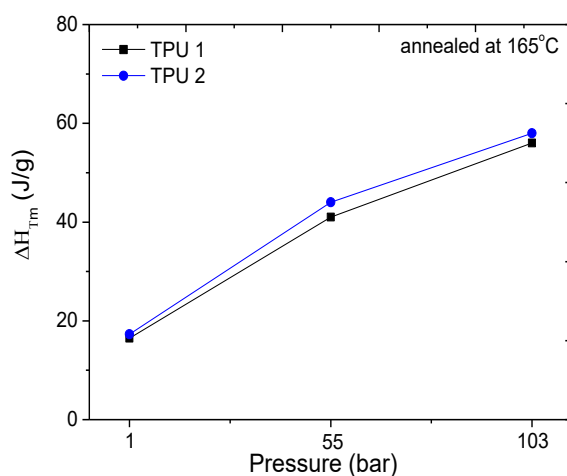


Figure 2.8: Comparison of total heat of fusion of TPU samples after annealing at ambient pressure (1 bar), 55 bar butane, and 103 bar butane [72].

They also pointed out that remaining the saturation pressure lowered free energy barrier of bubble nucleation, furthermore heterogenous nucleation was promoted by HS crystallites, consequently cell density increased and TPU foam with microcellular obtained.

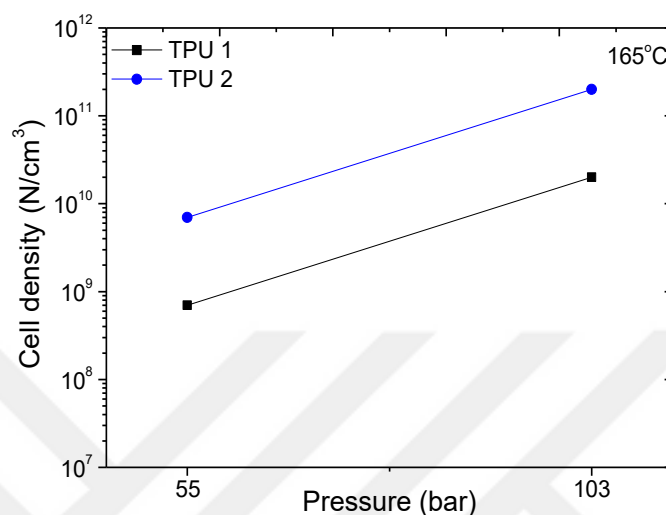


Figure 2.9: Cell density of TPU samples foamed at 55 and 103 bar [72]

Another research showed that the presence of glycerol monostrate (GMS) promoted the phase separation and crystallization behavior of TPU and influenced the cell nucleation during foaming, also increased the cell density [65].

Studies about the multiple endotherms, size and the position of melting peaks of TPU have been reported in few literatures. They attributed with changes in segments ratio, polyol length, annealing, processing temperature and mechanical deformations. Since annealing causes rearrangement of HS domains and improves crystallization of TPU, several studies investigated thermal annealing effect without present of high pressure gas on the crystallization evolution. In addition, the thermal annealing effect on TPU's structure in the presence of high pressure butane gas was performed by Hosseiny et al [72] as mentioned above.

Nonetheless, studies discussing crystallization of HS of TPU in the presence of high pressure gas is very limited. Creating multiple endotherms and effect of gas can be seen in some studies of other semicrystalline polymers. A study of Nofar et al. [73] on polylactide acid (PLA) bead foams with a double crystal melting peak structure showed the generation of the crystals with a high melting point during thermal

annealing with present of high pressure CO₂, significantly affect the foam structure. High saturation pressures of CO₂ caused to increase of gas content dissolved in polymer, which improved cell nucleation and decreased the high melting crystal sizes. Therefore, heterogenous cell nucleation around the small size crystals was enhanced which resulted in uniform foam structure, improved foam properties such as expansion ratio and cell density [74]. Nofar et al. [75] studied that EPP foam with a double crystal melting peak structure dependency on the annealing temperature, soaking time and saturation pressure. While annealing temperature was the most important parameter for creating double crystal melting peak, longer annealing time also promoted high melting temperature peak by giving time for rearrangement of unmelted crystals. Moreover, higher saturation pressures decreased required temperature for creating higher melting peak, since CO₂ acted as plasticizer [76].

One of the most important problems of ETPU bead foams is high shrinkage ratio which affects expansion ratio, surface morphology and properties of final product since the dissolved gas in ETPU beads lean to escape. There are some studies concentrating on modification of TPU by improving rheological and crystalline properties, hence recover the shrinkage of the foam. A study of Hossieny et al. [65] showed that the lubricating effect of GMS remarkably influences the HS crystallization of TPU during foaming process with butane, which improves cell density and expansion while reduces cell coalescence. Zhang et al. [77] studied foaming properties of TPU blended with acrylonitrile-butadienestyrene copolymer (ABS) to improve cell morphology and decrease the shrinkage ratio. Increasing ABS content enhanced the rheological and foaming properties of TPU blend. These improved properties helped to produce foams with better expansion ratio, cell morphology and anti-shrinkage properties.

Moreover, one the most recent study of ETPU by Zhao et al. [78] investigated the effect of process parameters on the expansion ratio, shrinkage ratio and foam morphology. According to results, temperature of foam process was the most significant parameter to expansion ratio and shrinkage ratio of ETPU bead foams. They observed that high saturation pressure had a great impact on shrinkage due to extending the concentration gradient between inside and outside of the bead foams (Figure 2.10), which promotes CO₂ to diffuse out. They obtained highest expansion ratio, medium cell diameter, and lower shrinkage in the process conditions of 150 bar, 60 min, 100°C.

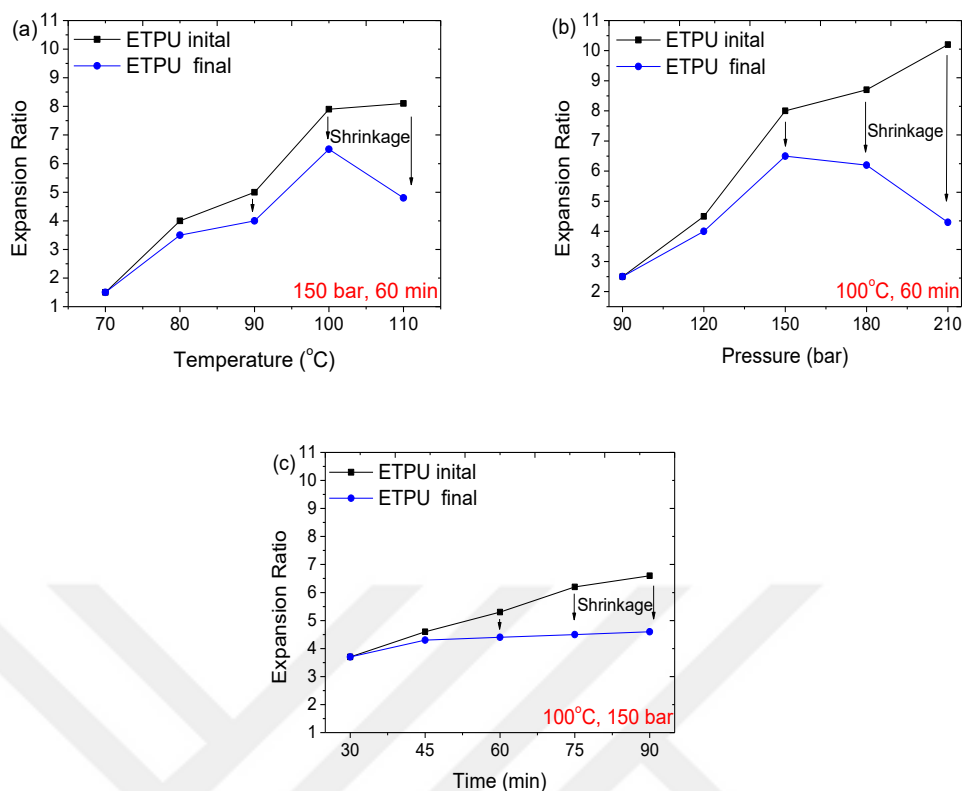


Figure 2.10: Expansion ratios of initial and final ETPUs at various a) saturation pressure; (b) saturation temperature; (c) soaking time [78].

Ge et al. [79] investigated microcellular TPU foaming different hard segment contents to evaluate cell structure and tensile properties using solid state batch foaming. They showed that after saturation at room temperature and immersing in hot oil, low hard segment content expanded more, while high hard segment content TPU creates more crystalline region, thus expansion ratio was restrained. Figure 2.11 shows the cell morphology of TPU samples, with higher cell density of low HS content of TPU, and lowest cell density of high HS content of TPU.

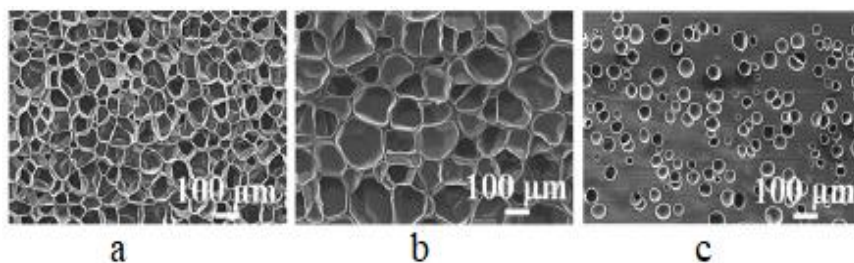


Figure 2.11: SEM images of the cell morphologies of a) low HS TPU b) medium HS TPU c) high HS of TPU saturated at 35 bar CO₂ for 12 hours then foamed at 100 °C hot oil bath for 30 sec. [79].

Yeh et al. [80] added nanoclay into TPU in their study to improve cell nucleation and cell density. Well expanded TPUs were obtained with high cell density by adding only 1%wt nanoclay. Increasing the nanoclay content resulted in decreasing foam density while the cell size stayed stable. A similar study by Keshtkar et al. [81] examined foaming behavior of PLA with nanoclay using CO₂ as blowing agent during foam extrusion process. Not only cell nucleation and cell growth increased, but also fast crystallization and nucleated crystals triggered by the adding nanoparticles. Moreover, studies of Nofar et al. [82-84] suggested that the adding nano/micro-sized particles such as talc, nanosilica, and nanoclay significantly affected foaming behavior of PLA using supercritical CO₂. Adding nanoparticles improved expansion ratio and cell density of PLA foams through increasing the low melt strength of PLA and promoting more cell nucleation around the nanoparticles and the nucleated crystals.

In this thesis, for the first time we explored the bead foaming behavior of ether based and ester based TPUs using supercritical CO₂ and furthermore explored the effect of TPU's soft segment molecular weight with constant hard-segment contents (using three different ester based TPUs) on hard segment crystallization and hence the TPU foaming behavior. A study of ETPU's foaming and crystallization behavior using butane gas has been done before, however the effect of CO₂ on crystallization behavior of microcellular ETPU bead foams is extensively explored by performing several experiments with different processing parameters such as saturation temperature, saturation pressure and saturation time in this research. We used several variations of TPU in terms of polyol type (ester or ether based) and changing Mw of polyol, to show dependency of foaming behavior on the chemical structure of TPUs. The DSC simulation were also conducted to see how the crystallization would develop and evolve with processing parameters and hence to create relationship between crystallization and foaming of TPU. We used one step foaming which is saturating TPU beads at elevated temperature for a given time and pressure where foaming occurs with fast depressurization.

3. EXPERIMENTAL PROCEDURE

3.1 Materials

All TPUs were supplied by Huntsman Polyurethanes, Belgium. Samples have almost same amount of hard segments consisting of 4,4'-MDI and 1,4-butanediol. PL1 are produced with pTHF as soft segment, while PL2 and PL4 series are based on polyester polyol of adipic acid and butanediol. Their molecular weights are given in Table 3.1. Chemical structure of the samples is illustrated in Figure 3.2.

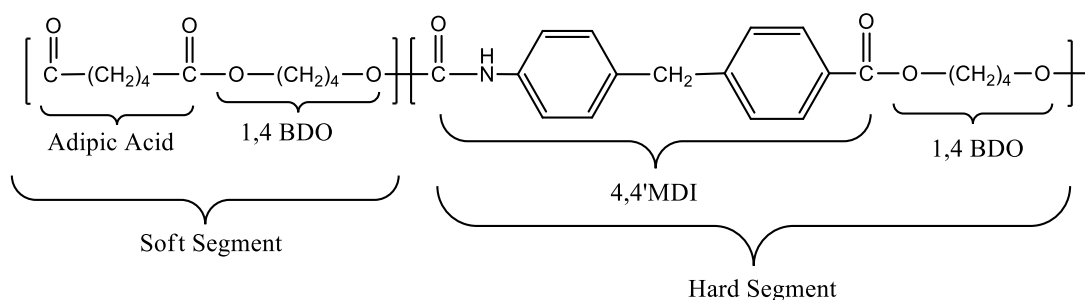
Table 3.1: List of samples.

Sample	SS Type	HS(%)	Mw of Polyol
PL1.A80	pTHF	37.2	1000
PL2.A80	AA-BDO	38.6	1000
PL4.28-58	polyester AA-BDO	35.3	2000
PL4.28-32	polyester AA-BDO	37.6	3500



Figure 3.1: Granules of samples.

Ester Based TPU (PL2&PL4 series)



Ether Based TPU (PL1)

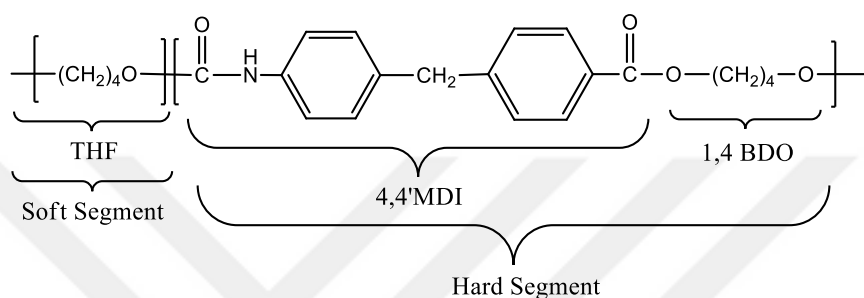


Figure 3.2: Chemical structure of TPU samples.

3.2 Thermal Analysis of TPU

3.2.1 Thermogravimetric analysis (TGA)

Before thermogravimetric analyses to investigate the onset of degradation and thermal decomposition behavior of TPUs, samples were dried in the vacuum oven at 100°C. Then they were heated from room temperature to 600°C at a heating rate of 10°C/min in the presence of N₂. The purging gas contacts and excess the vapor phase of samples and the remaining weight of the samples are recorded at those temperatures.

3.2.2 Crystallization analysis with differential scanning calorimeter (DSC)

Both non-isothermal and isothermal crystallization behaviors of TPU samples were examined using a DSC6200 (Seiko Instruments).

3.2.2.1 Non-isothermal melt crystallization analysis

Non-isothermal crystallization kinetics of the samples were investigated by DSC to understand the effect of molecular weight on TPUs phase separation and crystallization behavior. Samples were heated from 20°C to 230°C at a heating rate of 10°C/min and equilibrated at 230°C for 2 min. Then samples were cooled to -50°C at

a cooling rate of 10°C/min. Finally, samples were reheated to 230°C at a rate of 10°C/min.

3.2.2.2 Isothermal crystallization analysis

The isothermal crystallization kinetics of TPU samples were also investigated by DSC to simulate foaming process without gas. Samples were heated to annealing temperature from 20 °C at heating rate of 10 °C/min. Samples are annealed at temperatures of 120, 140, 160, 180°C for 30 min. Later samples were cooled to 20 °C at the rate of 10 °C/min. Then they were reheated to 230°C.

3.3 Rheological Analysis of TPU

The rheological behavior of the TPU samples were measured using an oscillatory rheometer and a melt flow indexer. To use in rheometer, samples were dried in a vacuum at 100°C and hot pressed and prepared with circular shapes of 25 mm in diameter and 1 mm in thickness as it seen in Figure 3.3.

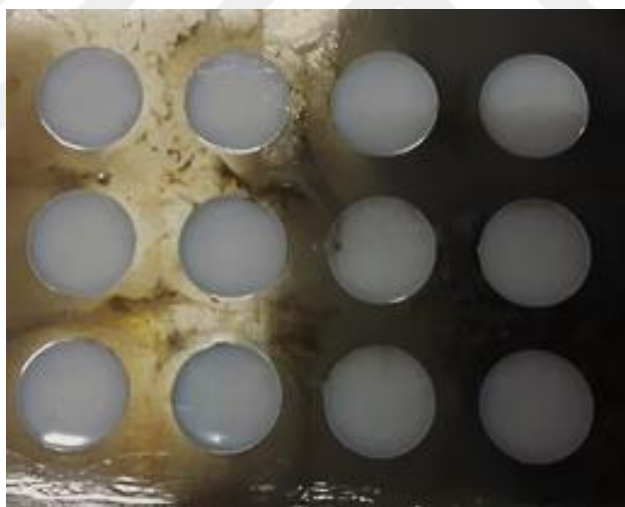


Figure 3.3: Mould for rheological measurements.

3.3.1 Rheological measurements with rheometer

To measure the complex shear viscosities, storage and loss modulus of TPU samples Rheometer MCR 302 (Anton Paar) with convection temperature device was used. The frequency sweep test was carried by varying the angular frequency range from 0.1 to 100 rad/s. Dynamic oscillatory tests were performed at a strain rate of 0.5% corresponding to the linear viscoelastic zone. The experiments were done in the

presence of a N_2 to eliminate any degradation. The linear viscoelastic zone was decided for each samples after repeating by changing temperatures during strain sweep experiments.

3.3.2 Melt flow index (MFI)

Melt flow index (MFI) device was used to explore the viscosity of TPU samples. Analyses were performed at 200°C with 2.16 kg. The weight of melt in grams flowing through the capillary in 10 minutes was measured.

3.4 Foaming Setup and Procedure

The autoclave foaming chamber setup is illustrated in Figure 3.4. Sytem contains CO_2 tank, blowing agent pump, high pressure vessel, and corresponding connections. TPU samples were first dried at 50°C overnight in vacuum oven. Melt temperatures were examined from DSC results to determine the process temperature range. Four samples were placed into high pressure vessel. It was saturated with CO_2 using a syringe pump and kept at constant pressure (2000 psi) and heated to saturation temperatures. Various temperatures were explored to find appreciable temperature. After the saturation of samples for 30 min, gas was released rapidly by a ball valve which was connected to the vessel, and vessel was dipped into water bath for fast cooling.

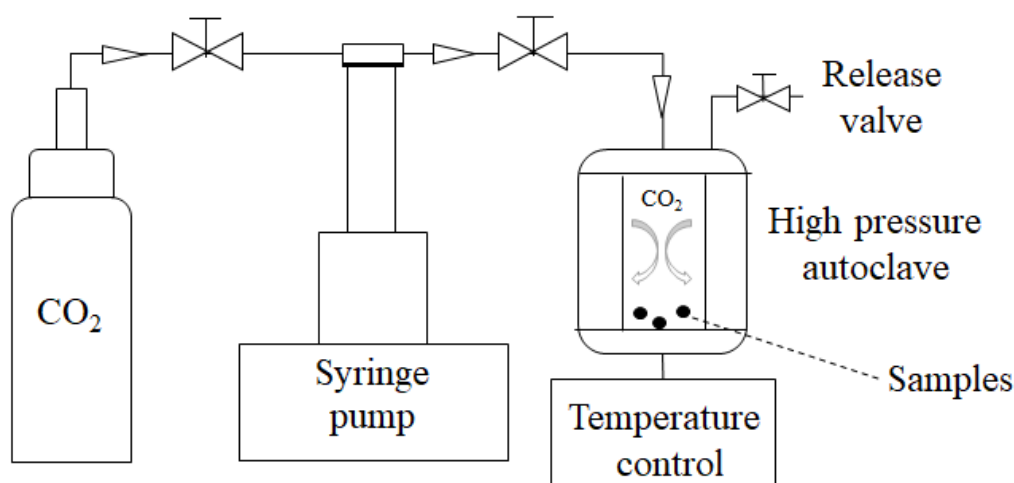


Figure 3.4: Schematic of batch foaming process.

According to most reliable structure of bead foams, saturation temperature was selected. Then, various conditions were studied to understand time and pressure effect. During the processes, one parameter was fixed while the others change. All

experiments were repeated with very slow pressure drop rates without inducing foaming experiments. All experiment conditions were shown in tables 3.2 to 3.5.

Table 3.2: Experiment conditions for PL1.A80.

Conditions	Temperature(°C)	Pressure(psi)	Time(min)
	85*		
P&t fixed	100	2000	30
	115		
T&t fixed	85	1000	30
		1500	
P&T fixed	85	2000	15
			60

Table 3.3: Experiment conditions for PL2.A80.

Conditions	Temperature	Pressure	Time
	80		
P&t fixed	100	2000	30
	110*		
	120		
T&t fixed	110	1000	30
		1500	
P&T fixed	110	2000	15
			60

Table 3.4: Experiment conditions for PL4.28-58.

Conditions	Temperature	Pressure	Time
	100		
P&t fixed	120*	2000	30
	130		
	140		
T&t fixed	120	1000	30
		1500	
P&T fixed	120	2000	15
			60

Table 3.5: Experiment conditions for PL4.28-32.

Conditions	Temperature	Pressure	Time
	110		
P&t fixed	120*	2000	30
	130		
	140		
T&t fixed	120	1000	30
		1500	
P&T fixed	120	2000	15
			60

3.5 Foam Characterization

3.5.1 Density & expansion ratio measurements

Foam density is one of the most important property for this study. Density measurement were done using Mettler A1201 density measurement device.

Pure water was used in order to measure the density of samples which has density of 1.00 g/cm³. Archimedes equation is used to calculate the density of foamed samples:

$$\rho_{foam} = \frac{(M_{air}) \cdot (\rho_{water})}{(M_{air}) - (M_{water})} \quad (3.1)$$

where M_{air} is the weight of sample in atmospheric condition, M_{water} is the weight of each sample in pure water condition, ρ_{water} is density of pure water. Expansion ratio of each foamed samples were calculated using equation:

$$E. R = \frac{\rho_{polymer}}{\rho_{foam}} \quad (3.2)$$

3.5.2 Morphological analysis and foam cell density calculations

Scanning electron microscope (SEM) (JEOL S410) was used to observe the cellular morphology and calculate the cell density by the equation;

$$\text{Cell density} = \left(\frac{N^2}{A} \right)^{3/2} \cdot \frac{\rho_{polymer}}{\rho_{foam}} \quad (3.3)$$

where N is number of cell, A (cm²) is the area. To calculate the average cell size D(μm) equation 3.4. was used, where Ø is expansion ratio and N is the cell density:

$$D = \left[\frac{(\emptyset - 1)^6}{\pi N} \right]^{1/3} \quad (3.4)$$

3.6 Thermal Behavior of ETPU Bead Foams

The thermal behavior of E-TPU beads was measured in a DSC by heating the foamed samples from 20 °C to 230°C at a rate of 10°C/min to understand the effect of foaming on crystallization of the foamed samples.

4. RESULTS AND DISCUSSION

In this study, the properties of ETPU foams prepared using low, medium and high molecular weight polyol of polyester type TPU and low molecular weight polyol of polyether type TPU were investigated. Foams were prepared in a laboratory scale autoclave foaming setup.

Firstly, to understand the onset of degradation and thermal decomposition of TPUs, samples were analyzed using TGA. Then, the effect of polyol length and types of TPU on the crystallization behavior was investigated with non-isothermal melt crystallization analysis in DSC. Isothermal crystallization analysis which could simulate the foaming process without gas was also performed to observe how isothermal annealing can affect the hard segment crystals and crystallization evolution. The evolution of crystallization and modifications in crystals during foaming process significantly influence the foaming behaviour that are cell nucleation and foam expansion. This simulation was later on conducted in the presence of dissolved CO₂ in the autoclave while minimizing the foaming effect and just to observe the saturation parameters effects on crystallization and hence foaming. Subsequently, the saturation the DSC experiments were run to implement the noted simulation. This is indeed much closer to the real foaming experiments where biaxial stretching caused by foaming would further influence the crystallization. The rheological properties of the samples were determined using an oscillatory rheometer and a melt flow indexer.

The foamed TPU samples were characterized in two steps. First step was calculation of expansion ratio of foams by archimedes equation via using the density data of foamed and raw samples. Second step was investigating cellular structure of foamed samples using SEM. Average cell density and cell size were calculated after the observation of cellular morphology. Thermal analysis performed for some foamed samples and unfoamed (as noted above) samples using DSC to observe the foaming and saturation effect on further modification of hard segment crystals, respectively.

4.1 Thermal Analysis of TPU

4.1.1 Thermogravimetric analysis (TGA)

The thermal degradation properties of TPU samples were studied by TGA. The results from the TGA are shown in Figures 4.1 and 4.2. In both two Figures, TPU samples showed a two-stage thermal degradation pattern corresponding to breaking of urethane bonds between MDI and BDO followed by the formation and escape of volatile THF from the released BDO, and then the decomposition of polyol (soft segment) at higher temperatures. This can be seen much more clearly in polyether based TPU, PL1.A80.

Figure 4.1 shows comparison of TGA curves between short polyol length of polyether based (PL1.A80) and polyester based TPU (PL2.A80). There is a slight improvement in the decomposition temperature for polyester based TPU, since polyether based TPU is slightly less stable than polyester based TPU. According to chemical composition of polyols, TPU shows different thermal behavior. Since there is hydrogen bond formation between the oxygen atom of carbonyl group of polyester in the soft segment and the urethane hydrogen atom in the hard segment, the interaction between the soft and hard segment is stronger in polyester based TPU. For this reason, thermal stability of polyester based TPU is higher than polyether based TPU. While pyrolysis of polyether based TPU started around 280°C, pyrolysis of polyester based TPU started around 295°C.

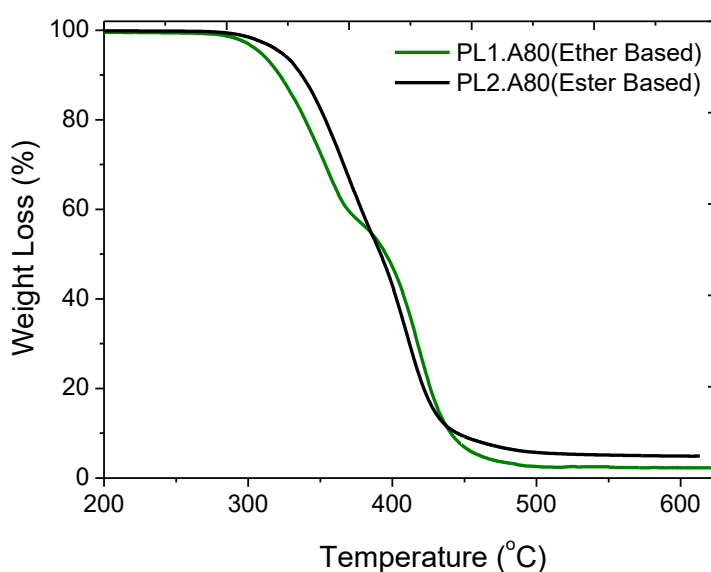


Figure 4.1: TGA curves of PL1.A80 and PL2.A80.

According to Figure 4.2, all polyester based TPUs started to pyrolysis around 295°C. But increase in polyol length of TPU resulted in increase in weight loss slightly, since the polyol is the main material and the energy source for the smoldering smoldering characteristics of TPU.

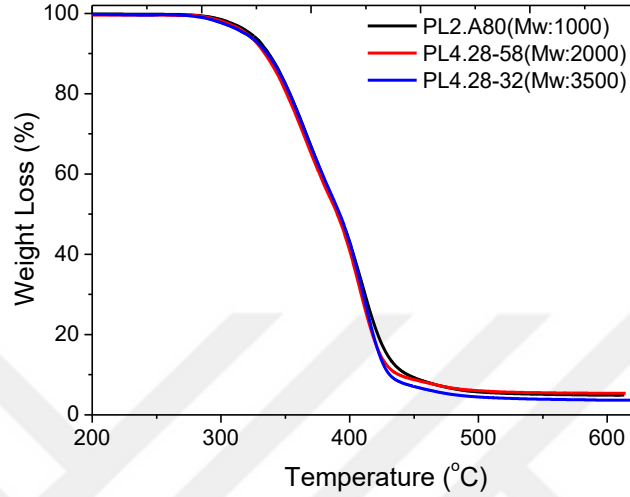


Figure 4.2: TGA curves of PL2.A80, PL4.28-58 and PL4.28-32.

4.1.2 Crystallization analysis with DSC

4.1.2.1 Non-isothermal melt crystallization analysis

The urethane linkages in TPU are steady in the solid state of the polymer. However, these bonds fall apart and a polydispersed system with short and long HS chains are created in elevated temperatures. When TPU is cooled down from the melt after extrusion, HS chains aggregates and creates different size of hard domains and crystallites. That is why, when a TPU is heated to high temperatures, it shows usually multiple melting endotherms. The crystallites formed with the small range HS chains order melted at a lower temperature labelling T_{m-low} and the crystallites formed with the larger range HS chains order melted at higher temperatures labelling T_{m-high} are shown in Table 4.1.

Table 4.1: Data of DSC measurements.

Sample	T_{m-low} (°C)	T_{m-high} (°C)	ΔH_T (J/g)
PL1.A80	127.7	152.7	11.65
PL2.A80	133.4	163.0	11.46
PL4.28-58	126.1	170.8	16.10
PL4.28-32	136.2	190.4	19.24

Figure 4.3 shows the first heating graph of different amount of polyols of polyether and polyester based TPUs. As it seen, the melting peak slightly shifted towards higher temperatures with increasing polyol amount. When having short polyol chains, the rigidity comes from reduced soft-segment content. The crystallization of hard segments in high Mw polyol case occurred in wider melting ranges and with various closed pack structures. The degree of hard segment crystallinity also increased as the Mw of polyols increased. This was due to the more flexibility that the soft segment could provide to form different size and closed packed hard segment crystals.

Hydrogen bonds between the urethane hydrogen in hard blocks and the carbonyl oxygen in a polyester soft phase are stronger than the hydrogen bonds between the urethane hydrogen and the oxygen of the ether function in a polyether soft phase. This difference can be the reason higher T_{m-low} and T_{m-high} obtained in polyester based TPU.

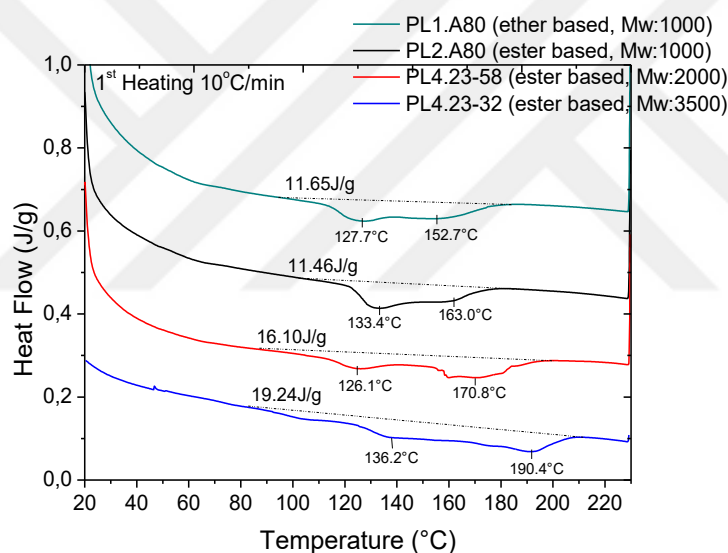


Figure 4.3: DSC thermograms of 1st heating of TPU samples.

As seen in the Figure 4.4, the polyether based TPU (PL1.A80) showed an earlier onset of the HS crystallization comparing to same Mw polyester based TPU (PL2.A80). The difference in crystallization temperature can be related to the difference in hydrogen bonding between a polyether and polyester. A difference in hard block-soft block compatibility between polyether and polyester based TPU may also play a role. Furthermore, higher the Mw of the polyol, faster the hard blocks crystallize again. Crystallites that are formed at higher temperature during cooling were also melted at higher temperatures (Figure 4.5), thus higher annealing temperatures were needed to reorganize the crystallinity of TPU samples with higher soft segment lengths. In

contrast to first heating, lower T_m peak is not seen clearly in the second heating graph. The reason of obtaining two melting peaks in first heating was the multiple structure of TPU. At low temperature is associative with short range order crystallites and at high temperature peak is relevant with disordering of HS crystallites with long range order [61]. After first heating, all crystals were melted and hard segments reorganized. In cooling step, because of the new perfected crystallites formation, broader peak produces at higher temperature in the second heating.

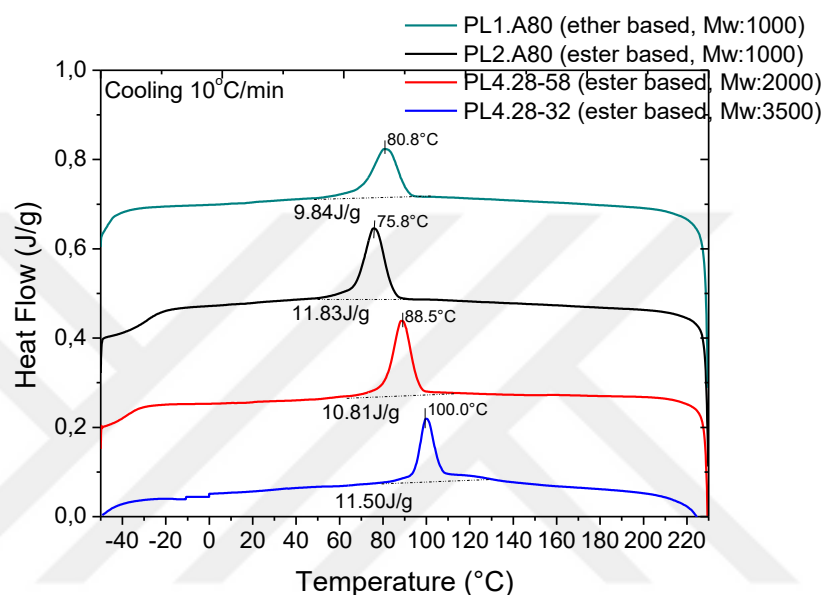


Figure 4.4: DSC thermograms of cooling of TPU samples.

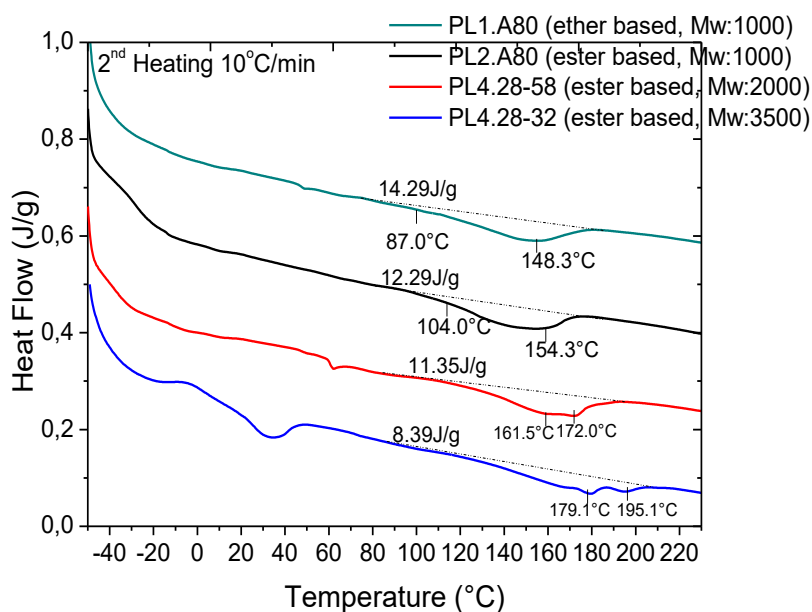


Figure 4.5: DSC thermograms of 2st heating of TPU samples.

Hydrogen bonding can be occurred also between SS carbonyl groups, which gives SS crystals with very low melting temperature [85]. These SS crystals were observed in literature in the case of SS having high molecular weight and high segregation degrees which is very low content of dissolved HS in SS. The endotherm due to SS crystals melting appears in low temperatures range of 40-60°C [85-87]. This phenomenon can be even better defined in DSC scan after a thermal treatment, which can also be seen in our study. A thermal treatment improves crystallization and shifts the endotherm towards higher temperatures. PL4.28-32 shows this phenomenon in DSC scan after heat-cool-heat treatment.

4.1.2.2 Isothermal crystallization analysis

When a TPU is enforced to an increasing temperature, especially above the T_g , the mobility of hard segment improves; hence, the hard segments reorganize and even crystallize/recrystallize at elevated temperature. The morphological modifications at elevated temperature can derive from the weakened interaction between hard segments.

TPUs produced from MDI and 1,4-butanediol as hard segment can crystallize when TPU annealed at the temperature above T_g for a long time [5]. Diminished interactions between hard segments at increasing temperature enable the rearrangement of hard segments. During the annealing process, hard segments in soft domain aggregate and create hard domains. TPUs are hence annealed at increasing temperature to improve the phase separation with the mechanical and thermal properties. In other words, thermal annealing of TPU helps the rearrangement of hydrogen bondings and hence the formation of HS domains and their crystallization kinetics.

The effect of isothermal treatment on the hard-segment crystallization of various TPUs were investigated in order to simulate the bead foaming process that requires time and isothermal temperatures and of course gas which is missing in the DSC analysis. The main purpose is to have an idea about the effects of annealing process on crystallization of hard segments and heterogeneous cell nucleation around those modified crystals, which is similar to foaming process but without dissolved CO_2 .

It can be seen in Figure 4.6 that the increased annealing temperature shifted the low temperature melting peak ($T_{m\text{-low}}$) to higher temperatures generally about 10-20°C above the annealing temperature.

It can be noticed that the total heat of fusion (ΔH_f) of both PL4.28-58 and PL4.28-32 samples decreased with raising annealing temperature. The reason for this less perfected crystals were melted at elevated temperature.

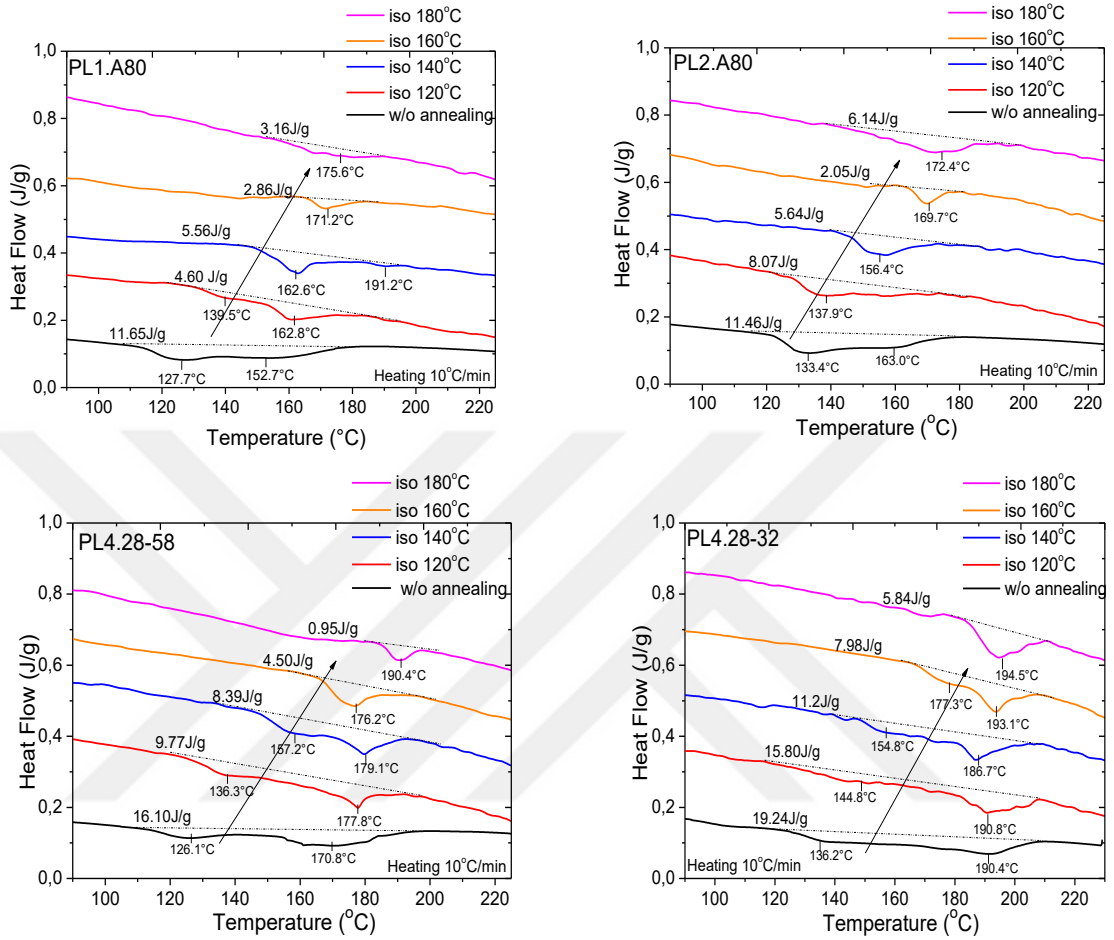


Figure 4.6: DSC thermograms of PL1.A80, PL2.A80, PL4.28-58 and PL4.28-32 after isothermal annealing at 120, 140, 160 and 180°C.

4.2 Rheological Analysis of TPU

In the rheological experiments, firstly, the linear viscoelastic region of the TPU samples was clarified at 210°C through strain sweep tests while applying 10 rad/sec and eventually the strain was fixed at 0.5%. Later the frequency sweep test was carried by varying the angular frequency range from 0.1 to 100 rad/s.

Figure 4.7 shows the complex viscosity versus frequency of TPU samples at 210°C. The chemical structure, hydrogen bondings, content of hard and soft segment, molecular weight and thermal history of TPU affect the rheological behavior of TPU. Moreover, long duration melt experiments are difficult for TPU since the urethane

linkage tend to decompose at higher temperatures. As shown, when the frequency changing from 100 to 0.1 rad/s, rising slope at low frequencies was obtained. This is because, as it is mentioned above, with the complex chemical structure and morphology of TPU, there might be bubble formation caused by the molecular decomposition at elevated temperatures which led to an increase in viscosity at low frequency. It can be seen in Figure 4.7 that higher molecular weight polyol TPU induces higher viscosity due to the molecular entanglement of chains. Besides, polyester based TPU shows higher viscosity comparing to polyether based TPU, likely due to higher mobility of its polyol structure. PL4.28-32 did not analyzed, but we can assume its viscosity would be the highest since it has the highest molecular weight polyol chain. MFI values of the TPUs were also measured and the results are shown in Table 4.2 which is consistent with the explained rheological data.

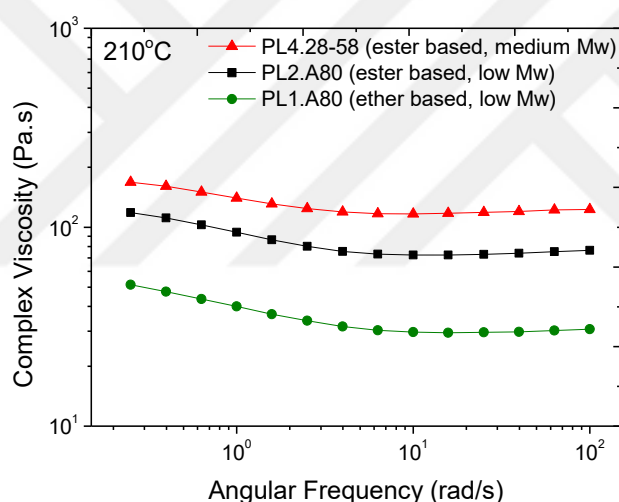


Figure 4.7: Complex viscosity plot of PL1.A80, PL2.A80 and PL4.28-58.

Table 4.2: MFI Results at 200°C.

Sample	MFI (g/10min)
PL1.A80	56.09
PL2.A80	38.51
PL4.28-58	28.13

4.3 Foam Characterization

To understand how process parameters, influence foam structure, TPU samples was studied at specified saturation temperatures, pressures and time. Firstly, temperature effect on foam structure was investigated for all samples under 2000 psi for 30 min.

Later the system was heated to a meaningful temperature for each sample and kept for 30 min under various pressures. The saturation pressure range was 1000, 1500 and 2000 psi. To understanding time effect on foam structure, pressure was fixed at 2000 psi and selected saturation temperature. The system was maintained for 15, 30 and 60 min under these conditions. Characterization analysis of foams were carried out using SEM to calculate cell densities and cell sizes of foamed samples. The density of the foams was also measured to calculate expansion ratios.

4.3.1 Saturation temperature effect on foam structure

Since it has an effect on cell nucleation, temperature is one of the most important process condition for foaming mechanism. It also influences the solubility of CO₂ in polymer/gas domains. The blowing agent which was supercritical CO₂ in our study has low critical temperature and better solubility at lower temperatures; however, polymers cannot be able to expand significantly at low temperatures. For this reason, it is critical to find the proper process temperature window for both the solubility of CO₂ and expansion. Starting temperatures were decided after running series of experiments and by monitoring the first heating DSC thermograms of TPU pellets. After obtaining the first foam, other temperatures were investigated by monitoring the expansion ratio of foamed samples. Figure 4.8 shows foamed samples under 2000 psi for 30 min at various saturation temperatures. All TPUs showed microcellular morphologies with fine cell sizes in the range of 5-50 μm , and cell densities between 10^8 cell/cm^3 and 10^9 cell/cm^3 as shown in Figure 4.9 and 4.11.



Figure 4.8: Foams of TPUs at various saturation temperatures.

While higher energy was needed to obtain better expansion for ester based TPU PL2.80, expansion ratio decreased at elevated temperatures for ether based TPU PL1.A80 (Figure 4.9). As seen in SEM results (Figure 4.10), higher temperatures increased the chain movement and led the reorganization of hard segments and further crystallization around diffused gas. Because of the rigid structure of crystallites, the melt strength increased which limits the cell growth and expansion.

Matsunaga et al [88] suggest that carbonyl group of ester based TPU suppress the diffusion of gas, which is not the case for ether based TPU; therefore, higher expansion might obtain for ester based TPU. The diffusivity and permability is higher in ether based polyols, which cause to coarsening of cell because it is easier gas to escape [88]. For that reason, cells cannot grow easily, and as seen expansion of ether based polyol TPU is lower.

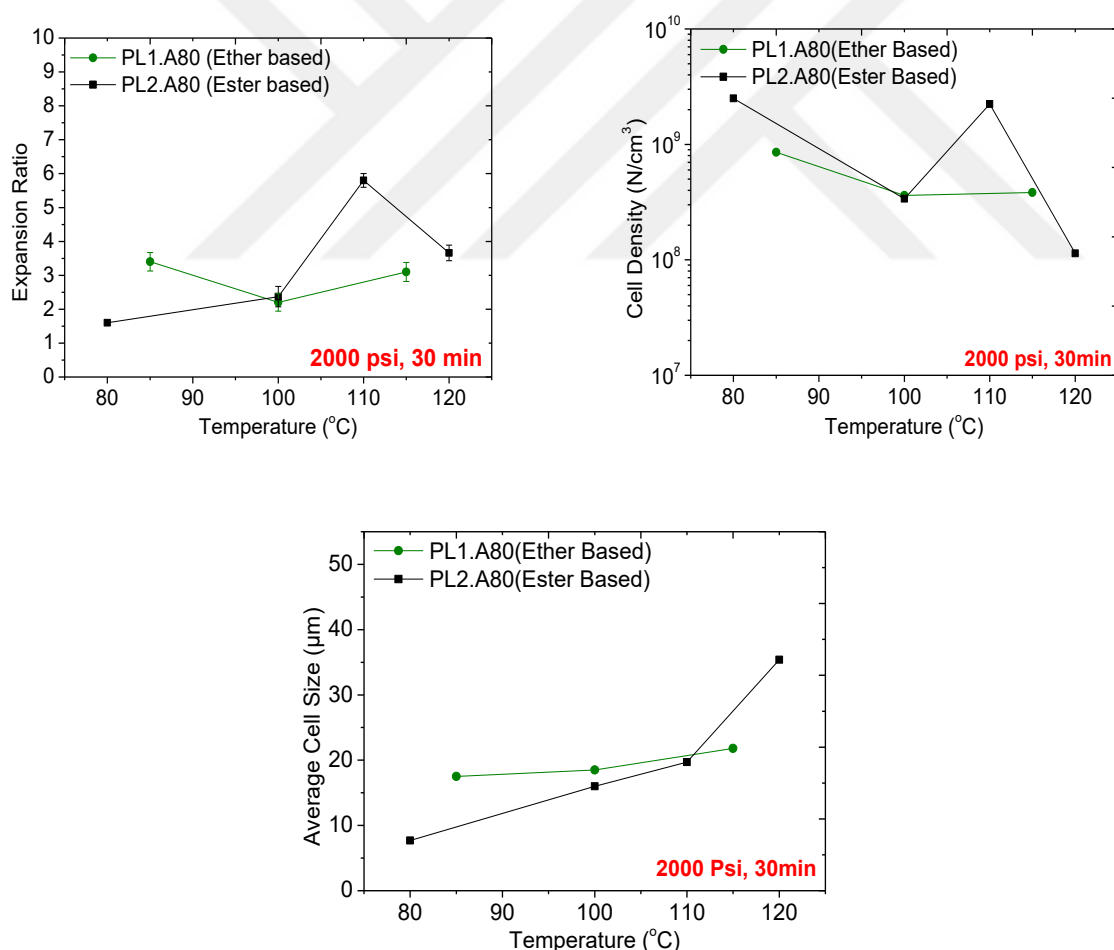


Figure 4.9: Expansion ratio, cell density, and average cell size graphs of PL1.A80 and PL2.A80 foams at various saturation temperatures.

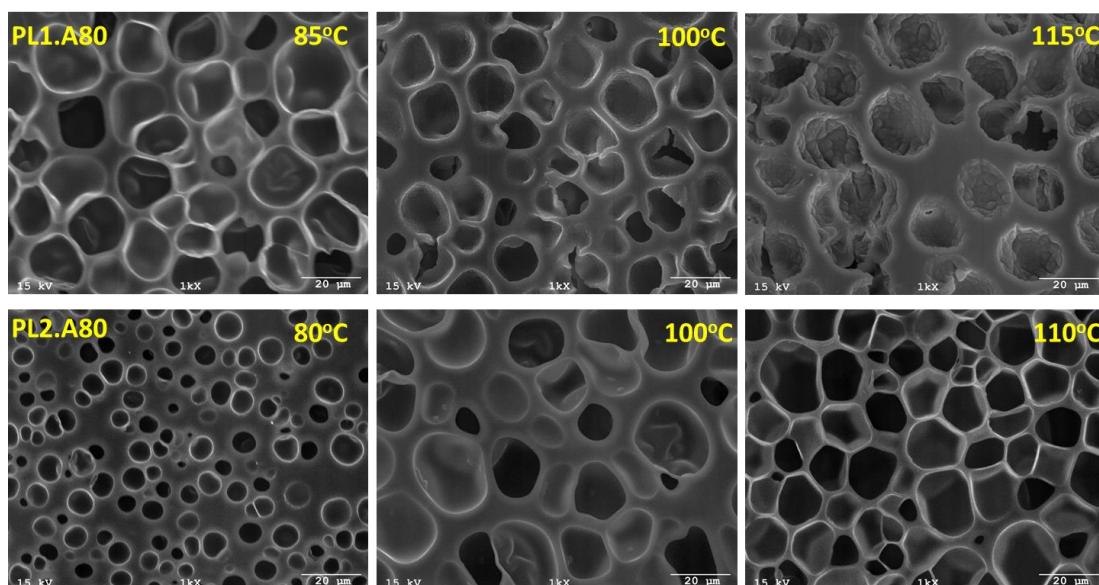


Figure 4.10: SEM images of PL1.A80 and PL2.A80 foams at various saturation temperatures (Magnification is 1000x)

Expansion ratio, cell density, and average cell size graphs of PL2.A80, PL4.28-58 and PL4.28-32 foams at different temperatures can be seen in Figure 4.11 and their SEM images in Figure 4.10 and 4.12. The hard domains of TPU is formed between the urethane groups of hard segments by hydrogen bonding, polar forces and intermolecular interactions, thus gas diffusion in those domains is very limited. On the other hand, soft segment chain is mobile and the gas can diffuse in the spaces between the molecular chains. Furthermore, it was reported that the higher molecular weight polyol caused the higher solubility of CO₂ in TPU due to the increase in free volume of soft segment chain and their more flexibility [89]. Since the solubility affects the cell nucleation rate, it also affects the cell density, which is the highest in highest molecular weight polyol TPU, PL4.28-32 at 120°C. On the other hand, solubility of CO₂ is also effected by viscosity of polymer melt, which is related to temperature as well as the molecular weight of polyol chain (shown in the section 4.2). When the saturation temperature increased to 130°C, medium molecular weight polyol TPU, PL4.28-58 showed higher expansion than highest molecular weight polyol TPU, PL4.28-32; however, cell density was the opposite (Figure 4.11). Since the longer polyol leads higher entanglement, movement of chains is harder than shorter polyol at elevated temperature. Besides in TPUs have short polyol chains have more free space for cell growth. Therefore, medium molecular weight polyol TPU, PL4.28-58 allowed

rapid cell growth and showed more expansion than highest molecular weight polyol TPU, PL4.28-32, however not the cell nucleation as much as PL4.28-32.

All ester based TPUs showed higher expansion with increasing temperature. However, low molecular weight polyol TPU, PL2.A80 shrunk at 120 °C, while medium and high molecular weight polyol TPUs showed better foam behavior at 120°C. This was reasonable since the longer polyol chain movement requires more energy. At saturation temperature 130 °C, medium and high molecular weight polyol TPU foams showed bigger cells with thinner cell walls and started to shrink after a time. At 140°C, very large shrinkage was observed for PL4.28-58, while PL4.28-32 showed a very rigid structure instead of shrinkage. This can be explained as molecular entanglement possibly prevented the cell coalescence, so cell walls could not collapse. Moreover, expansion ratios of PL4 series is higher comparing to PL2.A80, since the movement of SS chains serves the solubility of CO₂, provides better flexibility and causes a better cell growth. Therefore, longer polyol chains, which is longer the SS chains, help expansion significantly.

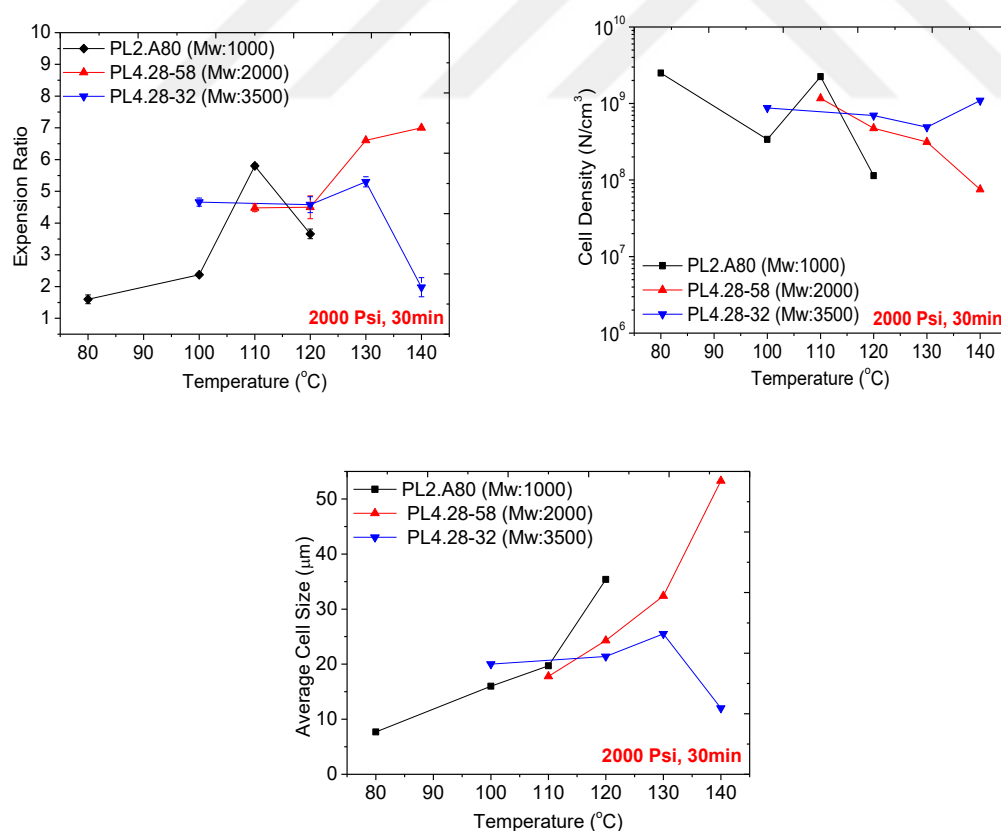


Figure 4.11: Expansion ratio, cell density, and average cell size graphs of PL2.A80, PL4.28-58 and PL4.28-32 foams at various saturation temperatures.

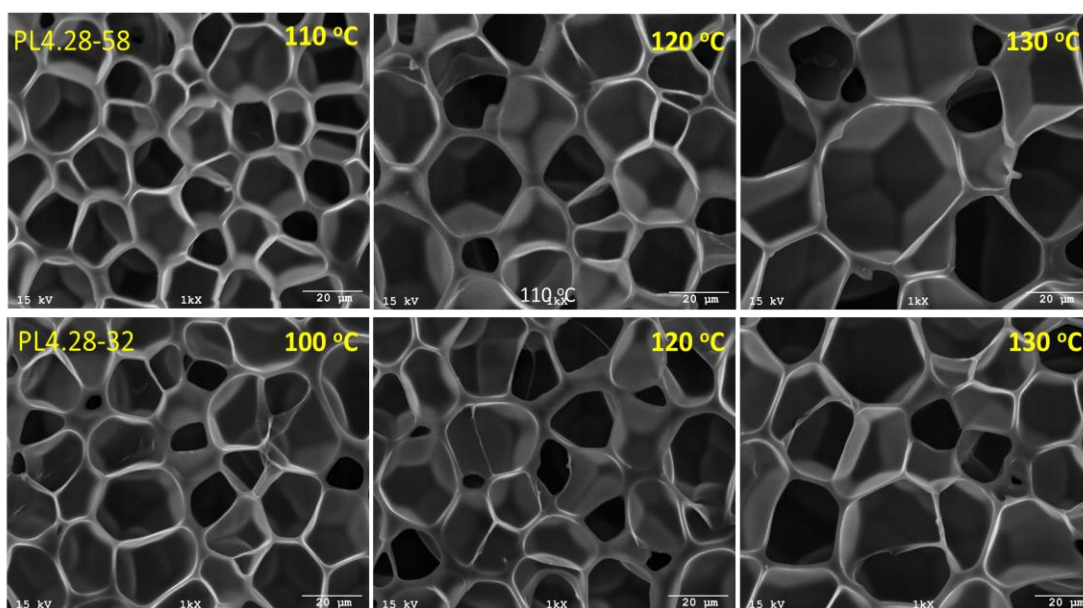


Figure 4.12: SEM images of PL4.28-58 and PL4.28-32 foams at various saturation temperatures (Magnification is 1000x)

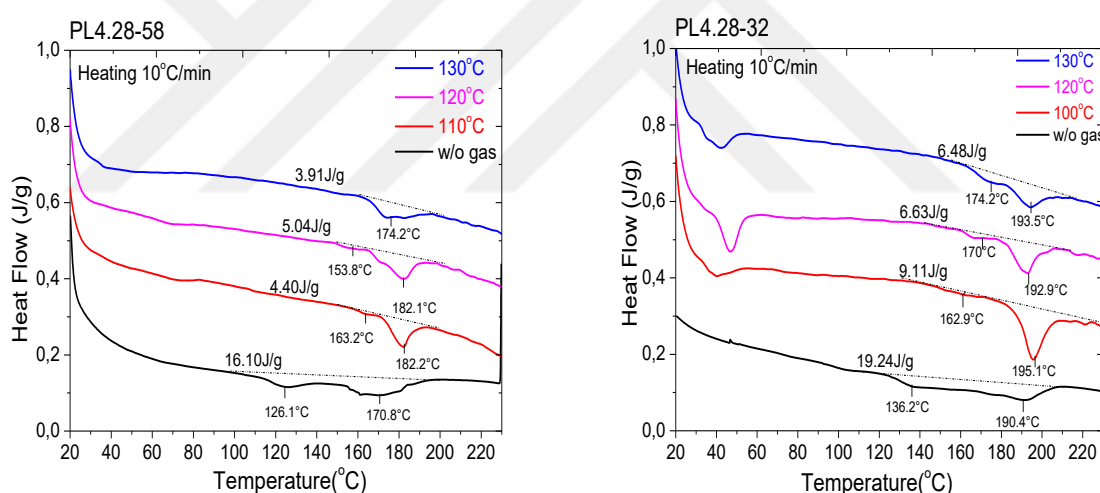


Figure 4.13: DSC thermograms of PL4.28-58 and PL4.28-32 under 2000 psi CO₂ at various saturation temperatures.

For better understanding of crystallization during foaming, we simulated the annealing with CO₂ at autoclave with same saturation temperatures without fast depressurization, and then analysed with DSC. Figure 4.13 shows the DSC graphs of PL4.28-58 and PL4.28-32 annealed with 2000 psi CO₂. As it seen, with increasing temperatures and effect of CO₂, the HS crystallinity was improved from less perfected crytalls to perfected crystalls. T_{m-low} shifted to higher temperatures and T_{m-high} became sharper. ΔH_T decreased at elaveted temperatures because more crystals were melted. Also the

reason why PL4.28-58 showed more expansion but not cell nucleation comparing to PL4.28-32 can be seen in Figure 4.13. The crystallinity of PL4.28-32 was very low at 130°C which could not promote the heterogenous cell nucleation but allowed to cells to grow.

4.3.2 Saturation pressure effect on foam structure

To understand effect of saturation pressure on foam structure, experiments were performed at 2000, 1500 and 1000 psi at the selected foam temperatures of each sample for a given saturation time of 30 min. Except the foaming at 1000 psi, other TPU foams showed microcellular morphologies with fine cell sizes in the range of 10-70 μm , and cell densities between 10^8 cell/cm^3 and over 10^9 cell/cm^3 as shown in Figure 4.16 and 4.17.

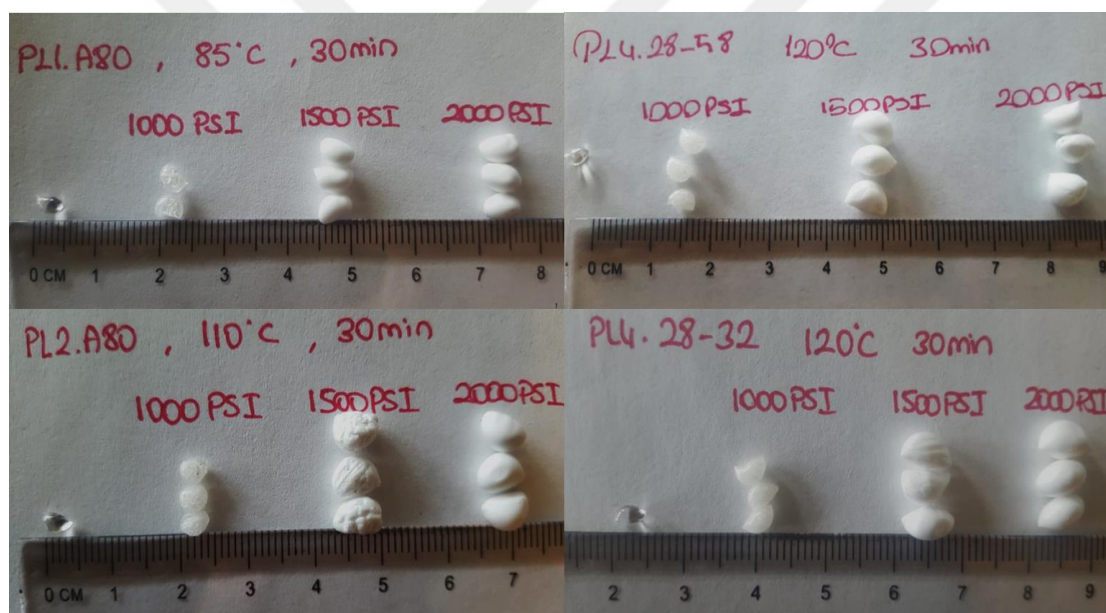


Figure 4.14: Foams of TPUs at various saturation pressures.

At higher pressures the solubility of CO_2 inside the polymer increases, therefore; the amount of CO_2 dissolved into the polymer is higher. This fact leads to an increase in the supersaturation of the polymer during the pressure release [90]. Moreover, as it has been mentioned in the section 2.1.3.2, CNT claims both homogenous and heterogeneous nucleation is strongly related to saturation pressure. For bubble nucleation, molecules need to overcome an energy barrier and gather together to form a new phase, which is very important process that affects the final size of the foam. Based on the equations in the section 2.1.3.2, increase in the saturation pressure, is

expected to decrease the free-energy barrier for bubble nucleation, and hence increase the nucleation rate, leading to smaller cells.

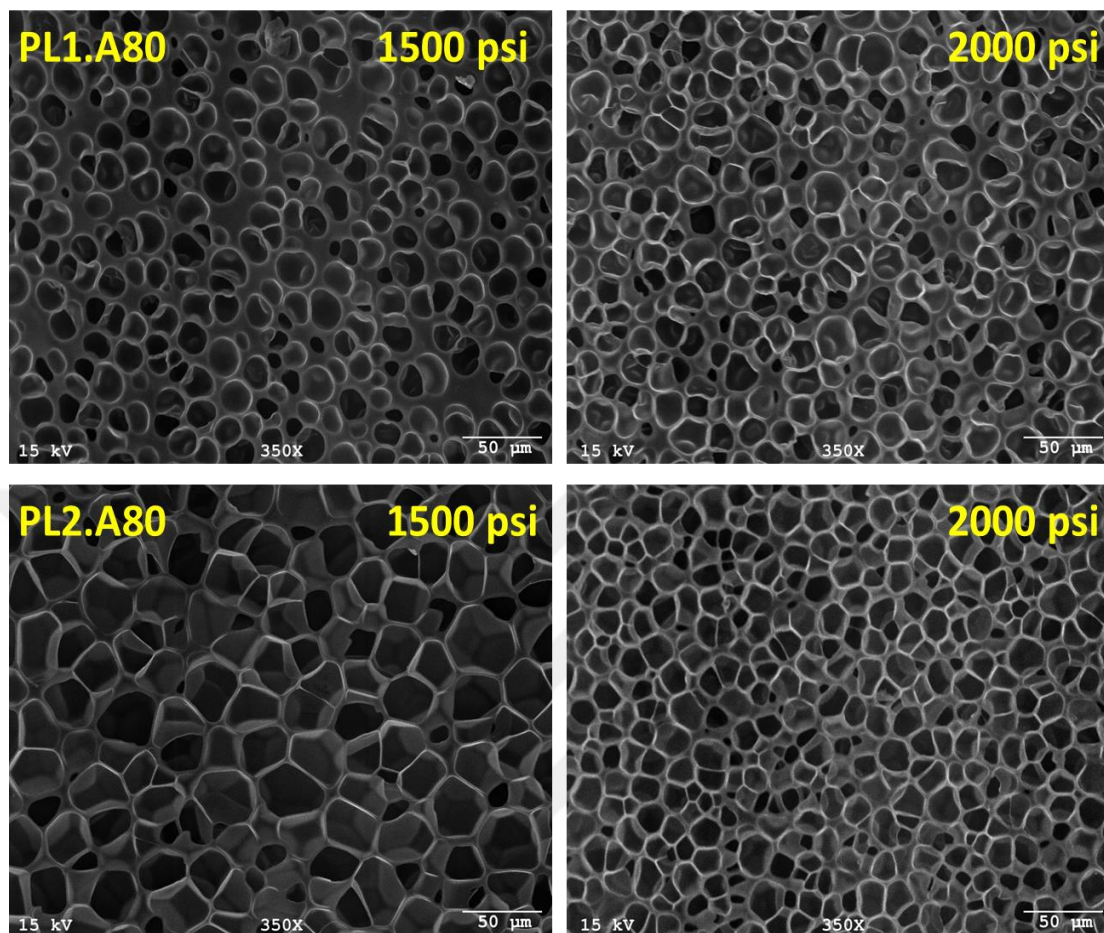


Figure 4.15: SEM images of PL1.A80 and PL2.A80 foams at various saturation pressures (Magnification is 350x)

Generally, for all TPU samples with ester or ether based and different molecular weight polyols, it can be said that increasing saturation pressure lead to an increase in foam expansion, increase in cell density and decrease in average cell size (Figure 4.16, Figure 4.17). As shown, under 1000 psi not a significant color or volume change for pellets was observed and foaming indeed could not happen.

On the other hand, expansion was observed under 1500 psi, and even more under 2000 psi. For ester based TPUs expansion was much larger than ether based TPU beacuse a strong interaction between the carbonyl group in polyester polyols and CO₂ inhibits the outward diffusion of gas [88]. The higher diffusivity and permability in polyether based polyols might lead gas bubbles to diffuse into bigger bubbles, known as cell coarsening.

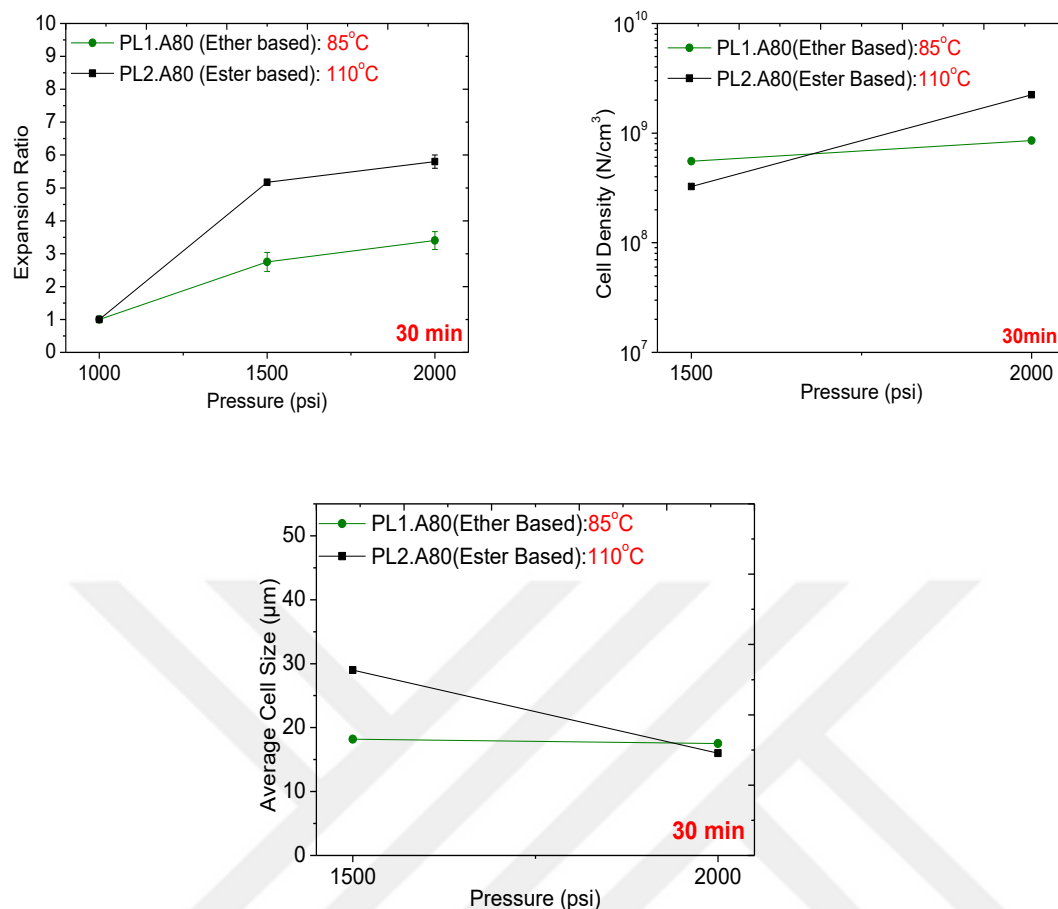


Figure 4.16: Expansion ratio, cell density, and average cell size graphs of PL1.A80 and PL2.A80 foams at various saturation pressures.

Expansion ratio, cell density, and average cell size graphs of PL2.A80, PL4.28-58 and PL4.28-32 foams at different saturation pressure are shown in Figure 4.17, and their SEM images can be seen in Figure 4.15 and 4.18. As was also discussed in ether and ester based lowest molecular weight polyol TPUs, increasing CO₂ concentration of the system resulted in higher expansion ratios of TPUs with higher molecular weight. Highest molecular weight polyol TPU, PL4.28-32 showed slower increase comparing to low and medium molecular weight polyol TPUs, since high molecular weight polyol needed more energy to movement of its SS chain, for diffusion of CO₂ and cell growth. As it seen in the Figure 4.18, at 1000 psi, while PL4.28-32 had more nucleated cells, PL4.28-58 has bigger cells. Since PL4.28-32 has longer SS chains, CO₂ dissolution was more even at low pressure, however its chain entanglement prevented cells to grow. Cell densities increased in all TPUs with increasing saturation pressure due to the increasing diffusivity of CO₂ leading cell nucleation.

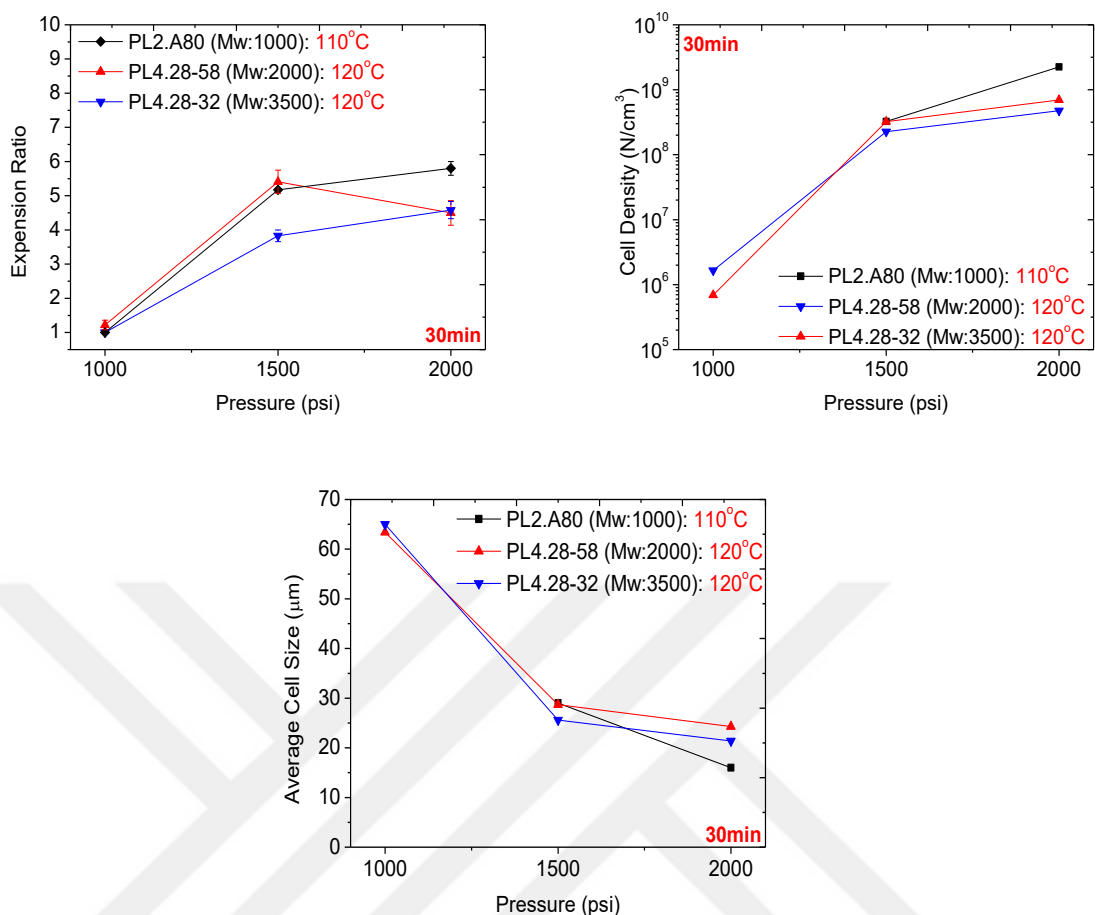


Figure 4.17: Expansion ratio, cell density, and average cell size graphs of PL2.A80, PL4.28-58 and PL4.28-32 foams at various saturation pressures.

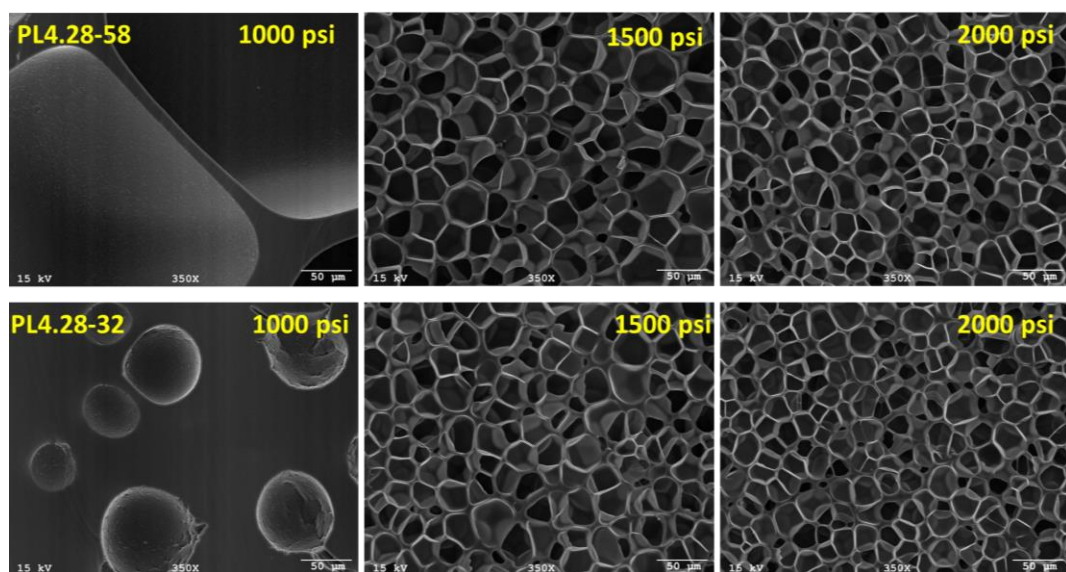


Figure 4.18: SEM images of PL4.28-58 and PL4.28-32 foams at various saturation pressures (Magnification is 350x).

From graphs of Figure 4.15 and Figure 4.17, it can be found that cell density can be significantly improved by increasing saturation pressure. Besides, it can also be seen that the average cell size decreased with increasing saturation pressure. According to CNT, the higher saturation pressure not only improves the CO₂ solubility in TPU melt but also decreases the free energy barrier for bubble nucleation. More nuclei are hence formed, causing decrease in cell size and increase in cell density, during the depressurization step.

Figure 4.19 shows the DSC thermograms of medium and high molecular weight polyol TPU samples saturated with CO₂ at 120°C under different saturation pressures but without foaming. Higher saturation pressure probably promoted the flexibility of TPU chain, and caused to recrystallization of less perfected HS crystallites toward more closed pack, therefore the shift of the lower melting peak, T_{m-low} , towards higher temperature. Saturation TPU with CO₂ did not significantly change the T_{m-high} as much as T_{m-low} , however with higher saturation pressure, T_{m-high} become more prominent. The increase in high perfection crystallites might be promoted by mobility of chains due to presence of CO₂.

As it seen, ΔH_T was also significantly decreased in the presence of dissolved CO₂, since the dissolution of CO₂ in TPU matrix enlarged the distance between molecular chains and decreased the crystallinity. Lowering crystallinity probably helped cell growth in the TPUs microstructure during foaming process.

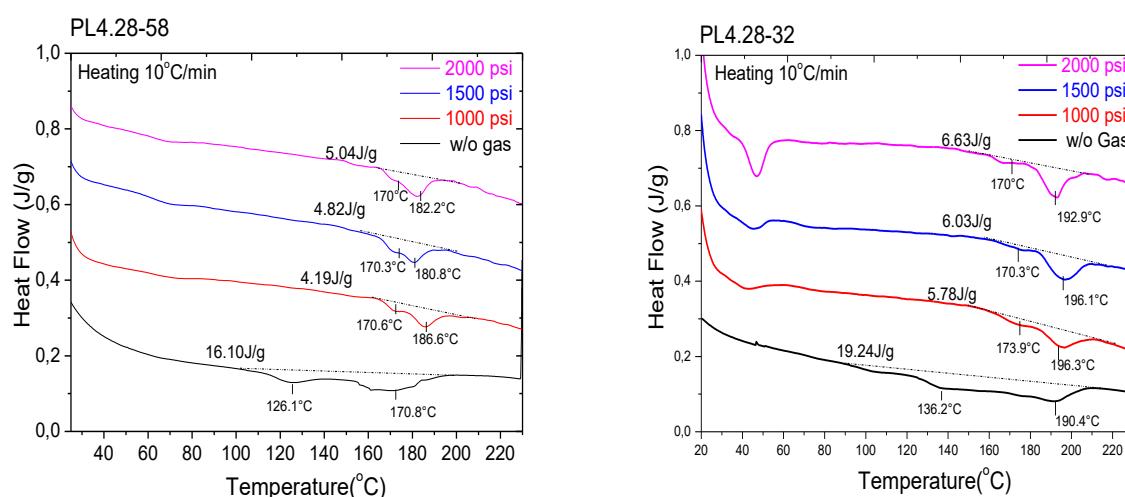


Figure 4.19: DSC thermograms of PL4.28-58 and PL4.28-32 annealed at 120 °C under CO₂ at various pressures.

4.3.3 Saturation time effect on foam structure

Saturation time has a great impact on crystallization and crystal evolution in presence of dissolved blowing agent and hence on foaming behavior of polymers. The effect of saturation time on foam structure was studied by saturating samples for 15, 30 and 60 min under 2000 psi at their selected foaming temperatures. All TPUs showed microcellular morphologies with fine cell sizes in the range of 10-40 μm , and cell densities between 10^8 cell/ cm^3 and over 10^9 cell/ cm^3 as shown in Figure 4.21 and 4.24.



Figure 4.20: Foams of TPUs at various saturation times.

The presence of CO_2 in system causes the polymer to swell, consequently longer time that polymer exposed to CO_2 lead to more chain movement, which causes newly growing HS crystallites. Moreover, longer saturation time serves further solubility of CO_2 within the polymer. However, as Figure 4.21 indicates the expansion ratio of ester based lowest molecular weight polyol TPU, PL2.A80 is much smaller at 60 min saturation time comparing to its foam at 30 min due to shrinkage at 60 min. As it seen in Figure 4.22, cell walls are much thinner at 60 min, which is the result of CO_2 dissolution with long impregnation time.

It can be seen in Figure 4.21 that the PL2.A80 sample shrunked after saturation for 15 min, which proved that the foam structure could not become stable at this given time. This may be explained by the fact that the CO_2 could not find enough time to be solved in TPU samples.

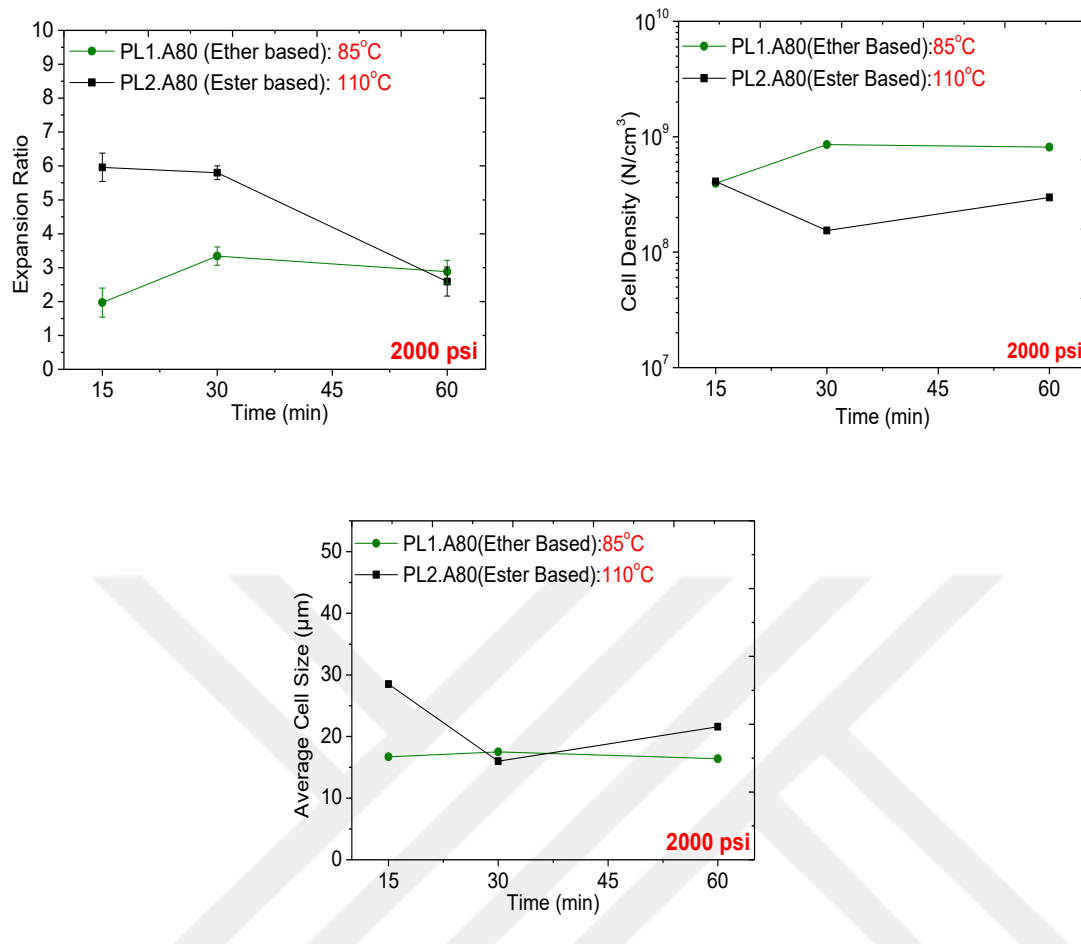


Figure 4.21: Expansion ratio, cell density, and average cell size graphs of PL1.A80 and PL2.A80 foams at various saturation times.

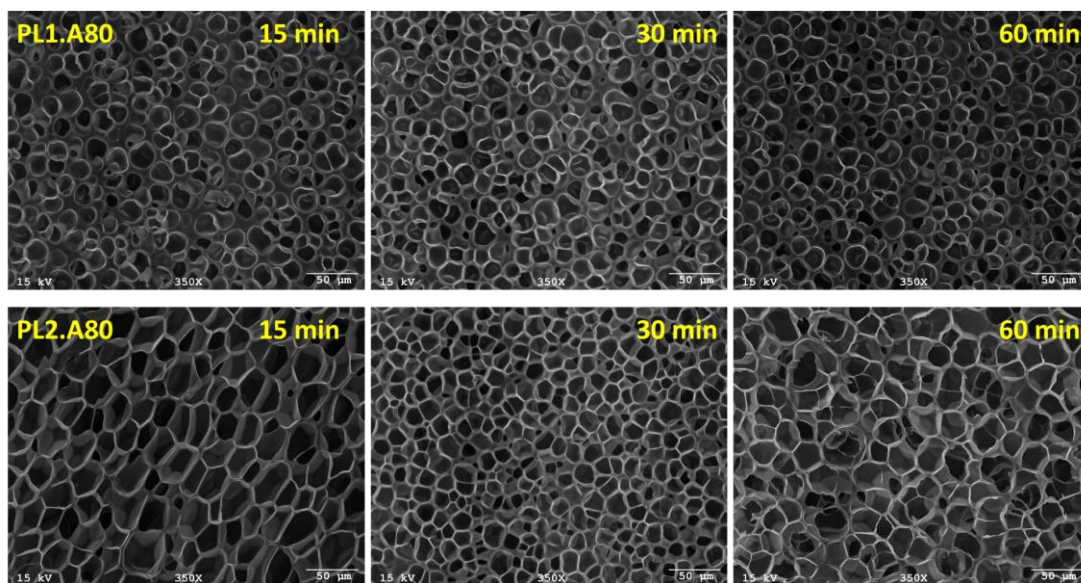


Figure 4.22: SEM results of PL1.A80 and PL2.A80 foams at various saturation times (Magnification is 350x).

Figure 4.24 shows that medium molecular weight polyol TPU, PL4.28-58 has highest expansion ratio and largest cell size at 15min, nonetheless rapid growth caused shrinkage since CO₂ dissolution could not be improved at such a short time. On the other hand, expansion ratio of the high molecular weight TPU, PL4.28-32 increased with longer saturation time. The reason of the difference in expansion behavior between the low and high molecular weight polyols versus saturation time is that PL4.28-32 has more entanglement because of its longer soft segment chains and more gas can dissolve with longer time. As mentioned before, longer saturation time resulted in obtaining more closely packed crystals. Like PL4.28-58 and PL2.A80, high perfect crystal parts form in PL4.28-32 polymer; however, because of SS segment flexibility, expansion ratio increased with time.

In Figure 4.25, the reason of high expansion ratio of PL4.28-58 comparing to PL4.28-32 at short saturation time can be explained by much lower ΔH_T value of PL4.28-58. As seen, the ΔH_T of PL4.28-58 at 15 min is 2.62 J/g, while it is 8.53 for PL4.28-32. Since CO₂ could dissolve more in shorter polyol chain in limited time, it might decrease the crystallization HS chains by increasing molecular distance between them. Moreover, at 60 min saturation time, T_{m-low} of PL4.28-58 was not only shifted to higher temperature but also became sharper, which is the result of newly growing short HS crystallites due to chain movement by CO₂ in a longer time.

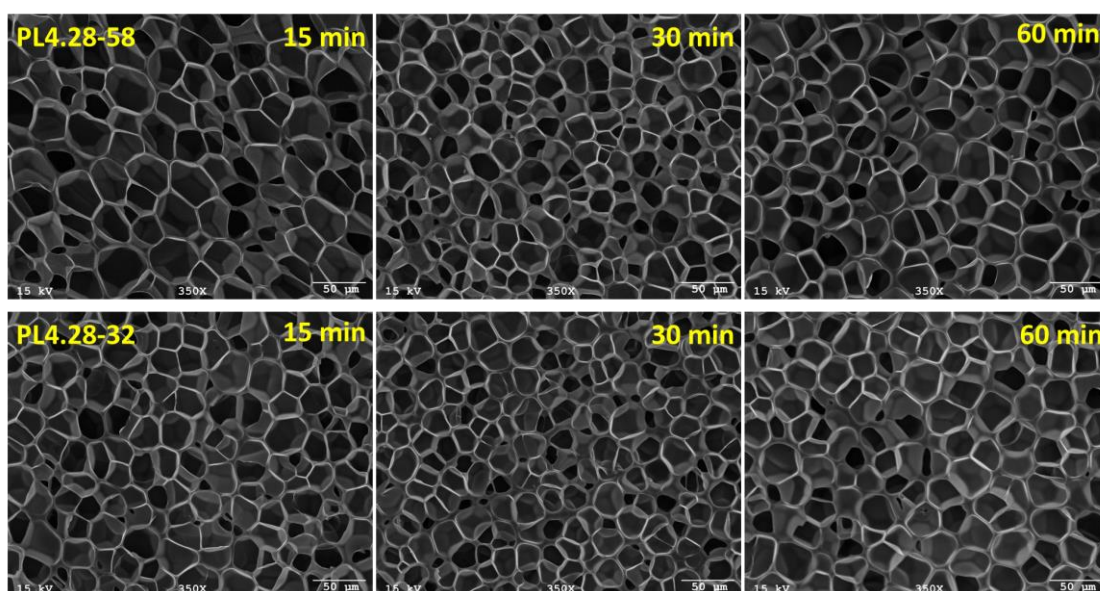


Figure 4.23: SEM results of PL4.28-58 and PL4.28-32 foams at various saturation times (Magnification is 350x).

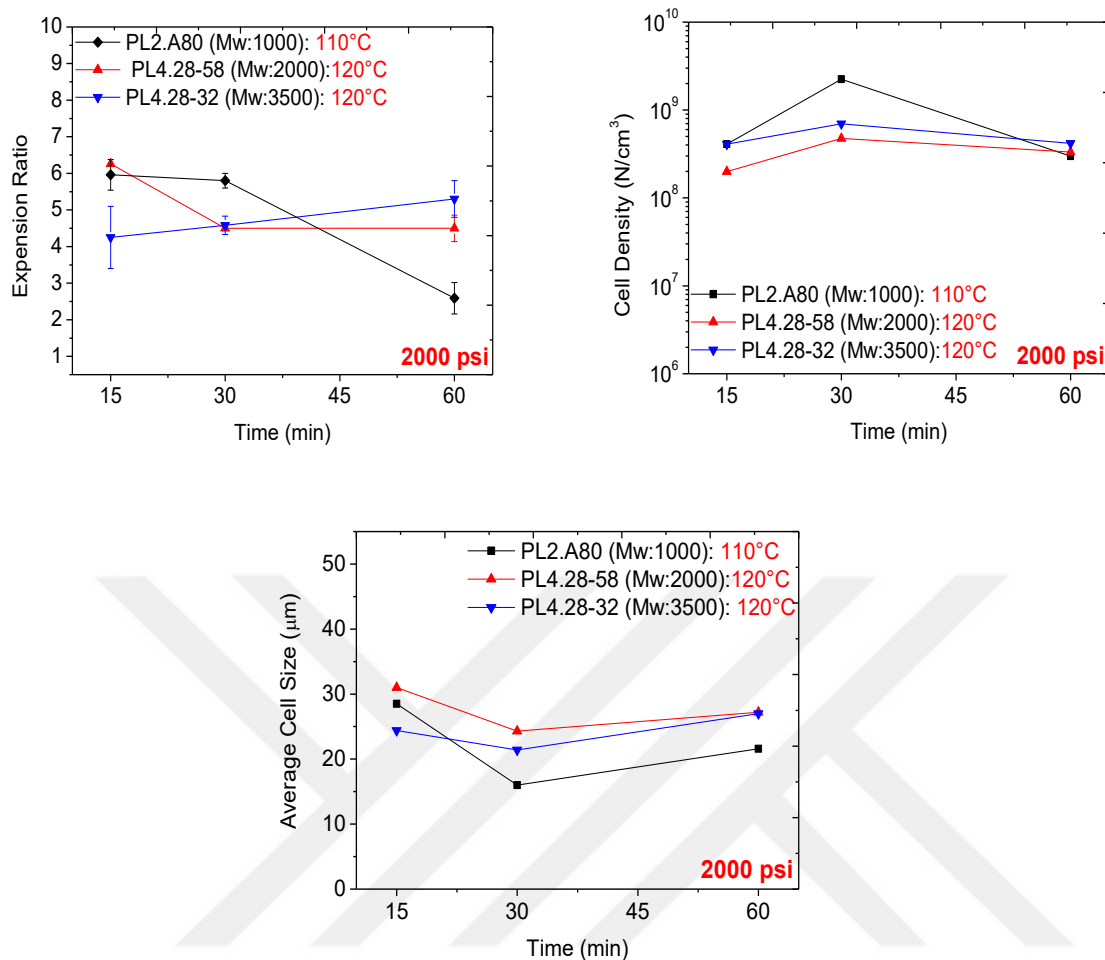


Figure 4.24: Expansion ratio, cell density, and average cell size graphs of PL2.A80, PL4.28-58 and PL4.28-32 foams at various saturation times.

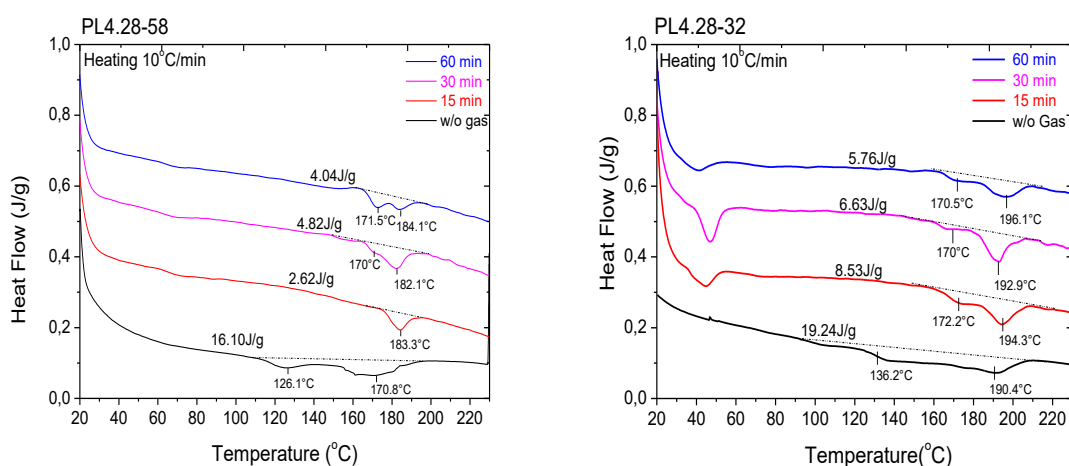


Figure 4.25: DSC thermograms of PL4.28-58 and PL4.28-32 annealed at 120 °C under 2000 psi CO₂ at saturation times.

4.4 Thermal Behavior of ETPU Bead Foams

The thermal behavior of foamed samples was investigated to understand the effect of foaming on HS crystalline domains in the ETPU foams. All foamed medium molecular weight polyol TPU with various processing parameters were analyzed using DSC. In Figure 4.26, 4.27 and 4.28, all DSC thermograms of both unfoamed and foamed PL4.28-58 samples can be seen. Unfoamed samples refer annealing with CO₂ in autoclave without inducing foaming.

For all samples which are foamed at 2000 psi, double melting peak with prominent T_{m-high} dissappeared, instead broad melting peak was observed. The reason of that might be the rapid expansion due to fast depressurization, which caused chains to stretch, high perfected crystals to break down and formed a more dispersed perfection of HS crystals. As a result, T_{m-high} decreased in a range of 3-15 degree.

Since foaming at saturation pressure of 1000 psi and 1500 psi did not form high expansion as much as foaming at saturation pressure of 2000 psi, double melting peak can still be observed (Figure 4.27). However, comparing to unfoamed DSC results, T_{m-low} decreased from 170.6°C to 158.5°C and T_{m-high} from 186.6°C to 171.8°C at 1000 psi foaming. T_{m-low} decreased from 170.3°C to 156.2°C and T_{m-high} from 180.8°C to 164.2°C at 1500 psi foaming.

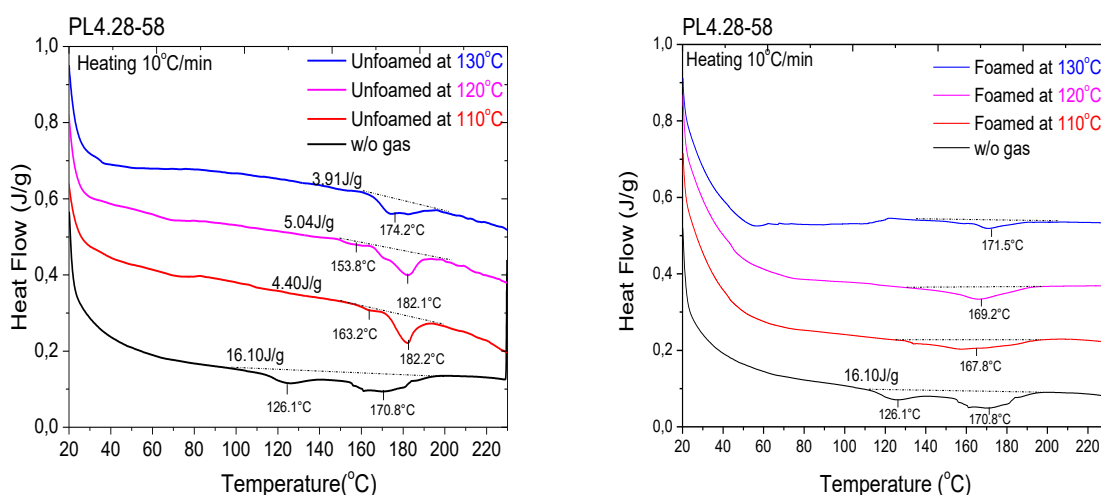


Figure 4.26: DSC thermograms of PL4.28-58 unfoamed and foamed samples at various saturation temperatures.

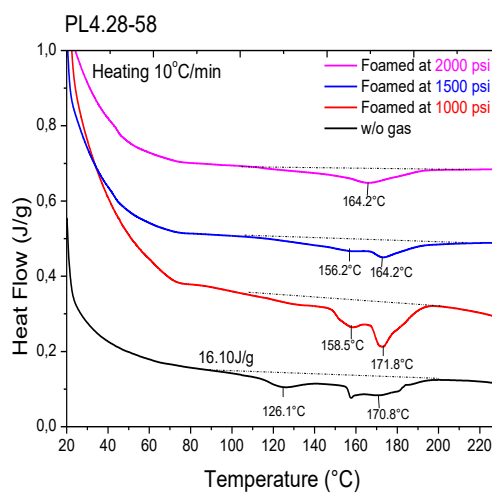
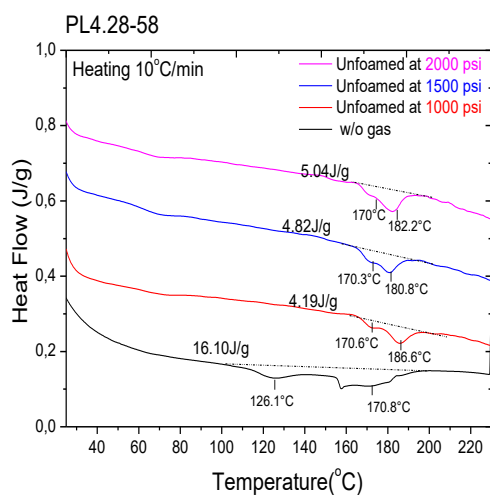


Figure 4.27: DSC thermograms of PL4.28-58 unfoamed and foamed samples at various saturation pressures.

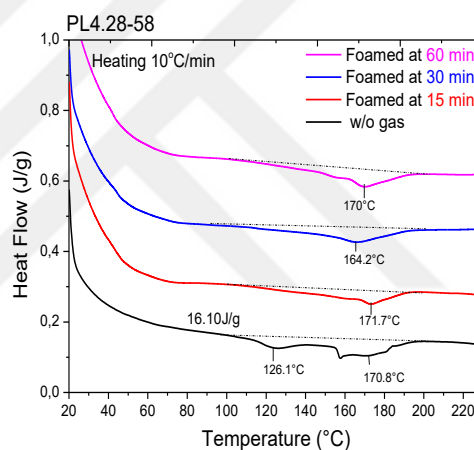
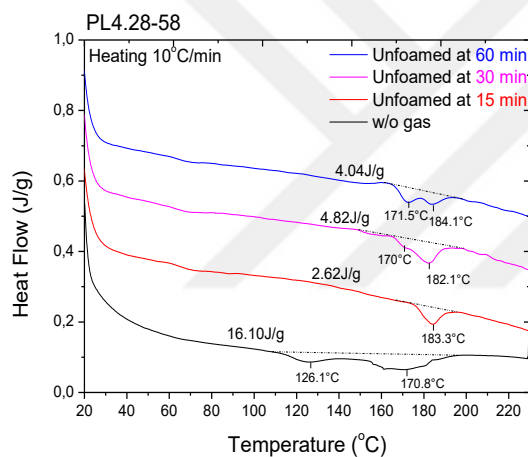


Figure 4.28: DSC thermograms of PL4.28-58 unfoamed and foamed samples at various saturation times.

5. CONCLUSION

In this thesis, ETPU bead foams with different length and type of polyols successfully developed in a lab-scale autoclave bead foaming setup. The effect of process parameters on foaming behavior of TPUs was investigated. The saturation temperature had a significant effect on foams. The expansion ratio and cell density was improved with increasing temperatures for polyester based TPUs; however, polyether based TPU required low temperatures comparing to polyester based TPU due to its thermal instability. Moreover, medium and high molecular weight polyol TPUs needed higher temperatures for better expansion because the movement of their soft segment chains was harder and required more energy. The saturation pressure was also important on foam morphology. Increasing saturation pressure increased CO₂ solubility, causing better cell nucleation, as a result better expansion and finer cells were obtained for all TPUs. On the other hand, the saturation time had different effect from other parameters. Increase in saturation time did not result in better expansions, on the contrary caused to increase in flexibility of soft segment chains and too much cell growth with thinner cell walls, which resulted in shrinkage. Highest molecular weight polyol TPU showed less cell growth comparing to medium and low molecular weight polyol TPU due to its high entanglement. Moreover, the short saturation time was not enough to CO₂ be dissolved, especially for high molecular weight polyol TPU. For low and medium molecular weight polyol, higher expansion was obtained at short saturation time; however, due to the fast cell growth, shrinkage was also observed. In general, the reason of high expansion was the higher cell nucleation for TPU with long soft segment chains, while it was cell growth for TPU with shorter soft segment chains.

For better understanding of crystallization during foaming, we simulated the annealing with CO₂ at autoclave without fast depressurization for medium and high molecular weight polyol TPUs, and then analysed with DSC. In general, ΔH_T showed significant decrease during annealing with CO₂. Not only the high temperatures melted less perfected crystals, but also the dissolution of CO₂ in TPU matrix increased the distance between molecular chains and hence decreased the crystallinity. Decreased

crystallinity likely helped cell growth in the TPUs microstructure during foaming process. Moreover, presence of CO₂ easily advanced the flexibility of TPU chain, and led to recrystallization of less perfected HS crystallites toward more closed pack. Hence, the lower melting peak, T_{m-low} shifted towards higher temperature. Saturation of TPU with CO₂ did not affect the T_{m-high} as much as it affected T_{m-low} . Nevertheless, T_{m-high} became more prominent since CO₂ increased the mobility of chains and promoted formation of high perfection crystallites. In the DSC thermograms of foamed samples, it was seen that increasing expansion caused to broader melting endotherms, result of deformation of large perfected HS crystals due to chain stretching.



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EDUCATION

- **B.Sc.** : 2011, Istanbul Technical University, Faculty of Science and Letters, Department of Chemistry

JOURNAL ARTICLES:

- **Kucuk, E.B., Bati, B. Nofar, M., Nijs, C., Klein, R., Tomei, G.**, “Development of microcellular expanded TPU bead foams using supercritical CO₂”, (to be submitted)
- **Kucuk, E.B., Bati, B. Nofar, M., Nijs, C., Klein, R., Tomei, G.**, “Effect of hard segment content on the microcellular bead foaming behavior of TPU”, (to be submitted)
- **Bati, B., Kucuk, E.B., Nofar, M., Nijs, C., Klein, R., Tomei, G.**, “Influence of molecular weight of the soft segment on microcellular bead foaming behavior of TPU”, (to be submitted).

CONFERENCE ARTICLES:

- **Bati, B., Kucuk, E.B., Nofar, M., Nijs, C., Klein, R., Tomei, G.**, “Effect of TPU soft segment molecular weight on TPU’s bead foaming behavior”, Polymer Processing Society 35, Izmir/Cesme, Turkey, May 26-30, 2019.
- **Kucuk, E.B., Bati, B. Nofar, M., Nijs, C., Klein, R., Tomei, G.**, “Effect of TPU hard segment on TPU’s bead foaming behavior”, Polymer Processing Society 35, Izmir/Cesme, Turkey, May 26-30, 2019.

