ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PRODUCTION AND CHARACTERIZATION OF MODIFIED PET FOAM

M.Sc. THESIS

Hatice Bilge ÇEBİŞLİ

Department of Polymer Science and Technology

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MAY, 2012

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Thesis Advisor: Prof. Dr. Nurseli UYANIK (ITU)
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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

MODİFİYE EDİLMİŞ PET KÖPÜK ÜRETİMİ VE KARAKTERİZASYONU

YÜKSEK LİSANS TEZİ

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To my family,

FOREWORD

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Hatice Bilge ÇEBİŞLİ
Polymer Science and Technology

TABLE OF CONTENTS

Page

ABBREVIATIONS

ABS : Acrylonitrile-Butadiene-Styrene Copolymer
ASTM : American Society for Testing and Materials
BMC : Bulk Molding Compound
C.A. : Contact Angle
CBA : Chemical Blowing Agent
DSC : Differential Scanning Calorimeter
DMA : Dynamic Mechanical Analysis
DTA : Differential Thermal Analysis
EVA : Poly(ethylene vinyl acetate)
HCFCs : Hydro Chlorofluoro Carbons
HDPE : High Density Polyethylene
IS : Isoprene–Styrene Copolymer
L.A. : Left Angle
LDPE : Low Density Polyethylene
LLDPE : Linear Low-Density Polyethylene
MCFs : Microcellular Foams
MFI : Melt Flow Index
Min : Minute
PBA : Physical Blowing Agent
PC : Polycarbonate
PCL : Polycaprolactone
PCL-PDMS-PCL : Polycaprolactone and Poly(dimethyl siloxane) Block Copolymer
PDMS : Poly(dimethyl siloxane)
PE : Polyethylene
PET : Poly(ethylene terephthalate)
PFA : Physical Foaming Agent
PPG : Poly(propylene glycol)
PS : Polystyrene
5-PT : 5-Phenyl-1H-tetrazole
PU : Polyurethane
PVA : Poly(vinyl alcohol)
R.A. : Right Angle
SAN : Styrene-Acrylonitrile Copolymer
SEM : Scanning Electron Microscopy
SMC : Sheet Molding Compound
TGA : Termogravimetric Analysis
T_g : Glass Transition Temperature
T_m : Melting Temperature

LIST OF TABLES

LIST OF FIGURES

Page

PRODUCTION AND CHARACTERIZATION OF MODIFIED PET FOAM

SUMMARY

Polymeric structural foams have been widely used in automotive, wind turbine, aerospace, construction, marine, electronic and packaging industries. Foam plastics are one of the fastest growing sectors of the plastics industry. As the consumption of plastic materials increased, the concept of generating cells or bubbles in plastics industry became an attractive option to reduce the cost of plastic material as long as the mechanical properties of products were not sacrificed.

Foaming of thermoplastics is an advanced technology used in extrusion, compounding, injection molding, blow molding, rotational molding, thermoforming, and compression molding. There are two general types of foaming agents: a physical foaming agent is metered directly under pressure into the polymer melt, is nearly always the primary source for low density foams; a chemical foaming agent is a pure chemical that reacts to produce blowing gas through heat-induced decomposition, is usually the primary source for higher density foams.

Nearly all thermoplastics can be foamed, but commercially important foams are mainly based on commodity plastics such that polyolefin (polyethylene, polypropylene), polyurethane, polystyrene, poly(vinyl chloride), poly(ethylene terephthalate), polycarbonate, and poly(methyl methacrylate) appeared as thermoplastic matrices. Among all important commercial thermoplastics, semi-crystalline poly(ethylene terephthalate) (PET) was chosen for foaming polymer recently due to its superior characteristics, i.e. good resistance to high temperatures and high compressive strength. The semicrystalline materials exhibit ten to one thousand times higher cell nucleation densities compared with the amorphous materials, resulting from heterogeneous nucleation contributions.

The aim of this study is to produce poly(etylene terephthalate) rigid foams in closed-cell structure with a chemical blowing agent (CBA), by compression molding method. A commercial ABA type triblock copolymer of polycaprolactone and poly(dimethyl siloxane) which is α,ω-dihydroxy polycaprolactone–poly(dimethylsiloxane) (PCL-PDMS-PCL) with $M_n = 6500 +/-600$; $M_{w\ \mathrm{PDMS}} = 3000$ and $M_{w\ \mathrm{PCL\ endblocks}} = 2000$ g/mol was used as additive.

The foaming of thermoplastic polymer was carried out with compression molding process, which provides a convenient method for quick evaluation of material formulations instead of labor and material intensive extrusion processing. The process parameters, which are processing temperature, processing time and processing pressure, can be optimized in this compression method.

Poly(ethylene terephthalate) is one of the high-temperature foaming polymers among other thermoplastic polymers, and foamed with an exothermic type of chemical blowing agent that is 5-phenyl-1H-tetrazole (5-PT). For most molding and extrusion applications, the general rule of thumb is to select a chemical blowing agent that has

a decomposition, or gas release, temperature closely matching with the processing temperature to be used for the polymer. Due to the fact that, 5-PT was chosen as a chemical blowing agent which decomposes into gas form at elevated temperatures (above 250 ^{o}C), and the decomposition temperature of 5-PT closely matching with the melting range of PET (around 250 ^{o}C) for foaming process.

Polymer foams were prepared by using hydraulic hot press with the processing temperature and pressure in the ranges of 255 - 275 ^{o}C and 10 - 100 bar, respectively. The process foaming time were taken from 6 to 22 minutes. The amount of 5-PT addition as chemical blowing agent was changed between 0.05 % and 0.25 % (wt) during the preparation of PET foam mixtures. After the foaming process in hydraulic hot press was carried out, the foamed products were cooled in hydraulic cold press with contant cooling time as 5 minutes under 50 bar pressure. Although the content of the chemical blowing agent was kept constant as 0.10 % and 0.20 % in PET foam samples, 0.10 % CBA content gave the best results. The optimum conditions were achieved after several experiments, and then the PET foam samples to be analysed were prepared by compression molding technique in hydraulic hot and cold presses. The optimum conditions were presented as at 260 °C the processing temperature, under 15 bar the processing pressure, 0.10 % (wt) CBA and 0.075 % (wt) PDMS contents with 10 minutes the processing time in hydraulic hot press, and 5 min cooling time under 50 bar pressure in hydraulic cold press.

The PCL-PDMS-PCL copolymer as surface modifying additive in polymer were mixed at low levels (0.050 % – 0.300 % by weight) with PET, the resulting systems displayed silicone-like, hydrophobic surface properties, as determined by critical surface tension measurements or water contact angles. The effect of PCL-PDMS-PCL content, the base polymer type and the morphology on the resulting surfaces are discussed. PCL-PDMS-PCL addition to the foamed PET samples gave increased toughness and better surface properties than those of the foamed PET samples without PCL-PDMS-PCL additive under the same conditions. The brittleness of the PET foams was also decreased although PCL-PDMS-PCL was added at very low weight percentages during the preparation of the PET foam mixture.

The prepared 27 samples were investigated structural, morphological, mechanical and processing points of view. The produced PET foams were analysed with contact angle measurement, density calculation, cell size analysis and three-point bending mode flexural test. A cellular foamed plastics were characterized by a cell size of one milimeter or less in diameter and a cell density of at least a thousand cells per cubic centimeter. These thermoplastic foams are produced by supersaturating a polymer with a gas and then using a thermodynamic instability to generate thousands of microvoids instantaneously. Elastic modulus, and contact angle measurements of the foamed PET samples were measured for different cell structures. The results showed that the mechanical properties are significantly affected by the foaming parameters; the PCL-PDMS-PCL additive and the chemical blowing agent contents of the thermoplastic polymer matrix. The prepared closed-cell PET foams were characterized morphologically, physically and mechanically in terms of contact angle measurement (ASTM D5946, ASTM D5725), density calculation (ASTM D1622-08), and 3-point bending mode flexural test (ASTM D790-10).

This study also focuses on the feasibility study of improving mechanical properties of high density poly(ethylene terephtlate) (PET) foams having closed-cell structure.

The bulk density values are changing between 0.945 g/cm^3 and 1.190 g/cm^3. These results shows that high density foams were formed.

The experimental results show that the elastic modulus of PET foam increased as PCL-PDMS-PCL additive increased. Besides, as the bulk density increased the elasticity of the foam was also increased, as the cell density increased the elasticity of the foam was decreased. In general, crystallized products are more brittle than amorphous products. PDMS addition to the foamed PET samples gave increased toughness and better surface properties than those of the foamed PET samples without PDMS additive under the same conditions. The weight reduction of PET was achieved without sacrificing much of the mechanical properties by introducing cellular structure in thermoplastic materials. It was observed that the elastic modulus increased nonlinearly as the relative foam density and PDMS additive content increased.

When the foaming time was more than 6 minutes, the tensile strength and elongation at break values of cellular PET started to decrease. This was because the longer the gas was allowed to diffuse into the cells, the larger the cell size was. Therefore, the larger cell size (larger to some extent) decreased the tensile strength and elongation at break. The foaming time had a relatively strong influence on cell nucleation and cell growth for the amorphous and semicrystalline polyester meaning there was an effect on the mechanical properties. Similar strong cell-size dependence on foaming time was reported for styrenic resins. The foaming time in our experiment did have effects on the mechanical properties, too.

The solubility of nitrogen in polymers increases linearly with pressure up to about 25 MPa. Therefore, increasing foaming pressure actually increased the foaming gas concentration inside of PET, and the net result was a cell-size decrease and a cell density increase. When the the cell density was larger, the elongation at break (% ε_b) became larger. This explains why the elongation at break increased with increasing foaming pressure under our foaming pressure scope. When the foaming pressure was smaller than 10 MPa, the PET sample showed no detectable cell structure. This means that the foaming pressure should exceed 10 MPa if one hopes to obtain microcellular PET foam.

The effect of foaming temperature on the mechanical properties occurred in the temperature range between 250 and 275 °C. When the foaming temperature was lower than 250 °C, there was no detectable cell structure. One of the reasons was that the foaming reagent 5-PT could not decompose completely at lower temperature; hence, there was probably not enough gas necessary to form microcellular PET. Another reason was that at lower foaming temperatures, the PET matrix stiffness may have been sufficiently large enough to prevent nucleated cells from growing to detectable size, even though the allotted foaming time should have allowed all of the available gas to diffuse into the cells.

The effects of polycaprolactone block poly(dimethyl siloxane) (PCL-PDMS-PCL) additive content on rigid PET foams were investigated mainly. There is an increasement in contact angle measurement results with certain amount of PDMS percentage increasement because of the migration of PDMS molecules to air-polymer surface in PET foam samples. According to the calculated results, for the samples which do not include PCL-PDMS-PCL, showed decrease in elongation at break. It was observed that when the PCL-PDMS-PCL additive content was increased, the elastic modulus of PET foams increased, and the elastic modulus was also increased as the relative foam density was increased.

Each sample description refers to a specific composition involving the components used in the preparation of the samples. This description code explanation is presented in results and discussion section.

MODİFİYE EDİLMİŞ PET KÖPÜK ÜRETİMİ VE KARAKTERİZASYONU

ÖZET

Polimer yapılı köpükler otomotiv, rüzgar türbini, uçak, uzay, inşaat, denizcilik, elektronik ve ambalaj sektörlerinde kullanılmaktadır. Termoplastik ve termoset olmak üzere iki ana gruba ayrılan polimerik köpükler plastik endüstrisi baz alındığında en hızlı büyüme gösteren sektörlerin başında gelmektedir. Son zamanlarda plastik malzemelerin tüketimindeki artış da bunu kanıtlamaktadır. Dolayısıyla, plastik üretiminde “hücre” ya da “habbecik” oluşturma konsepti, (mekanik özelliklerinden ödün verilmeden) hafif ürün eldesinin yanısıra maliyet düşürmede etkin bir seçenek olmuştur.

Termoplastik köpük üretimi ileri bir teknoloji bilgisi gerektiren ekstrüzyon, enjeksiyonla kalıplama, üflemeli kalıplama, döner kalıplama, ısıl şekillendirme (termoforming) ve basınçla kalıplama (pres) yöntemleriyle gerçekleştirilmektedir. Köpürtücü ajanların iki genel tipi vardır. Fiziksel bir köpürtücü ajanlar, basınç altında doğrudan polimer eriyiğine beslenir, ve düşük yoğunluklu köpüklerin üretiminde neredeyse her zaman birincil kaynak olarak geçmektedir. Kimyasal köpürtücü ajanlar ise köpük ürünü eldesi için gerekli olan gazı üretmek amacıyla yüksek ısı ile indüklenme sonucu bozunma reaksiyonu veren saf kimyasallardır.

Termoplastiklerin neredeyse tamamından termoplastik köpük ürün elde edilebilir; ancak ticari değeri olan köpükler, köpük malzemelerde termoplastik matrisler olarak beliren poliolefin (polietilen, polipropilen), poliüretan, polistiren, poli(vinil klorür), polikarbonat, poly(etilen tereftalat), poli(metil metakrilat) gibi yaygın olarak kullanılan plastiklere dayanır. Belirtilen önemli ticari termoplastik malzemeler arasından, üstün özellikli yarı-kristal termoplastik malzeme poly(etilen tereftalat) (PET), bu çalışmada köpük üretimi için seçilmiştir. Dolayısıyla, PET köpük eldesi bu çalışmanın ana konusu olarak belirlenmiştir, çünkü PET yüksek sıcaklık, basınç ve darbe dayanımı gibi üstün özelliklere sahiptir. Yarı-kristal malzemeler amorf termoplastiklere göre heterojen hücre yoğunluğuna katkı sağladıkları için, on ile bin kat arasında değişen hücre oluşumunu tetiklerler, dolayısıyla daha fazla hücre yoğunluğu elde edilir.

Bu çalışmanın amacı, kimyasal köpürtücü ajan kullanılarak presle kalıplama yöntemi ile kapalı-hücre morfolojisine sahip, yapısal olarak sert poly(etilen tereftalat) köpük üretmektir. Polikaprolakton (PCL) ve poli(dimetil siloksan) (PDMS) ‘in üç bloklu ABA tipi ticari bir kopolimeri olan α,ω-dihidroksi polykaprolakton–poly(dimetil siloksan) (PCL-PDMS-PCL) Mn = 6500 (+/-600); Mw_{PDMS} = 3000 ve $Mw_{\text{PCL uç blokları}}$ = 2000 gr/mol, katkı maddesi olarak kullanılmıştır.

Bu çalışmada termoplastik polimer köpük üretimi presle kalıplama prosesi ile gerçekleştirilmiştir. Bu proses, oldukça zahmetli ekstrüzyon prosesine kıyasla malzeme formülasyonlarının çok daha hızlı geliştirilmesine olanak sağlar. Presle

kalıplama metodunda optimize edilebilen proses parametreleri ise proses sıcaklığı, proses süresi ve proses basıncıdır.

Termoplastik polimerler arsında oldukça yüksek sıcaklıklarda köpük elde edilebilen bir polimer olan poly(etilen tereftalat), ekzotermik tipteki kimyasal şişirici maddesi 5-fenil-1H-tetrazol (5-PT) ile şişirilerek köpük eldesi sağlanmıştır. Birçok kalıplama ve ekstrüzyon uygulamalarında, geçerli olan genel kural kimyasal şişirici ajanının bozunma sıcaklığı ya da diğer bir deyişle gaz salınımının gerçekleşmesi için gereken sıcaklığın, polimer işleme koşulları için gerekli olan sıcaklık değerinde seçilmesidir. Bu genel kural baz alınarak, bu çalışmada PET’in işleme sıcaklığı (~250^{o}C) ile uyumlu olan ve dolayısıyla yüksek sıcaklıklarda (~250 ^{o}C), parçalanıp gaz formuna geçebilen ekzotermik bir kimyasal şişirici ajan olan 5-fenil-1H-tetrazol (5-PT) kullanılmıştır.

Polimer köpükler hidrolik sıcak pres makinesi kullanılarak 255 - 275 ^{o}C aralığındaki işleme sıcaklığı, 6 – 22 dakika aralığında değişen proses süresi ve 10 - 100 bar aralığındaki proses basıncı ile üretilmiştir. Köpük üretiminde kimyasal şişirici madde olarak kullanılan 5-PT miktarı kütlece % 0,05 ve % 0,25 aralığında değişmiştir. Hidrolik sıcak pres makinesinde yüksek sıcaklıklarda elde edilen eriyik karışımı, 50 bar basınç altında 5 dakika boyunca hidrolik soğuk pres makinesinde soğutulmuş ve sert formdaki PET köpük eldesi sağlanmıştır. Şişirici kimyasal madde miktarı kütlece % 0,10 – % 0,25 aralığında değişmesine rağmen en iyi sonucu kütlece % 0,10 kimyasal şişirici madde içeriği vermiştir. Kütlece % 0,10 kimyasal şişirici ajan ve kütlece % 0,075 PCL-PDMS-PCL katkısı içeriği ile oluşturulan karışım sıcak pres makinesinde 260 °C proses sıcaklığı, 15 bar basınç uygulaması, 10 dakika proses süresi ile ısıtma işlemi yapıldıktan sonra, soğuk pres makinesinde 15 bar basınç altında 5 dakika süreyle soğutma işlemi yapılarak PET köpük üretimi için optimum koşullar belirlenmiştir.

Polikaprolakton blok poli(dimetil siloksan), (PCL-PDMS-PCL) kopolimeri yüzey modifikasyon katkısı olarak kullanılmış ve PET ile düşük oranlarda (kütlece % 0,050 – % 0,300 aralığında) karıştırılmıştır. Eklenen PCL-PDMS-PCL miktarının etkileri, elde edilen köpük ürününün morfolojik yüzey özellikleri ve baz alınan polimer tipi tartışılmıştır. Sonuçta, kritik yüzey gerilimi ölçümleri veya su ile temas açısı ölçümlerinden yararlanılarak, ürünlerin silikon benzeri bir hidrofobik yüzey özelliği gösterdiği belirlenmiştir. PCL-PDMS-PCL katkısı maddesi eklenerek elde edilen PET köpük örnekleri, aynı koşullar altında PCL-PDMS-PCL katkı maddesi olmadan elde edilen PET köpük örneklerine göre artan bir tokluk ve daha iyi yüzey özelliği sağlamıştır. PET köpük karışımı hazırlanması sırasında çok düşük miktarlarda PCL-PDMS-PCL katkısı kullanılmasına rağmen elde edilen PET köpüklerde kırılganlık da azalmıştır.

Deneyler sonucunda hazırlanan 27 örnek farklı proses parametreleri denenerek, yapısal, yüzeysel ve mekanik özellikleri açısından incelenmiştir. Farklı hücre özellikleriyle elde edilen tüm PET köpük örnekleri temas açısı ölçümü, yoğunluk hesaplaması, hücre boyutlarının analizi ve üç-nokta eğme mekanik testi ile analiz edilmiştir. Termoplastik köpük örnekleri, hücresel olarak 1mm veya daha düşük çap uzunluğunda, ve santimetreküp başına en az bin tane hücreden oluşan hücre yoğunluğuyla karakterize edilmiştir. Bu termoplastik köpükler, bir gazla bir polimerin süper-doygunlaştırılmasını takiben, aynı anda milyonlarca mikro-boşluk yaratılması sırasında oluşan termodinamik bir kararsızlık etkisiyle üretilmiştir. Farklı hücre yapıları için elastik modülü ve temas açısı ölçümleri yapılmıştır. Sonuçlar, değişken proses parametrelerinin; PET matrisindeki PCL-PDMS-PCL katkısı ve kimyasal şişirici madde içeriği, elde edilen ürünlerdeki mekanik özellikleri önemli ölçüde etkilediğini göstermiştir. Hazırlanan kapalı hücre yapısındaki PET köpük örnekleri için morfolojik, fiziksel ve kimyasal olarak; ASTM D5946 ve ASTM D5725 standartlarına uygun olarak yapılan temas açısı ölçümleri, ASTM D1622-08 standartına uygun olarak yapılan yoğunluk hesaplamaları ve ASTM D790-10 standartına uygun olarak yapılan 3-nokta eğme testleri ile karakterize edilmiştir.

Bu çalışma ile kapalı hücre yapısına sahip yüksek yoğunluklu poli(etilen teraftalat) (PET) köpüklerinin mekanik özelliklerinin iyileştirilmesine odaklanılmıştır. Çalışmalar sonucunda yoğunluk değerlerinin 0,945 g/cm^3 ve 1,190 g/cm^3 aralığında değiştiği gözlemlenmiştir. Bu sonuçlar yüksek yoğunluklu köpük eldesinin gerçekleştiğini göstermektedir.

Deneysel sonuçlar, PET köpük elastik modülünün PCL-PDMS-PCL katkısı arttıkça arttığını göstermektedir. Ayrıca, köpük yoğunluğu arttıkça köpük elastisitesi de artarken, habbecik yoğunluğu arttıkça köpük elastisitesi azalmıştır. Kristal yapıdaki ürünler, amorf yapıdaki ürünlere göre daha çok kırılganlık gösterir. PCL-PDMS-PCL katkısı içeren PET köpük örnekleri, aynı koşullar altında PCL-PDMS-PCL katkısı olmadan elde edilen PET köpük örneklerine göre artan bir tokluk ve daha iyi yüzey özellikleri sergilemiştir. Termoplastik malzemelerden hücresel yapılı köpük üretimi eldesi, sarf edilen PET ağırlığındaki azalma avantajı ile mekanik özelliklerden ödün verilmeden sağlanmıştır. Bağıl köpük yoğunluğu ve PCL-PDMS-PCL katkı içeriği arttıkça, örneklerde doğrusal olmayan bir elastik modül artışı gözlenmiştir.

5-PT kimyasal şişirici ajanının bozunarak gaz formuna dönüşmesi ve PET granüllerinin tamamıyla erimesiyle oluşan eriyik karışımı sisteminda bir dengeye ulaşıldıktan sonra, üründe homojen baloncuk dağılımı gözlenebilmesi için, PET köpük üretimi 6 dakikadan daha uzun sürelerde gerçekleştirilmiştir. Süre ilerledikçe, oluşan hücresel yapıdaki PET köpüğün çekme mukavemeti ve uzamada kopma mekanik özellikleri azalmaya başlamıştır. Bunun nedeni, gazın süre ilerledikçe hücre içine difüzlenmesindeki artış ile hücre boyutunun büyümesidir. Bu yüzden, büyük bir çap değerine ulaşan hücreler (belli bir dereceye kadar büyüme), çekme dayanımı ve uzamada kopma değerini düşürmüştür. Amorf ve yarı kristal yapıdaki polyester köpük eldesinde, habbecik oluşum süreci ve proses süresinin mekanik özellikler üzerine etkisi olduğu ispatlanmıştır. Benzer özellik stirenli reçineler için de hücre-boyutunun, köpük oluşumu için gerekli olan proses süresi ile bağıntılı olduğu rapor edilmiştir. Bizim deneyimizde de habbecik oluşum süresi ürünlerin mekanik özelliklerini etkilemiştir.

Polimerlerdeki azot çözünürlüğü yaklaşık 25 MPa basınca kadar doğrusal olarak artmaktadır. Bu nedenle, köpük oluşumunda basıncın artırılması aslında PET içinde çözünen köpürtücü gaz konsantrasyonu artırmıştır, ve bu durumun net sonucu ise hücre boyutunda küçülme ve hücre yoğunluğunda artış şeklinde olmuştur. Hücre yoğunluğu ne kadar fazlaysa, uzamada kopma (% ε_b) değeri de o kadar büyüktür. Bu durum, mekanik testlerimizin deneysel sonuçları kapsamındaki uzamada kopma değerlerinin, basınç yükselmesiyle neden arttığını açıklamaktadır. Köpük oluşum basıncı 10 MPa ‘dan daha düşük iken, PET örneği saptanabilir bir hücre yapısı göstermemiştir. Bu durum, PET köpük elde edilmek isteniyorsa 10 MPa basıncın aşılması gerektiği anlamına gelmektedir.

Köpük oluşum sıcaklığının ürünlerdeki mekanik özelliklere etkisi, 250 ve 275 °C sıcaklık aralığındaki çalışmalarda sonuç vermiştir. Köpük oluşum sıcaklığı 250

°C’den daha düşük iken, oluşmuş herhangi bir hücre yapısı saptanamamıştır. Bu durumun nedenlerinden biri, 5-PT kimyasal şişirici ajanının düşük sıcaklıklarda tamamiyle bozunmuş olmamasından dolayı hücresel yapı formundaki PET köpük eldesi için gerekli olan gaz miktarının bu ortamda muhtemelen yeterli miktarda bulunmamasından kaynaklanmış olmasıdır. Diğer bir nedeni ise, düşük sıcaklıklarda gerçekleşen köpük üretiminde, mevcut olan bütün gazın hücrelerin içine doğru difüzlenebilmesi için gerekli olan habbecik oluşum süreci sağlanmış olsa bile, hücre oluşumu sürecinde saptanabilir bir hücre boyutuna ulaşılmasını engelleyen PET matrisinin sertlik değerinin yeterince büyük olmasından dolayı kaynaklanmaktadır.

Elde edilen sert PET köpüğün özellikleri üzerine, polikaprolakton blok poli(dimetil siloksan) (PCL-PDMS-PCL) katkısının etkisi çalışmalar sırasında önemli ölçüde araştırılmıştır. Belirli miktarlarda PCL-PDMS-PCL yüzdesi artışı ile orantılı olarak, PET köpük örneklerinde bulunan PCL-PDMS-PCL moleküllerinin hava-polimer yüzeyine göç etmesinden dolayı, temas açısı ölçüm sonuçlarında artış gözlemlenmiştir. Deneysel sonuçlara göre, PCL-PDMS-PCL katkısı içermeyen örneklerin uzamada kopma değerlerinde azalma olmuştur. PET köpük örneklerinde PCL-PDMS-PCL katkısının yüzdesi arttıkça, elastik modül artmıştır. Bağıl köpük yoğunluğundaki artış ile de elastik modülün arttığı gözlemlenmiştir.

Her örnek tanımlaması, örneklerin hazırlanılmasında kullanılan bileşenleri içerecek şekilde yapılmıştır. Bu kod sistemi sonuçlar ve yorumlar kısmında figürlenerek açıklanmıştır.

1. INTRODUCTION

Polymeric structural foams came into being in the 1910s and have been widely used in automotive, aerospace, construction, electronic and packaging industries since that time. Foam plastics are one of the fastest growing sectors of the plastics industry. At the beginning of the 21st century, about 23 billion pounds of foamed products were consumed each year around the world [1], and this number is expected to increase significantly in the future as more applications are discovered. Foam processing in general has gained a significant technical and scientific sophistication [2], [3]. However, notwithstanding the capability to develop new classes of cellular materials by foaming, the literature is still limited.

Over the last decades, foaming of polymers has evolved into a well-developed technology for equipping materials with a set of desired properties. The achieved scientific understanding, the technological progress as well as the broad range of realized commercial applications have further driven the significant growth of this particular field. Besides the continuous enhancement of foam formulations and the ever-increasing improvement of processing technologies, the evolution of new fields of research related to foams and their successful technological transfer into industrial applications are steadily proceeding.

Nearly all thermoplastics can be foamed, but commercially important foams are mainly based on commodity plastics. Foamed thermoplastic matrices are polyolefin, polyurethane, polystyrene, poly(vinyl chloride), poly(methyl methacrylate), poly(ethylene terephthalate), generally.

There are several categories of polymeric foams; however, only structural polymeric foams (i.e., high density foams with closed-cell structure) are of concern in the thesis.

The recent European ban of the use of azo based foaming agent “azodicarbonamide” in gaskets and other products that come in contact with food [38] result in the fact that the preference of environmentally friendly blowing agent “5-phenyl tetrazole” usage in this study.

Recently a number of leading materials suppliers have tried to place clarified polypropylene, polystyrene, and even new grades of nearly transparent high-density polyethylene as potential substitutes for poly(ethylene terephthalate). So far, market acceptance of these appears to be very limited. PET remains a favorite among brand owners, who value its appearance, ease of processing and performance in packaging lines, and its positive environmental image [4]. Foaming of polyesters in particular can be identified as a topic of potential interest, both from a scientific as well as from a commercial point of view.

Poly(ethylene terephthalate) (PET) is a low-cost engineering polymer with good mechanical and thermal characteristics and exhibits high elastic moduli, high glass-transition temperature (T_g), and good crystallinity and solvent resistance, appearing one of the most versatile plastics in the world [5].

The availability of foams based on PET could be very interesting, mainly for the temperature range allowed by the high melting temperature (T_m) of the bulk polymer and its crystallinity. Such foams can be used in applications such as packaging, thermal insulating panels, transportation, construction, and cores for sandwich structures.

Although the market finds excellent utilities for PET, the low shear and elongational viscosities and low melt strength of conventional PET prevents from being easily foamed by typical technologies such as gas extrusion foaming, and complex procedures have to be used [6]. In many cases PET has to be modified chemically or physically to have homogeneous cell distribution in polymer matrix. In chemical modifications, different treatments have been developed to improve the PET macromolecular characteristics, in particular, to extend the polymer chain lengths [7]. In physical type modification, PET is processed with additives to achieve specific physical properties such as flexural, tensile, and barrier properties.

Microcellular semicrystalline polymers such as poly(ethy1ene terephthalate) show great promise for engineering applications because of their unique properties, particularly at higher densities. Recent studies reveal some high-density microcellular polymers have longer fatigue lives and/or equal strengths to the neat polymer. Relatively few microcellular-processing studies of semicrystalline polymers have been presented. In general, semicrystalline polymers are relatively difficult to microcellular process compared to amorphous polymers. The semicrystalline materials exhibit ten to one thousand times higher cell nucleation densities compared with the amorphous materials, resulting from heterogeneous nucleation contributions [8].

Considering everything, PET was chosen recently among thermoplastic polymers due to its superior characteristics, i.e. good resistance to high temperatures and high compressive strength.

Furthermore, to produce polymeric cellular structures the blowing agents are needed. Chemical blowing agents (CBAs) are made of a class of solid or liquid compounds that decompose to form gases under processing conditions [9]. Most CBAs are solids and decompose within a given temperature range. For most molding and extrusion applications, the general rule of thumb is to select a CBA that has a decomposition, or gas release, temperature closely matching the processing temperature to be used for the polymer [10]. PET melts at higher temperatures around 250 °C, and 5-PT decomposes at around 250 °C, too. Due to the fact that, 5-phenyl tetrazole (5-PT) was chosen as the suitable chemical blowing agent to foam poly(etylene terephthalate) PET in this study.

In this study, closed-cell structured poly(ethylene terephthalate) rigid foams were produced with the help of a chemical blowing agent (5-PT) by compression method. A commercial α,ω-dihydroxy polycaprolactone–poly(dimethylsiloxane) (PCL-PDMS-PCL) additive were used at very low weight percentages to improve surface properties of the PET foam samples, and to decrease the property of brittleness of the PET foams. The PET foams produced with and without PCL-PDMS-PCL triblock copolymer additive were analysed with structural, morphological and mechanical testing methods. Besides, bubble formation characteristics were reviewed in a thermoplastic polymer matrix.

2. THEORETICAL PART

2.1 Thermoplastic Polymers

Plastics are an important group of raw materials for a wide array of manufacturing operations. Applications range from small food containers to large chemical storage tanks, from domestic water piping systems to industrial piping systems that handle highly corrosive chemicals, from toys to boat hulls, from plastic wrap to incubators, and a multitude of other products. When properly designed and applied, plastic provides light weight, sturdy/economic/resistant, and corrosion products. Plastics are polymers. The term plastic is defined as “capable of being easily molded,” such as putty or wet clay. The term plastics was originally adopted to describe the early polymeric materials because they could be easily molded. Unfortunately, many current polymers are quite brittle, and once they are formed they cannot be molded [11].

Polymers can be subdivided into three main categories; *thermoplastics* consist of individual long chain molecules, and in principle any product can be reprocessed by chopping it up and feeding it back into the appropriate machine; *thermosets* contain an infinite three dimensional network which is only created when the product is in its final form, and cannot be broken down by reheating whilst *rubbers* contain looser three dimensional networks, where the chains are free to change their shapes.

Table 2.1 : Thermoplastics commonly used for closed-cell foams.

Polymer name	Abbreviation	Type
Polyethylene	PE	Semi-crystalline
Ethylene-vinyl acetate copolymer	EVA	Semi-crystalline
Polypropylene	PP	Semi-crystalline
Polystyrene	PS	Glass
Polyvinylchloride	PVC	Glass + 10% crystalline
Polyphenyleneoxide blend with PS	PPO	Glass

The foam behaviour depends on the properties of the polymer from which it is made. Nearly all thermoplastics can be foamed, but commercially important foams are mainly based on commodity plastics – PE, PP, PS, and PVC (Table 2.1). This partly reflects their low cost, and partly the availability of grades with highly elastic melts [12].

In terms of microstructure thermoplastics can be divided into amorphous and semi-crystalline solids. The amorphous ones are glassy up to a temperature called the glass transition temperature $\boldsymbol{T}_{\mathbf{g}}$, whereupon they change into a rubbery liquid, the viscosity of which falls as the temperature is raised further. Semi-crystalline thermoplastics can be regarded as two phase materials, with an amorphous phase, and a crystalline phase with a melting temperature $\boldsymbol{T}_{\mathbf{m}}$. The chemical structures and transition temperatures of several thermoplastics can be considered to control the mechanical properties. The melting values are not as precise as the melting points of pure metals; the crystalline phase of polymers melts over a temperature range that ends at T_m, and the exact values of T_g, and T_m, depend on the molecular weight. For semi-crystalline polymers the percentage crystallinity is another important parameter due to possibility of fabricating highly anisotropic forms of semi-crystalline polymers [13].

The thermoplastic polyester resin such as poly(butylene terephthalate) and poly(ethy1ene terephthalate) are the examples of semi-crystalline polymers. The melting point of PBT resins is about 30 °K lower than that of PET resins, resulting in lower melt temperatures during moulding as well as slightly lower allowable design temperatures for moulded parts. PET and PBT are mentioned on the ‘green list’ of the European Regulation EEC 259/93, Annex II [14].

The class of thermoplastic polyesters has two major subclasses – polybutylene terephthalate and polyethylene terephthalate - and two minor subclasses - PET copolymer such as Eastman's PETG, and polyethylene naphthanate or PEN.

2.1.1 Poly(butylene terephthalate)

Polybutylene terephthalate (PBT) is a thermoplastic engineering polymer that is used as an insulator in the electrical and electronics industries, produced by the polymerization of butanediol and terephthalic acid. It is a thermoplastic (semi-crystalline) polymer, and a type of polyester. PBT is resistant to solvents, shrinks very little during forming, is mechanically strong, heat-resistant up to 150 °C (or 200

°C with glass-fibre reinforcement) and can be treated with flame retardants to make it noncombustible.

PBT is closely related to other thermoplastic polyesters. PBT is similar in structure to polyethylene terephthalate (PET), the difference being in the number of methylene (CH_2) groups present in the repeating units of the polymer molecules. Compared to PET (polyethylene terephthalate), PBT has slightly lower strength and rigidity, slightly better impact resistance, and a slightly lower glass transition temperature. The mechanical properties of the two materials are also similar. However, PBT has a lower melting point (223 °C [433 °F]) than PET (255 °C [491 °F]), so it can be processed at lower temperatures. This property, combined with its excellent flow when molten and its rapid crystallization upon cooling, makes PBT highly suitable for injection-molding into solid parts. Either unmodified or reinforced with glass fibres or mineral fillers, it is used in numerous applications, especially electrical and small machine parts, owing to its excellent electrical resistance, surface finish, and toughness.

2.1.2 Poly(ethylene terephthalate)

Polyesters are produced commercially by melt polymerization, ester interchanges, and interfacial polymerization. Commercial poly(ethylene terephthalate) is produced traditionally by two successive ester interchange reactions. In the first step, dimethyl terephthalate is heated with ethylene glycol at temperatures near 200 °C. This yields an oligomeric dihydroxyethyl terephthalate ($x = 1$ to 4) and methanol, which is removed. In the second step, the temperature is increased, leading to polymer formation, while ethylene glycol is distilled off (Figure 2.1) [15].

Commercially important polyesters are based on polymers with the *p*-phenylene group in the polymer chain. In contrast to the low melting, linear aliphatic polyesters, the stiffening action of this group coupled with the high degree of symmetry results in a high melting point and other important engineering properties. For example, all commercial polyester fibers are based on terephthalic acid as the primary building block. Different products are obtained by varying the difunctional alcohols used in polycondensation reaction with this acid. However, the major engineering polyesters are poly(ethylene terephthalate) and poly(butylene terephthalate).

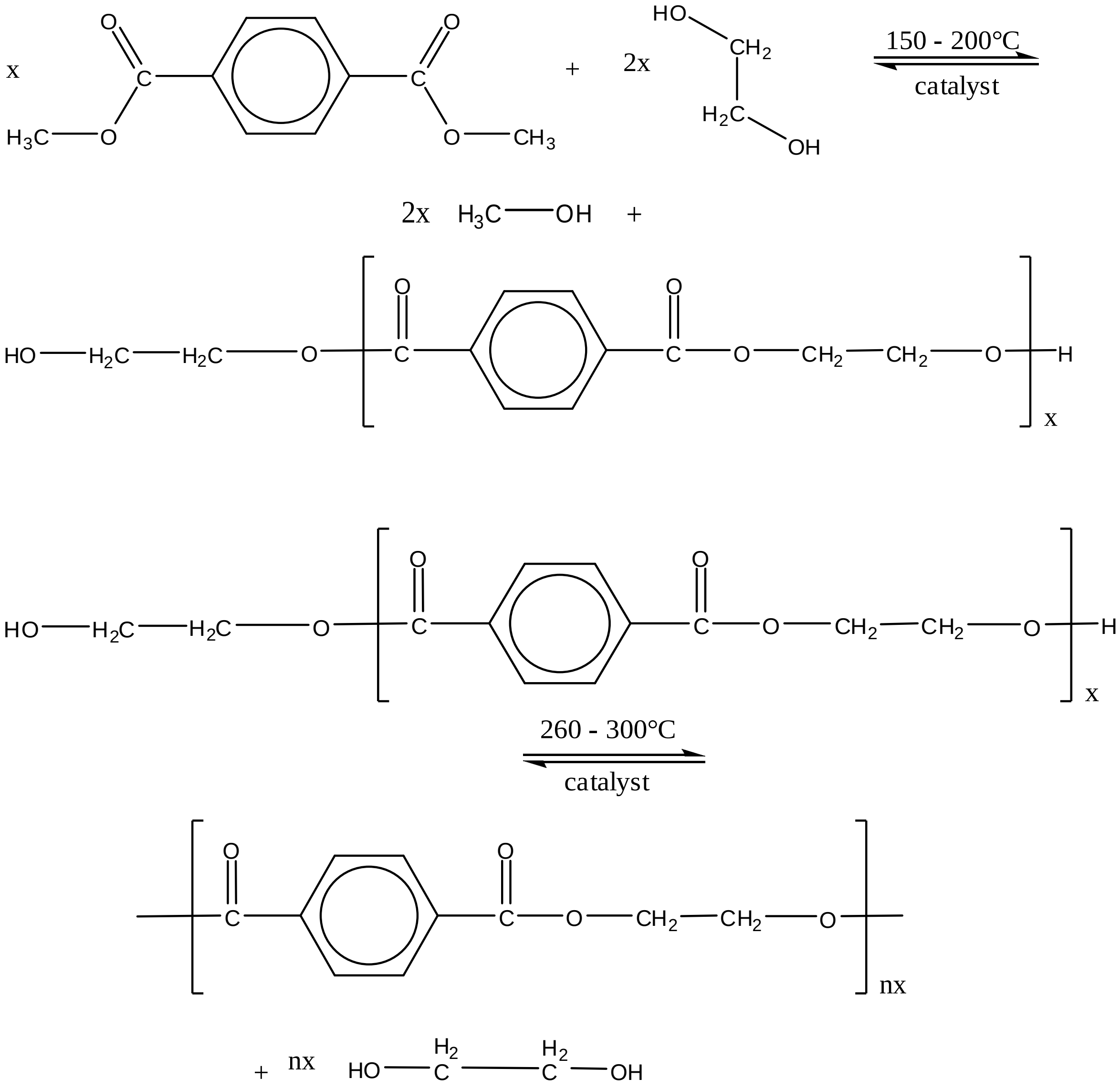


Figure 2.1 : Polymerization reaction mechanism of PET.

PET is characterized by high strength, rigidity, and toughness; low creep at elevated temperatures; excellent dimensional stability; low coefficient of friction; good chemical, grease, oil, and solvent resistance; minimal moisture absorption; and excellent electrical properties (Table 2.2).

PET has many advantages, which include:

- Lightweight: reduces transport fuel consumption and the cost of distributing products.
- Performance: provides insulation and protection from contamination and impact.

- Economy: usually less expensive than alternative materials resulting in savings to the consumer.
- Energy Savings: PET manufacture requires less energy than alternatives resulting in lower "greenhouse" emissions. As insulation, PET foams enable enormous energy savings in commercial installations such as cool stores.

Table 2.2 : Properties of engineering polyester, PET.

Property		Property	
Specific gravity	1.34–1.39	Flexural strength (MPa)	96.5–124.1
Melting temperature (°C)	265	Flexural modulus (MPa)	2413–3102
Tensile strength (MPa)	58.6–72.4	Impact strength (Izod) (ft-lb/in)	0.25–0.65
Tensile modulus (MPa)	2758–4136	Water absorption (24 hr)	0.1–0.2

Microcellular semicrystalline polymers such as poly(ethy1ene terephthalate) show great promise for engineering applications because of their unique properties, particularly at higher densities. Recent studies reveal some high density microcellular polymers have longer fatigue lives and/or equal strengths to the neat polymer. Relatively few microcellular processing studies of semicrystalline polymers have been presented. In general, semicrystalline polymers are relatively difficult to microcellular process compared to amorphous polymers. The semicrystalline materials exhibit ten to one thousand times higher cell nucleation densities compared with the amorphous materials, resulting from heterogeneous nucleation contributions. The amorphous materials show a strong dependence on cell density, while the semicrystalline materials show a weaker dependence. Moreover, classical nucleation theory is not adequate to quantitatively predict the effects of saturation pressure on cell nucleation for either the amorphous or the semicrystalline polyesters. Both the semicrystalline and amorphous materials exhibit constant nucleation cell densities with increasing foaming time. Foaming temperatures near the glass transition are found to influence the cell density of the amorphous polyesters, indicating some degree of thermally activated nucleation. Furthermore, classical nucleation theory is not adequate to predict the cell density dependence on foaming temperature. Similar to the amorphous polyesters above the glass transition temperature, nucleation in the semicrystalline materials is found to be independent of the foaming temperature [8].

Melt strength of poly(ethylene terephthalate)

Melt strength, a property of the polymer melt which indicates its ability to withstand drawing without breaking. Melt strength is improved by the presence of high molecular weight tail or long chain branches [117]. It is well-known that a melt viscosity is a primary material property in the formation of stable bubbles.

High melt strength polypropylene is an example for foaming. It was first presented by Himont [17], in which, by chain extension, semicrystalline polypropylene demonstrates a wider processing window and a much better foaming structure over the nonextended conventional PP. As a result, more polypropylene research and development has been initiated. It is anticipated to have more grades of better structured PP in the market for foaming. Recently, a polyethylene terephethalate (PET) resin supplier reported solid state polymerization technology enhancement to allow improved polymer strength PET for foaming [18]. In brief, resin structure development opens interesting possibilities to further enhance foamed plastic strength/weight performance.

In this study, the complexity is the non-uniform distribution of pressure and temperature throughout the product that may cause a non-uniform cell structure. The polymer could not be cooled sufficiently to prevent bubble collapse before it crystallized. Among engineering plastics poly(ethylene terephthalate) is relatively difficult to process microcellularly compared to general thermal plastics because of its low melting viscosity.

In chemical modifications, different treatments have been developed to improve the PET macromolecular characteristics, in particular, to extend the polymer chain lengths. In fact, the molecular weight increase, through chain extension or branching, is responsible for the increases in both viscosity and melt strength; these, in turn, facilitate the production of expanded structures [19].

The evolution of shear and extensional behavior as a function of molecular weight (M_w), degree of branching, and molecular weight distribution (MWD) studies showed that an increase in the degree of branching and M_w and the broadening of the MWD induce an increase in Newtonian viscosity, relaxation time, flow activation energy and transient extensional viscosity, while the shear thinning onset and the Hencky strain at the fiber break decreased. The semicrystalline polymers had considerably higher cell densities than the amorphous polymers, which was attributed to the significant heterogeneous nucleation contributions in the amorphous crystalline interfacial regions. The amorphous foam experienced diffusional controlled cell growth, whereas the semicrystalline foams experienced viscoelastic controlled cell growth, and the longer the gas was allowed to diffuse into the cells, the larger the cell size was.

Chain branching in some polymers is known to improve certain properties and is practiced commercially (e.g., polyethylene and polycarbonate). In PET, many types of branch structures have been synthesized and the effect of branch structure on properties studied. Some of the branch structures possible in PET are star, comb, H-, random, hyper, POM POM branched. Most of the recent studies of branched PET have focused on new synthetic methodologies and on rheological properties.

2.2 Polymer Foams

Foams can be defined as a gaseous void surrounded by a much denser continuum matrix, which is usually in a liquid or solid phase. It exists widely in nature, in cellulositic wood, marine organisms, and other phenomena, and it can be made using synthetic processes (i.e., foamed plastics). The presence of gas voids can be outside, encapsulation, or inside, irreversible volume expansion. In most cases, a gas phase possesses dramatically different properties and structures (or states) than the surrounding solid phase, as opposed to different property and similar structure (or state) blends, to make a lighter heterogeneous composite structure [20].

Foamed plastics can be classified in different ways, for instance, by nature as flexible and rigid, by dimension as sheet and board, by weight as low density and high density, by structure as open cell and closed cell, and by cell size as foam and microcellular [2].

The cellular plastics encompass a range of materials with widely varying properties and fields of application. Virtually any polymer, thermoplastic or thermoset, can be made into a cellular or foamed form with the resulting products having densities ranging from 60 pounds per cubic foot (pcf) (0.96 g/cm^3) all the way down to 0.1 pcf (0.0016 g/cm^3).

2.2.1 Types of polymer foams

The cellular plastics can have either of two structural configurations: (a) the closed-cell type, in which each individual cell, more or less spherical in shape, is completely enclosed by a wall of plastic, or (b) the open-cell type, in which the individual cells are intercommunicating. The foams can be rigid, semirigid, or flexible. In general, the properties of the respective plastics are present in the foamed products, except, of course, those that are changed by conversion to the cellular structure.

Currently achievable apparent foam densities range from 2 kg/m^3 to 960 kg/m^3

[22]. Based on these values, plastic foams can be classified into one of three classes:

1. *Low Density Foams:* foams having an apparent density value between 2 kg/m^3 (0.002 g/cm^3) and 50 kg/m^3 (0.050 g/cm^3).

2. *Medium Density Foams:* foams having an apparent density value between 50 kg/m^3 (0.050 g/cm^3) and 350 kg/m^3 (0,350 g/cm^3).

3. *High Density Foams:* foams having an apparent density value between 350 kg/m^3 (0,350 g/cm^3) and 960 kg/m^3 (0.960 g/cm^3).

In terms of cell size and cell density, plastic foams can be classified into one of three categories [23]:

1. *Conventional foams:* foam structures with an average cell size greater than 300 μm and a cell density less than 10^6 cells/cm^3.

2. *Fine celled foams*: foam structures with an average cell size between 10 and 300 μm and a cell density between 10^6 and 10^9 cells/cm^3.

3. *Microcellular foams:* foam structures with an average cell size less than 10 μm and a cell density greater than 10^9 cells/cm^3.

2.2.1.1 Thermoplastic and thermoset polymer foams

The thermoplastics that can be produced as structural foams already run a wide gamut - ABS, acetals, acrylics, styrenes, polyethylenes, nylon, PVC, PC, modified polyphenylene oxide, PP, polysulfone, thermoplastic polyesters, and various glass-reinforced nylons, polyethylenes, polypropylenes, and other thermoplastics. Among the thermosets, urethane structural foams are most in use.

Bubble formation theory

In polyurethane foam production, the correct foaming process requires that these two reactions take place at the same rate.

Isocyanate + Polyol $\longrightarrow$ Polymer (First Reaction)

Isocyanate + Water $\longrightarrow$ CO_2 for Foaming (Second Reaction)

If the polymerization (the first reaction) is faster, the polymer formed will have final strength before foaming and the result will be a high density foam (low degree of foaming). If the second reaction is much faster, the evolved gas will blow the foam. Due to the low 'green' strength and viscosity of the polymerizing mixture, the gas will leave the mixture, and the foam will collapse to a high density foam, as in the first case. In the balanced process, the polymerization should proceed fast enough to give high viscosity and melt strength of the mixture, which will trap fast evolving gas and finish the polymerization at the end of foam growth [24 - 29]**.**

The initial polyol and isocyanate mixture is a low molecular weight, low viscosity fluid, which is reflected in the low strength of the bubble wall formed during foaming. The wall of such a bubble breaks easily and gas escapes. Therefore, it is necessary to increase the strength and elastic properties of the bubble wall (gel strength), which is achieved by increasing the molecular weight of the polymer. The mechanism of the bubble formation is a science 'per se', and it is essential to understand the basics of the process. This process is similar to bubble generation during boiling of a liquid. Gas which is formed in the chemical reaction, or by evaporation of the added low boiling foaming agent, is partially soluble in the polymer mass. When the limit of solubility is reached, i.e., when enough gas is generated to exceed the solubility limit (saturation), the excess separates in the form of bubble. First stage of bubble formation is called nucleation. The number of bubbles will depend on the number of nuclei (seeds) present in the system. Nucleation can be homogeneous (in the absence of foreign particles, nucleants) or heterogeneous (in the presence of nucleants). The bubble nucleus is usually a small amount of air caught in the crevasses or in the roughness on the surface of the solid or liquid particle, in case of heterogeneous nucleation. The beginning of foam formation is characterized by formation of large number of nuclei. Their creation causes refraction of light on the walls of nuclei, which is manifested as whitening of the mass without significant volume increase. The next stage is bubble growth from the nucleus due to the incoming evolved gas, and the volume increase of the foaming mixture. This stage is observed as the foam rise. Stability of a growing bubble depends on the surface tension. If the surface tension is too large and there is no nucleation, a small number of large bubbles will grow, and the shape should be elongated in the direction of rise. Such foams are usually not desirable since they show anisotropy in their mechanical properties. Regulation of bubble growth is achieved by the addition of surfactants (usually silicone copolymers). The surfactant has multiple role, to lower surface tension and facilitate division of cells into smaller, and since it is a separate phase, to act as a nucleant. Increasing the amount of surfactant gives finer cells with thinner walls until the limit is reached above which it causes foam collapse, more regularly shaped bubbles [29], [30].

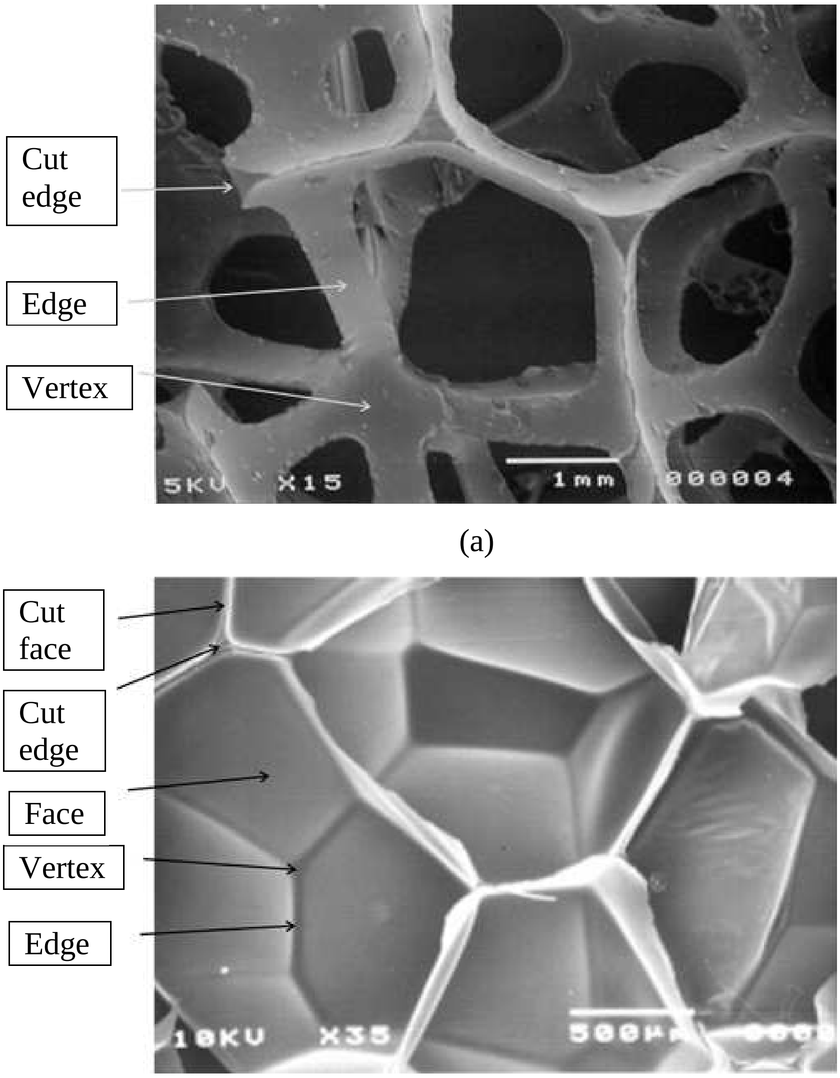
2.2.1.2 Open- and closed-cell polymer foams

During foaming, two types of foam cells are observed: open- and closed- cell. Closed-cell structure may entrap hydrogen, carbon dioxide and volatile liquids. The entrapped fluid (e.g. air) plays a major role in increasing in compressive strength and energy absorption capability for closed- cell foams [31]. On the other hand, open-cell foamed plastics have a higher absorptive capacity for water and moisture, a higher permeability to gas and vapor, less insulation capabilities for heat or electricity and a better ability to absorb and damp sound.

Foams may have open or closed cells. Open cells are obtained by crushing the foam after gelation, but the amount of open cells is regulated by the selection of catalysts. Foams used in the furniture industry contain open cells while those used for thermal insulation (rigid foams) are required to have closed cells, since they contain a gas of low thermal conductivity. Polyester urethane flexible foams have better strength and oxidative stability but lower hydrolytic stability than polyether urethane foams. They also show higher hysteresis in the stress–strain cycling test. Polyester urethane foams are more resistant to chemicals, particularly those used for chemical cleaning, but are also more expensive than PPG based foams [32].

Figure 2.2 compares typical microstructures of open- and closed-cell polymer foams, respectively, as seen in a scanning electron microscope (SEM). The good depth of focus allows complete cells to be seen in the interior of open-cell polyurethane (PU) foams. Air can pass freely between the cells of such foams.

Although in Figure 2.2(a) all the cell faces are open, only a small fraction of cell faces need to be open to create continuous air passages. In a typical closed-cell foamed thermoplastic, each cell is surrounded by connected faces.



(a)

(b)

Figure 2.2 : SEM photograph of (a) PU open-cell foam of density 28 kg m^{-3}, (b) Closed-cell LDPE foam of density 24 kg m^{-3} [12].

Partial cells, with cut faces and edges, are visible on the cut surfaces (Fig. 2.2(b)), while complete cells exist in the interior of the sample. The cell faces can sometimes be split or otherwise damaged [12].

Closed-cell foam development

Compared with the five stages of PU foaming, the only two stages in thermoplastics are the growth of isolated spherical bubbles and the formation of polyhedral closed cells.

Isolated bubble growth in a melt, the first stage of bubble growth occurs in a polymer melt under pressure, containing dissolved gas. A variety of gases have been used. CFCs have ideal physical properties of low diffusivity, low thermal conductivity, and low boiling point, but have been phased out as they deplete the ozone layer in the stratosphere. Hydrocarbon gases, hydro chlorofluoro carbons (HCFCs), carbon dioxide, and nitrogen are all used.

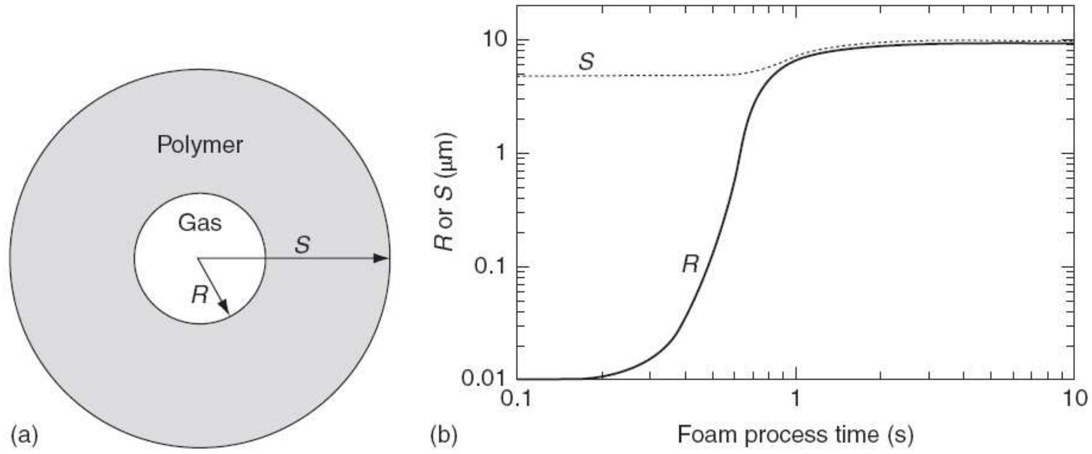


Figure 2.3 : (a)Modelling the growth of an isolated spherical bubble in a PE melt. (b)The predicted growth in the radii of the bubble and melt with time [3].

A pressure reduction, or the generation of more gas, causes bubbles to nucleate. Figure 2.3 (a) shows an isolated spherical bubble in a polymer melt, the first stage of the foaming process.

Shafi et al. [35] assumed that there are spherically symmetric flows:

(a) radial heat flow;

(b) radial gas diffusion from the melt to the bubble;

(c) extensional polymer melt flow, in directions tangential to the sphere, and compressive melt flow in the radial direction.

It is assumed that no further bubble nucleation occurs during bubble growth. The pressure balance of the bubble depends not only on its curvature and surface tension, but also on the biaxial tensile stresses in the melt. In Figure 2.3(a), the outer radius of the melt sphere indicates the approximate amount of melt per growing bubble. The viscosity of the polymer melt is a function of its temperature and the amount of dissolved blowing agent. The coupled equations were solved by finite difference methods. Figure 2.3(b) shows the predicted increase in the cell radius with time in a PS melt. Since the model does not consider the interaction between touching bubbles, it is unlikely to be correct at long times.

Multiple bubble growth in a melt, melt extensional flow in cell faces draws melt from the vertices. Everitt et al. [36] modelled the interaction of a sheet of large and small bubbles in a 2-dimensional (2D) polymer melt. The bubble array had hexagonal symmetry, so it was possible to consider a small representative unit cell (RUC), containing parts of a small and a large bubble plus a mirror symmetry plane.

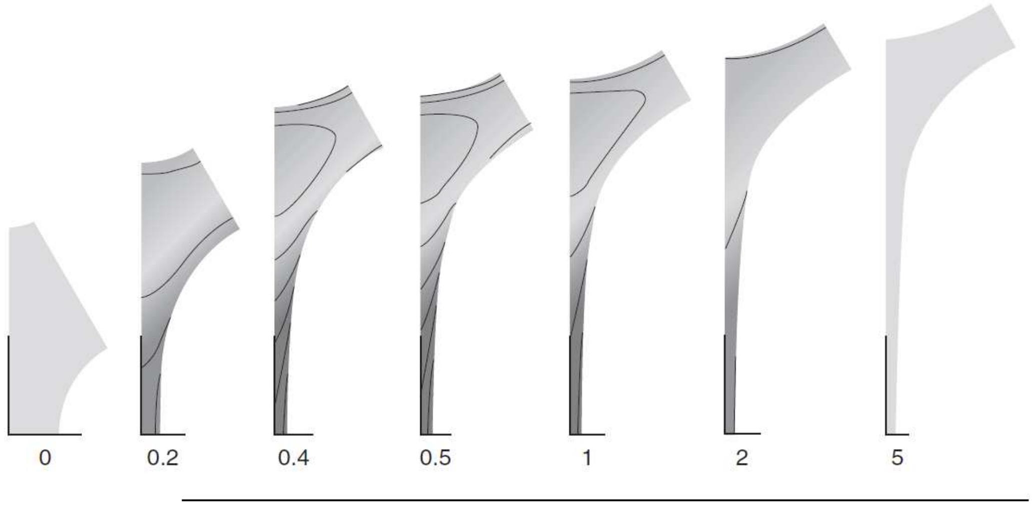


Figure 2.4 : Developing foam in a structure with two large to every small bubble, at the dimensionless times indicated (the grey scale indicates orientation) [36].

There are separate time scales for polymer viscoelasticity, bubble growth, and for gas diffusion in the melt. Figure 2.4 shows how, with increasing bubble expansion, the melt is elongated between two neighbouring large bubbles. The dimensionless time in the simulation is time divided by the fluid relaxation time. A full 3D consideration of such flow will eventually lead to better models of foam development.

2.2.1.3 Flexible, semirigid and rigid polymer foams

Polyols, one of the major ingredient of a PU foam, are active hydrogen-containing compounds, primarily variations of polyesters and polyethers. As a rule of thumb, high molecular weight, low fuctionality polyols produce molecules with a low amount of cross-linking and, consequently, a flexible foam. Conversely, low molecular weight polyols of high functionality produce a structure with a high degree of cross-linking, a rigid foam. Also, it is possible to vary the formulation to produce any degree of flexibility or rigidity between the two extremes [37].

Flexible foams differ from the aforementioned rigid foams in that they can be elastically deformed and return to their original contours when the force is removed. They are usually in the 1 to 6 pcf density range. The two major production techniques in the flexible foam area are the slabstock and the molded foam processes.

When foams are made either by free foaming or in a mold, a skin is formed on the foam surface called Integral Skin Foams, in which the foam comes out of the mold with a continuous skin that can replace the separate vinyl or ABS surface (e.g., RIM process). This fact is utilized to prepare foamed products with a controlled thickness of the skin. The formulation for integral foams generally does not contain water but it has physical blowing agents. The objects are made in closed molds. Density of the skin can be regulated by the mold temperature, amount of the mixture poured in the mold (larger amount exerts higher pressure) and mold release agents (usually silicones). As a rule lower temperature favor thicker skin. Higher pressure and release agents, which act as antifoaming agents in contact with the skin, also favor thicker skin [32].

Rigid foam compositions differ from those of flexible foams as they use short triols or higher functionality polyols, typically with $M_n = 400$. They are made with crude MDI, and main part of foaming is done with physical blowing agents. Due to the high concentration of crosslinks the foams are rigid. Rigid foams are used primarily for heat insulation in refrigeration and construction, and partly in automobile industry [38].

A variety of rigidity grades of flexible foams are manufactured, with grades having rigidity between soft and rigid foams being called semirigid. Semi-rigid foams are used for automobile seats and components for interior and exterior safety. These foams are characterized by low resilience, in that they recover very slowly from compression, and by high-energy-absorbing characteristics. Semirigid foams also are cold-curing in nature and usually involve special polymeric isocynates [37].

2.3 Production of Polymer Foams

The cellular plastics can be produced in the form of slabs, blocks, boards, sheets, molded shapes, and sprayed coatings. Some can also be “foamed-in-place” in an open cavity. The type of process used (casting, extrusion, injection molding) will affect the properties of the endproduct.

As originally conceived, most foamed plastics were completely cellular in structure; today, it is possible to arrange the cells so that a product may have an essantially solid skin surface and a cellular core.

The ways in which the cellular structure is produced in plastics vary widely. The following are the basic ones among them:

1. Air is whipped into a suspension or solution of the plastic, which is then hardened by heat or catalytic action or both.
2. A gas is dissolved in the mix and expands when pressure is reduced.
3. A component of the mix is volatilized by heat.
4. Water produced in an exothermic chemical reaction is volatilized within the mass by the heat of reaction.
5. Carbon dioxide gas is produced within the mass by chemical reaction.
6. A gas, such as nitrogen, is liberated within the mass by thermal decomposition of a chemical blowing agent.
7. Tiny beads of resin or even glass (e.g. micro-balloons) are incorporated in a plastic mix.

Moreover, many different processes, the most popular ones being injection molding and extrusion, can produce thermoplastic foams. In the extrusion process, the extruder offer relevant unit operations for foam production, such as melting, mixing and metering in continuous mode.

Furthermore, processing has become more sophisticated, especially in the area of producing high-quality surfaces on foam parts. Sandwich molding and coextrusion are being used to manufacture “foam core” thermoplastic products with low density, rigidity, and smooth surfaces for a variety of applications.

2.3.1 Blowing agents

The term *blowing agent* in the broadest sense denotes an inorganic or organic substance used in polymeric materials to produce a foam structure. There are two major types of blowing agents: physical and chemical.

Among physical blowing agents, the chlorofluorocarbons (CFCs) used in the past, such as CFC_{11} (CCl_3F), had several advantages; the heat of fusion of the low boiling point liquids aided foam temperature control, the low diffusivity of the gases made stable cell structures easy to achieve, and the gases were non-flammable. In contrast, pentane and butane are gases at room temperature, flammable, and have a high diffusivity through molten polyolefins.

When a high melt strength PP was foamed using butane [39] the maximum expansion ratio was a function of the extrudate temperature; it increased with temperature in the low temperature range where the expansion was limited by crystallisation, then decreased at higher temperatures due to butane loss from the extrudate. The extrudate swelled from the die, then foaming caused further expansion. Several strategies were used to achieve ultra-low-density PP foams [40] branched PP prevented cell face fracture, lowering the melt temperature reduced the gas loss during expansion, and optimisation of the die design avoided too-rapid crystallisation. Hydrocerol, a mixture of sodium bicarbonate and citric acid which decomposes to liberate CO_2 and a mixture of other products, was used [41]: the CO_2 and isobutane acted as blowing agents. The extruder screw speed and hydrocerol concentration controlled the nucleation density, hence the foam density and mean cell size. Branched PP had a slightly larger cell size than linear PP when CO_2 was used as the foaming agent, but there were a significant number of open cells in the foamed linear PP [42].

Sims et al. considered the efficiency of azodicarbonamide and sodium bicarbonate blowing agents for PE foams made by compression moulding [43]. These systems generate CO_2 gas. Blends of the blowing agents have a reduced exotherm, so are more suitable for polymer systems with that are temperature sensitive, such as ethylene copolymers.

According to Shutov [44], there are various requirements that have to be met when choosing a CBA:

- Decomposition temperature of the CBA should be slightly higher than the melt or processing temperature of the material.
- Gas must be liberated within a narrow temperature range.
- Rate of gas liberation must be sufficient and controllable.
- Gas and decomposition products must be noncorrosive, nontoxic, and nonflammable.
- CBA must be adequately dispersed in the polymer matrix.
- Polymer matrix should not be destroyed by CBA or heat generated during decomposition.
- Internal gas pressure should be controlled.
- Diffusion rate of the gases generated by CBA should be adequate for the chosen polymer matrix.

Due to the fact that, 5-phenyl tetrazole was chosen as the chemical blowing agent in this thesis study.

2.3.1.1 Physical blowing agents

Physical blowing agents (PBA) are volatile liquids or compressed gases that change state during processing to form a cellular structure within the plastic matrix. The gases or low-boiling liquids that are dissolved in the resin, evaporate through the release of pressure or the heat of processing. The compounds themselves do not experience any chemical changes. Cell size is influenced by the pressure of the gas, the efficiency of dispersion, melt temperature, and the presence of nucleating agents. The most common gases used are carbon dioxide, nitrogen, and air. The liquid blowing agents are typically solvents with low boiling points, primarily aliphatic hydrocarbons and their chloro- and fluoro- analogs.

The blowing agents should be soluble in the polymer under reasonably achievable conditions but excessive solubility is not desirable. The permeability of the gas within the polymer is also significant, as is the volume of gas released per unit weight of agent. This latter measure is called the *blowing agent efficiency,* and is an important yardstick for all types of materials. Effective blowing agents should yield at least 150 to 200 cm^3 of gas (measured at standard temperature and pressure) per gram of agent [45].

2.3.1.2 Chemical blowing agents

Chemical blowing agents (CBAs) are products that decompose at high temperature. At least one of the decomposition products is a gas, which expands the plastics material to give a foam structure. The amount and type of the blowing agent influencethe density of the finished product and its pore structure. Two types of pore structures are possible: open and closed cell. Factors that determine the formation of a fine-celled plastic foam with a regular cell structure are the particle size of the blowing agent, dispersion properties of the plastics processing machine used, decomposition rate of the blowing agent, and the melt viscosity of the resin processed.

CBAs are mainly solid hydrazine derivatives. The gas formation must take place in a temperature range close to the processing temperature range of the polymer. In addition, the decomposition products must be compatible with the polymer. Typically, these additives decompose over a relatively narrow temperature range. CBAs can be mixed with the polymer at room temperature, requiring no special processing equipment. In most operations, they are self-nucleating and are stable under normal storage conditions. In addition, CBAs may be reformulated with such other additives as blowing agent catalysts or nucleating agents. Blowing agent catalysts lower the temperature of decomposition for the CBAs while nucleating agents provide sites for formation of a cell in the foamed plastic.

Blowing agents are used in plastics for several reasons: weight reduction, savings in cost and material, and achievement of new properties. The new properties include insulation against heat or noise, different surface appearance, improved stiffness, better quality (removal of sink marks in injection molded parts), and/or improved electrical properties. [45].

From automotive to medical products, packaging to housing, CBAs are applied in wide variety of applications within today’s plastics sector. Typically offered as a powder or a pelletized master batch, CBAs can be added like any other additive to the process. Less commonly used, but also available, are liquid CBAs where the powder is let down into a compatible liquid.

CBAs offer various advantages with the most commonly known being weight or density reduction. This can typically be achieved without entirely compromising the physical properties of the end product. Some other common uses are as nucleating agents in direct gas operations and structural foam, and sink mark removal. In some cases the CBA is used to provide a “spongy” feel to the finished product.

Activated by temperature, the CBA generates gas via a decomposition reaction. Ideally, this gas is mixed into solution with the polymer melt. When the melt and gas solution is introduced to a pressure drop, gas pockets or bubbles begin to form within the polymer matrix. Over time the gas diffuses out of the polymer matrix and is replaced with air.

There are two basic types of chemical foaming agents, known as *endothermic* and *exothermic*. These two can be blended together to make a third type of foaming agent known as an *endo/exothermic*. The decomposition of endothermic foaming agents absorbs heat and typically generates carbon dioxide and water vapor. Exothermic foaming agents generate heat upon their decomposition and produce nitrogen and/or ammonia gas and are typically said to produce higher volumes of gas. The exothermic decomposition is also known to generate higher pressures than the endothermic.

The *endo/exo* blends are used in applications where the properties of both the endothermic and exothermic are required. An example would be in profile extrusion of rigid PVC. The exothermic provides a large volume of gas at a high pressure allowing the gas to enter the PVC matrix, while the endothermic provides gas and absorbs heat thus preventing distortion in the profile and allowing for faster line speeds.

The endothermic products typically decompose in the range of 130 - 230 ºC, while exothermic decomposition typically takes place around 200 ºC. However, particle size plays an important role in the decomposition rate as well as the decomposition temperature for both. In addition, the decomposition temperature of the exothermic products can be lowered by adding an “activator” or “kicker.”

Selection of the proper CBA for the application is crucial, and is done based upon compatibility of the gasses generated with the polymer of interest, as well as compatibility of the carrier resin (if applicable), desired amount of gas evolution, and the processing window [38].

Generally CBAs are used for high-density foams. Among them endothermic CBAs have desirable property for wood polymer composites as during foaming they absorb heat at decomposition, which cools the polymer, increases the viscosity of the melt, stabilizes the cellular structure, and reduces cell coalescence [47 - 49].

Exothermic blowing agents

Exothermic foaming agents generate heat upon their decomposition and produce nitrogen and/or ammonia gas and are typically said to produce higher volumes of gas.

Azodicarbonamide (AZ), the most widely used exothermic CBA. In its pure state, this material is a yellow-orange powder, which will decompose at about 390°F. Its decomposition yields 220 cm^3/g of gas, which is composed mostly of nitrogen and carbon monoxide with lesser amounts of carbon dioxide and, under some conditions, ammonia. The solid decomposition products are off-white, which not only serves as an indicator of complete decomposition but also does not normally adversely affect the color of the foamed plastic. Unlike many other CBAs, AZ is not flammable. In addition, it is approved by the FDA for a number of food-packaging uses. AZ can be used in all processes and with most polymers, including PVC, PE, PP, PS, ABS, and modified polyphenylene oxide (PPO).

Modified AZ systems have been developed which offer improved performance and increase versatility in a wide variety of applications. Each system has a formulated cell nucleation system (usually silica) and gas yield is approximately the same as unmodified AZ. Modified types are also available in several particle size grades.

The simplest form of modified AZ is a paste. It is composed of a plasticizer, which forms the liquid phase, and may also contain dispersing agents and catalysts. Its principal field of application is the expansion of PVC plastisols. The agents facilitate the dispersion of the blowing agent when it is stirred into the PVC plastisol, while catalysts lower the decomposition temperature.

Other modified AZs have been developed for the manufacture of integral-skin foams by extrusion and injection molding. These contain additives that modify the usual decomposition process of AZ and suppress the formation of cyanuric acid, which causes plateout on the surfaces of molds, dies, and screws. The additives used include zinc oxide and/or silicic acid (a colloidal silica) with a very low water content. The additives also act as nucleating agents, producing a cell structure that is both uniform and fine-celled.

There are also grades that have been flow-treated. This type contains an additive to enhance the flowability and dispersability of the powder. These grades are very useful in vinyl plastisols, where complete dispersion of the foaming agent is critical to the quality of the final foamed product.

Another method of modifying AZ is to mix it with such other CBAs as those from the sulfonyl hydrazide group. These “auxiliary” blowing agents decompose at lower temperatures than AZ, broadening the decomposition range.

Sulfonyl hydrazides have been in use as CBAs longer than any other type. The most important sulfonyl hydrazide is 4,4′-oxybis (benzenesulfonyl hydrazide) (OBSH). OBSH is the preferred CBA for low-temperature applications. It is an ideal choice for the production of LDPE and PVC foamed insulation for wire where it does not interfere with electrical properties. In addition, it is capable of cross-linking such unsaturated monomers as dienes. Additional applications include PVC plastisols, epoxies, phenolics, and other thermosetting resins. Like AZ, it is approved by the FDA for food-packaging applications and is odorless, nonstaining, and nontoxic.

Sulfonyl semicarbazides are important CBAs for use in high-temperature applications. TSS (*p*-toluene sulfonyl semicarbazide) is in the form of a cream colored crystalline powder. Its decomposition range is approximately 440 to 450 °F with a gas yield of 140 cm^3/g, which is also a mixture of nitrogen, CO_2, CO, and NH_3 [50]. TSS is flammable, burning rapidly when ignited and producing a large amount of residue. TSS is used in polymers processed at higher temperatures such as ABS, PPO, polyamide (PA), and HIPS.

Dinitropentamethylene tetramine (DNPT) is one of the most widely used CBAs for foamed rubber. Its use is limited in plastics because of its high decomposition temperature and the unpleasant odor of its residue. DNPT is a fine yellow powder that decomposes between 266 °F and 374 °F, producing mainly nitrogen and a solid white residue.

With the increased use of engineering plastics in recent years, the need for chemical blowing agents having higher decomposition temperatures to match the processing temperatures of these materials has also grown. In the tetrazole class, *5-phenyltetrazole* is the only available product, which is a white crystalline powder with a melting point of 212 °C [51]. This high temperature CBA is a solid with a decomposition temperature range of around 250 °C, and generates 200 cc/grams (measured at STP) of predominantly nitrogen gas [52]. Its primary area of application is in polycarbonate, but it may be used in other engineering plastics. It should be noted that incomplete decomposition of this material will result in a pink colored intermediate product.

Hydrocarbyl tetrazoles (the class of materials to which 5-PT belongs) may be synthesized via the reaction of an aromatic amine with a metal azide in the presence of a Friedel-Crafts catalyst [53]. Hence, 5-PT can be obtained from the reaction of benzonitrile and sodium azide.

An alternative route to 5-PT has been demonstrated via cyclization of benzamidrazone with nitrous acid [54].

The most commonly reported solid decomposition product of 5-PT is 3,5-diphenyl-1,2,4-triazole [51], [54]. Other solid decomposition products claimed are aminodiphenyltriazole and triphenyl-S-triazine [54].

The decomposition mechanism of 5-PT has not been extensively studied, although the nature of the decomposition products permits some speculation. Clearly, more than one reaction pathway is allowed. Also, the decomposition must involve some interaction between pairs of 5-PT molecules and/or decomposition intermediates. As is generally the case with this sort of mechanism, the gas yield and the residue composition can be affected by the conditions under which decomposition occurs (e.g., heating rate and decomposition media) [55].

The main decomposition products of Expandex 5-PT are heterocyclic nitrogen compounds, such as triphenyl-s-triazine, 3,5-diphenyl-1,2,4-triazole, 4-N-amino-3,5-diphenyl-1,2,4-triazole as shown in Table-A.1 [56].

Gas pressure development

The pressure exposure during the decomposition is particularly important in regards to the cooling time, the tendency of uncontrolled post-expansion of the molded parts, and the cell structure. This can also influence the physical properties of the parts, depending on the grade of expansion rate. It is quite obvious that CBAs that liberate nitrogen have the highest gas pressure development.

Table 2.3 : Maximum gas pressure at decomposition and remaining pressure in room temperature for various chemical blowing agents.

Substance	Maximum Pressure (Bar)	Remaining Pressure (Bar)
ADC	85.4	30.3
5–PT*	40.6	21.1
ADC/endo 1:1	42.2	15.8
Standard endo	41.6	11.9
ADC/bicarbonate 1:4	28.1	11.2
Bicarbonate	24.2	11.0

*****[59]

The chemical blowing agents are added to the polymer pellets in solid form and are activated through addition of heat, releasing a fluid, mostly nitrogen, carbon dioxide, or water [60].

Table 2.4 : Properties of chemical blowing agents.

Product	Decomposition Range (°C)	Gas Evolution (mL/g)	Main Gases
ADC (ADCA)	200-215	220	CO, CO_2, NH_3
ADC (ADCA) act.	140-215	130-220	N_2, CO, CO_2, NH_3
DNPT	190-200	190-200	N_2, NH_3, CH_2O
THT	245-285	180-210	N_2, NH_3
TSH	105-110	115	N_2, H_2O
OBSH	155-165	110-125	N_2, H_2O
TSSC	225-235	120-140	N_2, CO_2, NH_3
5-PT	240-250	190-210	N_2
$NaHCO_3$	110-150	160-190	CO_2, H_2O
$NaHCO_3$/citric comp.	130-230	110-180	CO_2, H_2O

However, the appearance of residual products is a disadvantage, given the fact that they can represent up to 70 % of the final composition of the agent [61], [62]. Their decomposition can lead to a degradation of the polymer matrix, to a decrease in mechanical properties, to coloration of the part and to corrosion and contamination of the mold. For these reasons only a defined amount of foaming agent ought to be incorporated into the polymer melt when using chemical blowing agents. A list of chemical blowing agents is provided in Table 2.4 [63].

Endothermic blowing agents

Endothermic CBAs are used primarily in the injection molding of foam where the rapid diffusion rate of carbon dioxide gas through the polymers is essential. This allows postfinishing of foamed parts right out of the mold without the need for a degassing period. Nucleation of physically foamed materials, especially those used for food packaging, has become a well-established application area for endothermic CBAs.

Sodium borohydride ($NaBH_4$) is an effective endothermic blowing agent because its reaction with water produces 10 to 20 times the amount of gas produced by other CBAs that give off nitrogen. Sodium borohydride must be blended with the polymer to be foamed to prevent reaction with water during storage.

Sodium bicarbonate ($NaHCO_3$) decomposes between 212 and 284 °F giving off CO_2 and H_2O and forming a sodium carbonate residue. Its gas yield is 267 cm^3/g. At 287 °F or higher, decomposition becomes more rapid, facilitating its use as a blowing agent for such higher-temperature thermoplastics as styrenic polymers.

Polycarbonic acid decomposes endothermically at approximately 320 °F and gives off about 100 cm^3/g of carbon dioxide. Further heating will release even more gas. In addition to being used as the primary source of gas for foaming in some applications, this class of materials is frequently used as a nucleating agent for physical foaming agents [64].

2.3.1.3 Determining the amount of gas generated

The dimensionless volume V_{g0} of gas generated (volume at STP per volume of LDPE) can be calculated from the concentration of the chemical blowing agent. Lee and Flumerfelt (1995) found that the solubility of nitrogen in LDPE melts increases with temperature [35]. The relationship between the mass X of nitrogen dissolved, expressed as g N_2/g LDPE, and the pressure p measured in bar, at 135 °C is (2.1)

$$X = 0.24 \times 10^{-3}\, p - 1.7 \times 10^{-6}\, p^2 \quad (\text{for } p < 20) \tag{2.1}$$

Since the molar mass of nitrogen is 28 g/mol, and the molar volume of a gas at 135 °C is 31,600 ml/mol, 0.22 volumes of nitrogen dissolve in one volume of LDPE at 135 °C under an absolute pressure of 1 bar. Since the foam relative densities are typically less than 0.08 in the later stages of expansion, and the gas pressures are less than 0.2 bar, the fraction of the nitrogen gas dissolved in the LDPE is insignificant.

It is assumed that no gas loss occurs by diffusion through the cell faces to the outside of the foam. If the foam density is ρ (kg m^{-3}) at the process temperature T, the dimensionless gas volume $V_g(T,p)$ under the process conditions is (2.2)

$$V_g\left(T,p\right) = \frac{918}{\rho} - V_P(T) \tag{2.2}$$

The dimensionless LDPE relative volume $V_P(T)$ at temperature T °C is given by Hellwege et al. [65] as (2.3)

$$V_P(T) \equiv \frac{V(T)}{V(20)} = 1.057 + 7.93 \times 10^{-3} T \tag{2.3}$$

The absolute gas pressure p is determined from V_g and V_{g0} using the ideal gas laws, hence the relative gas pressure p_r is obtained.

2.3.1.4 Control of cell size and cell stability

Nucleating agents can be used to reduce cell size. Cheung and Park [66] described the use of talc in PP foam. Talc is more effective than calcium carbonate [67], probably due to its platelet geometry; the concentration of nuclei appeared to increase almost exponentially with the concentration of talc, with the smallest particle size 0.8 μm talc being most effective. Low-density foams of HDPE can be extruded with fine cells, using CO_2 as a blowing agent [68]. The melt temperature was reduced to the lowest possible value of 121 °C at the die, to avoid cell coalescence and achieve high expansion ratios. In related research [69], a blend of LDPE and LLDPE, blown with CO_2, was extruded at 220 °C. It was necessary to cool the extrudate surface to temperatures as low as 0 °C to stabilise the foam.

Park and Malone [70] defined a foamability factor *F*, from the tan δ of the PE melt (at 190 °C and 1 Hz).

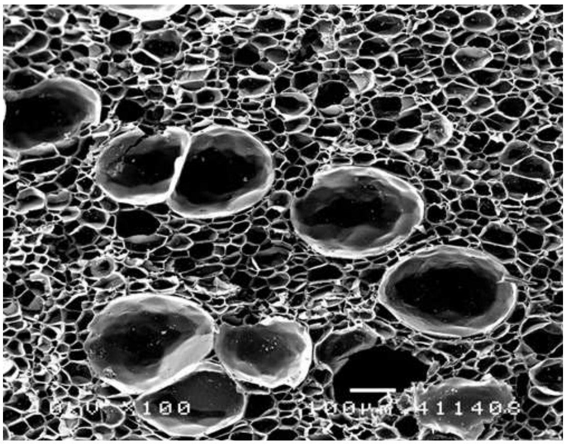


Figure 2.5 : Abnormally large cells, with >20 faces, formed by cell face collapse in EVA foam of density 150 kg m^{-3}, with a background of normal cells [71].

The LDPE blown film process is successful, since the melt bubble cooling occurs in a few seconds, allowing little time for the viscous extensional flow of the thermoplastic melt. However, due to the low thermal diffusivity of foams, it takes the order of 20 min for a PE foam melt to cool to the solid state. During this time, the melt bubbles must remain stable. The typical gel content, from 30 % to 70 %, causes the low-shear-rate viscosity to be extremely high. However, if gelations were taken further, the tensile stresses in the expanded foam would be too high.

2.3.2 Production Methods of Polymer Foams

The manufacturing of plastic foams extends to most plastics processing technologies [57]. Foams can be processed in extrusion, injection molding, compression molding, blow molding, coating, calendaring, rotational molding, etc.

Regardless of the processing technique, the foaming of polymers by using physical blowing agents, such as carbon dioxide or nitrogen, relies on the same principles: (1) the polymer is saturated with the blowing agent at high pressures, (2) the polymer-gas mixture is quenched into a supersaturated state by reducing the pressure and/or increasing the temperature, (3) the thermodynamic instability of supersaturation leads to nucleation of foam cells, (4) the growth of the foam cells, driven by the diffusion of the blowing agent, proceeds until the cells either stabilize or rupture. The growth rate is primarily controlled by the diffusion rate, the rheological properties of the polymer, the temperature, the state of supersaturation, and the hydrostatic pressure applied to the polymer matrix. Although these principles controlling the foaming behavior are fairly well understood, most commercial thermoplastic foams are still based on a limited number of polymers such as polystyrene (PS), polyvinyl chloride (PVC), polyethylene (PE), and polypropylene (PP) [73].

2.3.2.1 Extrusion of thermoplastic foam sheet

Foaming plastics has been developed as an extension of the extrusion application while extruder evolution is primarily based on its function optimization. Extrusion of thermolastic foams is largely controlled by the relatively complex rheological behavior of the polymer melt and physical foaming agent (PFA) mixture [74].

In 1941, the first foam extrusion based product was Styrofoam, created by Dow and in 1958, the first commercialized LDPE foam was introduced by Dow again [75].

The complexity arises first from the moderate to large plasticization due to the adequate dissolution of the small molecules of the foaming agent. They act as a diluent with respect to the polymeric macromolecules, which forms a single phase (zone #1, Figure 2.6). This solution should remain in that state until the nucleation step occurs at the die exit, as shown in Figure 2.6. This is usually accomplished by maintaining a pressure that is sufficiently high inside the extruder, i.e., above the solubility pressure for such conditions of temperature and PFA concentration, thereby preventing any phase separation. In the extruder, the deformations occur mainly in a shearing mode. Elongational and shear flows coexist in the die, where the PFA should still be kept dissolved in the polymer melt [10].

The melt, leaving a slot-shaped die, spreads on a moving belt. As the foaming process proceeds, the thermal conductivity of the foam decreases significantly, while the heat conduction distance increases as the foam sheet thickens. The time scale for foam expansion is of the same order as that for heat conduction. Gas diffusion occurs, under the pressure differential from the centre to the surface of the sheet. The lower pressure in the surface cells could allow these to shrink in size and relieve the tensile stresses in the oriented faces. Hence the foam density is expected to be higher near the foam skin. The high tensile viscosity of the molten polymer resists, but does not prevent, the thinning of cell faces and the drawing of melt from cell edges. If neighbouring cells have different diameters, larger bubbles will try to grow at the expense of neighbouring smaller bubbles, lessening the overall surface energy of the system. However, as bubble coarsening is rarely observed, this process must be slow compared with the solidification process. Occasional large cells in foams appear to be the result of face fracture followed by a reshaping of the joined cells.

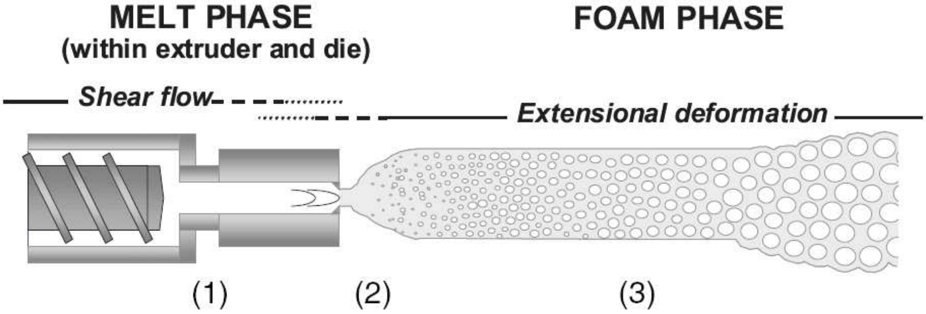


Figure 2.6 : Schematic of the extrusion foam process.

(1) A single-phase, gas-laden melt is pumped toward die exit.
(2) Nucleation occurs outside the die due to the large pressure drop.
(3) Cells expand and the structure stabilizes as the polymer is cooling.

When the melt passes through the short extrusion die, its pressure falls rapidly to atmospheric and a fine cell size is produced. The process of gas diffusion from the melt to the bubbles occurs on a time scale of the order of seconds. Faster pressure reduction allows less time for gas diffusion, so the effective gas diffusion distance is smaller. This allows new bubbles to nucleate closer to growing bubbles, reducing the average cell size in the final foam. Shafi et al. [35] predicted cell size distributions for freely expanded LDPE/nitrogen system from measured parameters. However they did not predict the mean bubble size in terms of directly measurable process variables.

2.3.2.2 Compression molding method

Compression molding is a forming process in which a plastic material is placed directly into a heated metal mold, then is softened by the heat, and forced to conform to the shape of the mold as the mold closes. The mold is closed with a top force or plug member, pressure is applied to force the material into contact with all mold areas, while heat and pressure are maintained to the molding material. The advantage of compression molding is its ability to mold large, fairly intricate parts. Also, it is one of the lowest cost molding methods compared with other methods such as transfer molding and injection molding; moreover it wastes relatively little material, giving it an advantage when working with expensive compounds.

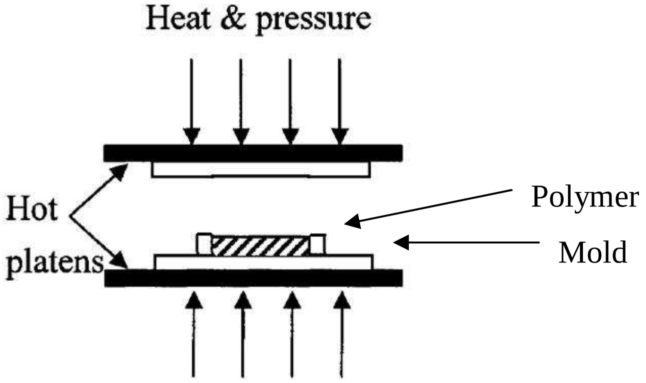


Figure 2.7 : Schematic of the compression molding foam process.

Compression molding was first developed to manufacture composite parts for metal replacement applications, compression molding is typically used to make larger flat or moderately curved parts. This method of molding is greatly used in manufacturing automotive parts such as hoods, fenders, scoops, spoilers, as well as smaller more intricate parts. The material to be molded is positioned in the mold cavity and the heated platens are closed by a hydraulic ram. Bulk molding compound (BMC) or sheet molding compound (SMC), are conformed to the mold form by the applied pressure and heated until the curing reaction occurs. SMC feed material usually is cut to conform to the surface area of the mold. The mold is then cooled and the part removed. Materials may be loaded into the mold either in the form of pellets or sheet, or the mold may be loaded from a plasticating extruder. Materials are heated above their melting points, formed and cooled. The more evenly the feed material is distributed over the mold surface, the less flow orientation occurs during the compression stage [78].

In compression molding system compression force is applied among molds to get the desirable shape of molten materials through solidification. In this process good optimization could be obtained between the flow of material and the mechanical properties [79]. Meij [80] investigated non-isothermal effects on the flow of Glass Mat reinforced Thermoplastics (GMT) during moulding and suggested process control tools.

The compression molding processing of cellular samples is based on three sub-processes which include the processing of the polymer matrix, the processing of the cellular structure, and the processing of the net shape. The creation of a cellular structure is achieved by dissolving large gas concentrations into a polymer matrix and subjecting the saturated system to a rapid thermodynamic state change. This creates an unstable or supersaturated matrix that drives the nucleation of billions of microcells. Stable cells then grow as gas diffuses into the cells reducing the bulk density of the material [81].

In compression molding there are six important considerations that an engineer should bear in mind.

- Determining the proper amount of material.
- Determining the minimum amount of energy required to heat the material.
- Determining the minimum time required to heat the material.
- Determining the appropriate heating technique.
- Predicting the required force, to ensure that shot attains the proper shape.
- Designing the mold for rapid cooling after the material has been compressed into the mold.

Commercial moulding prediction tools issued from work on non-isothermal moulding are available [82 - 84]. It was found that the fiber content and the polymer viscosity both have a large influence on the work of compression [80]. However, not much is known about the influence of each of the constituent materials on processing and about the evolution of the temperature and deformation fields during non-isothermal flow [86]. During industrial flow molding processing, composites are preheated and then transported to the mould, which is maintained at a temperature below the solidification temperature of the matrix. The mould is then closed at a high speed. When the flow is almost complete, the press is switched from displacement control to pressure control and a pressure is maintained until the mould is full and the material inside has cooled sufficiently. The material in the inlay zone cools first and its rheology and solidification behavior determines the extent of flow in the rest of the mould. The void content during dwell and initial compression is high due to lofting of the preforms at preheating. When the hot preform is compressed between the platens, the macro-voids are removed. During the initial phase of flow, some voids, still remain in the material are rapidly suppressed. The material then flows out from between the platens and flow ends until the material between the platens is solidified throughout thickness. However, surface void formation is still a major problem, especially for application in automotive industry [87]. Such voids require costly after treatment to enable good appearance after painting.

In compression molding, compounding step can be eliminated and mixing and molding can be done in one step [88], [89]. This will allow minimizing length reduction of the fibers and the time the fibers spend at high temperature. In this method the cellulose fibers get distributed evenly between polymer films and then the “sandwich” is created by pressing in a compression molder at adequate time and temperature. Bullions et al. [90], [91] prepared composites of kenaf bast, wood pulp, and poultry feather fiber by mixing with polypropylene and then passing them through a hot oven at a fast rate to melt the PP fibers but not degrade the natural fibers and a formed a prepreg. The prepreg is then compression-molded into laminate plates under pressure (4.44 MPa) and temperature (180 °C) [92].

Park [93] and Gendron [10] cover the processes for polyolefin foams and the blowing agents used. The compression moulding of EVA foam shoe midsoles use a different technology, with crosslinking and expansion in a heated mould. Eaves and Witten [95] described the Zotefoams process, in which nitrogen is dissolved into molten crosslinked polyolefin sheets in a high-pressure autoclave, which are then expanded into foams in two stages. Recent research has concentrated on process refinement. The development of rotomoulded [96] and microcellular foams [97] are peripheral to the products discussed.

2.3.2.3 Reaction injection molding of foams

Reaction injection molding is a processing technique for the formation of polymer parts by direct polymerization in the mold through a mixing activated reaction. A simplified process schematic is shown in Figure 2.8. Two reactive monomeric liquids, designated in the Figure 2.8 as A and B, are mixed together by impingement and injected into the mold. In the mold, polymerization and usually phase separation occur, the part solidifies, and is then ejected. Primary uses for RIM products include automotive parts, business machine housings, and furniture [98].

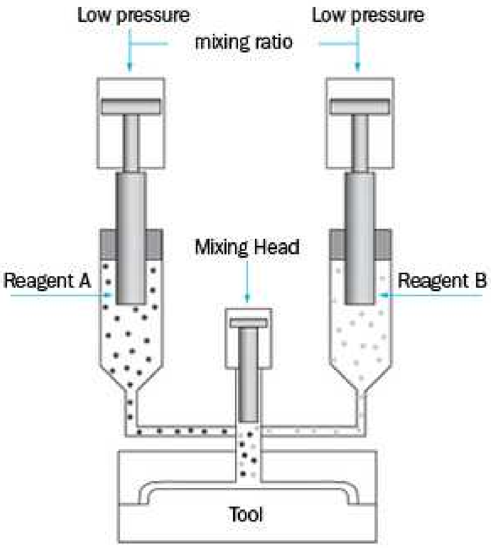


Figure 2.8 : Schematic of the reaction injection molding foam process.

Reaction injection molding is a variation of the standard high pressure molding with impingement mixing. A very low viscosity mixture is injected into the mold to produce quickly the final part. RIM differs from regular molding in that the formulation of the polyurethane system has to be very fast. This is achieved by replacing the diol crosslinker with diamine crosslinker to obtain polyurea. This technique can be used to produce ‘structural foams’ (high density rigid foams with a skin) for auto body parts, dashboards and bumpers and also to obtain elastomers and microcellular foams. Components are injected in the mixing chamber of the mixing head under high pressure and mixed by impingement. The piston then injects the accumulated mass into the mold and cleans the chamber for the new shot. When the piston is in the down position the polyol and isocyanate components are recycled. Because of the low viscosity and low pressures RIM technology can be used to mold large parts with metal inserts. The molds for RIM can be made from steel, aluminum or zinc alloys. They are cheaper than the molds for injection molding of thermoplastics. Total consumption of energy is lower than in the competing techniques, and the investment in equipment is lower.

The most common RIM processable material is polyurethane, [99] but others include polyureas, polyisocyanurates, polyesters, polyphenols, polyepoxides, and nylon 6.

Reaction injection molding can produce strong, flexible, lightweight parts which can easily be painted. It also has the advantage of quick cycle times compared to typical vacuum cast materials. The bi-component mixture injected into the mold has a much lower viscosity than molten thermoplastic polymers, therefore large, light-weight, and thin-walled items can be successfully RIM processed. This thinner mixture also requires less clamping forces, which leads to smaller equipment and ultimately lower capital expenditures. Another advantages of RIM processed foam is that a high-density skin is formed with a low-density core [100]. The disadvantages are slow cycle times, compared to injection molding, and expensive raw materials.

If glass fibers are added to get reinforcement, the method is known as RRIM (Reinforced Reaction Injection Molding). Structural RIM (SRIM) is the process whereby the reinforcement fabric or mat (glass, carbon) are placed in the mold and the resin is injected to impregnate the reinforcement [101], [102].

2.3.2.4 Injection molding method

Injection molding is a manufacturing process for producing parts from both thermoplastic and thermosetting plastic materials. Material is fed into a heated barrel, mixed, and forced into a mold cavity where it cools and hardens to the configuration of the cavity [103].

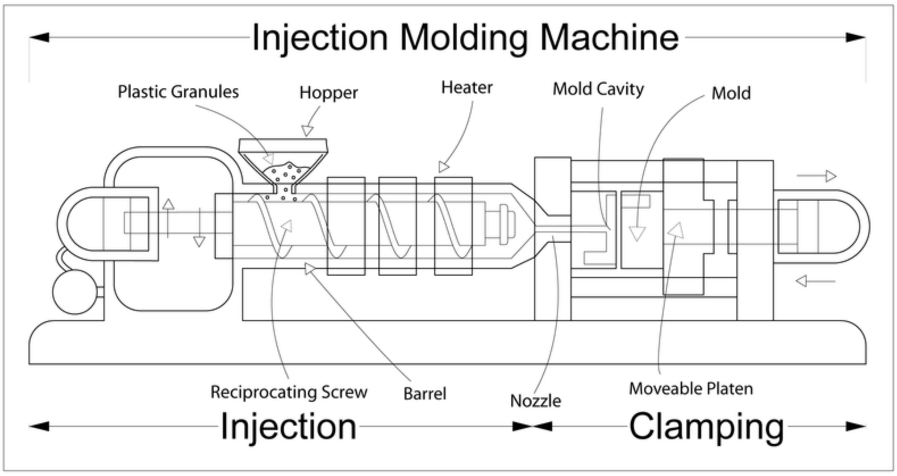


Figure 2.9 : Schematic of the injection molding machine.

The structural foam process is a low pressure injection molding process where an inert gas is introduced into melted polymer for the purpose of reducing density and hence weight of the finished product.

Low pressure foams (Figure 2.10/1) have the characteristics of the injection of a physical blowing agent, usually gaseous nitrogen, into the extruder with the melt. The charge is collected in an accumulator and injected in the mold at something less than the mold volume through valved injection points called nozzles. The mold is not filled when the injection phase is complete and the expanding blowing agent provides the energy to force the polymer to the extremes of the mold cavity [104].

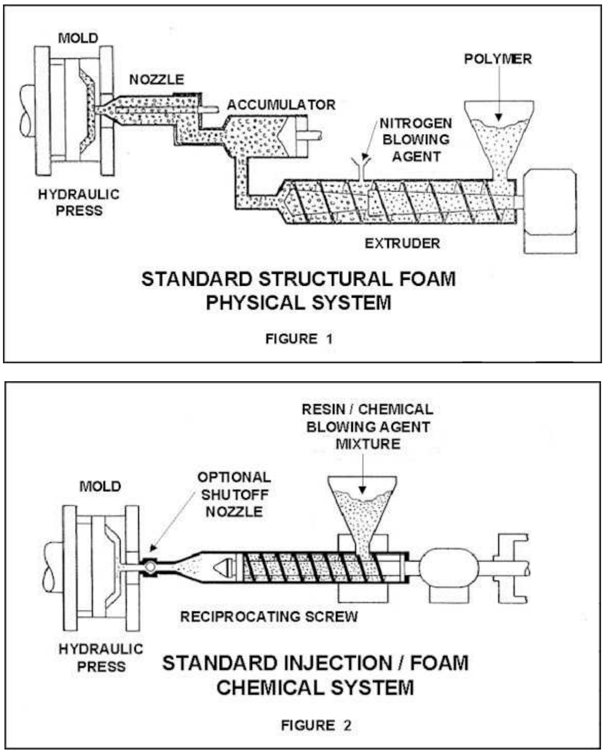


Figure 2.10 : Schematic of the injection molding foam processes.

High or medium pressure foam process (Figure 2.10/2). A chemical blowing agent is typically used. The blowing agent decomposes under the influence of elevated temperature over a time to produce a gas or series of gases leaving a small quantity of a residue. The injected charge is incomplete to fill the mold cavity leaving the expansion of the chemically liberated gas to provide the energy to fill the mold [105].

The performance advantages of injection molded thermoplastic foams have been known and exploited for some decades now, but only the recent developments in processing technologies and blowing agents have given them a steady growth into new market applications. Automotive products, electric and electronic equipment and industrial appliances are profiting from the reduction in war-page and shrinkage associated with foam injection molding, as well as from the diminution in the required clamping tonnage. An obvious benefit, the potential of material saving, is gaining relevance in the automotive field, because of the ever tightening environmental legislations toward the reduction of CO_2 emissions. Facing the demand of reducing the vehicles' weight, the implementation of foamed parts stands as one of the most straightforward answers.

It is however known that the enhancement of the molded part properties has a price to be paid in terms of mechanical performance. Given the typical structure of a foam injection molded part, where a compact outer layer surrounds a foamed core, this loss in properties is caused by an obvious reduction of the stress-bearing area, as well as by the actuation of the foam cells as stress concentrators. The reduction in properties has traditionally been studied as a function of the foam density reduction, but there is little understanding of the effect played by morphological parameters of the foam, such as cell size distribution, anisotropy or outer layer thickness.

In the injection of thermoplastic foams the morphology can be drastically affected by the molding parameters, and the change in variables as injection velocity, melt temperature and mold temperature can deliver, for the same density reduction, a very dissimilar spectrum of properties [106].

Injection molding in the presence CBAs is the major manufacturing method to produce high foams. On the other hand, up to 90 % of density reduction versus the unfoamed polymer can be achieved by low density foaming with PBAs such as volatile hydrocarbons, CFCs, HCFCs and atmospheric gases [107].

2.3.2.5 Rapid rotational foam molding

Conventional rotational molding, or rotomolding, is a plastics fabrication technology that is advantageously utilized to manufacture single-piece, hollow or doublewalled, large-sized, complex-shaped, seamless, stress-free plastic articles. Rotomolding is best implemented in manufacturing environments that practice medium to low production runs of large parts; this is due to the intrinsically lengthy cycle time of the process, as it is required to elevate the temperature of a mold, while rotating it bi-axially, from room temperature to beyond the melting temperature of the plastic to allow shaping, and then cool it back to room temperature for part removal [108 - 113].

All rotomolding machines must allow accomplishing four distinct fabrication tasks; these are: (i) heating, (ii) cooling, (iii) servicing, and (iv) bi-axial rotation during the first 2 stages.

Rapid Rotational Foam Molding (RRFM) is a novel patent-pending process that was designed and developed to maximize the synergistic effects resulting from the deliberate combination of extrusion and rotational foam molding and thereby serve as a time and energy efficient technology for the manufacture of integral-skin rotationally molded foams of high quality.

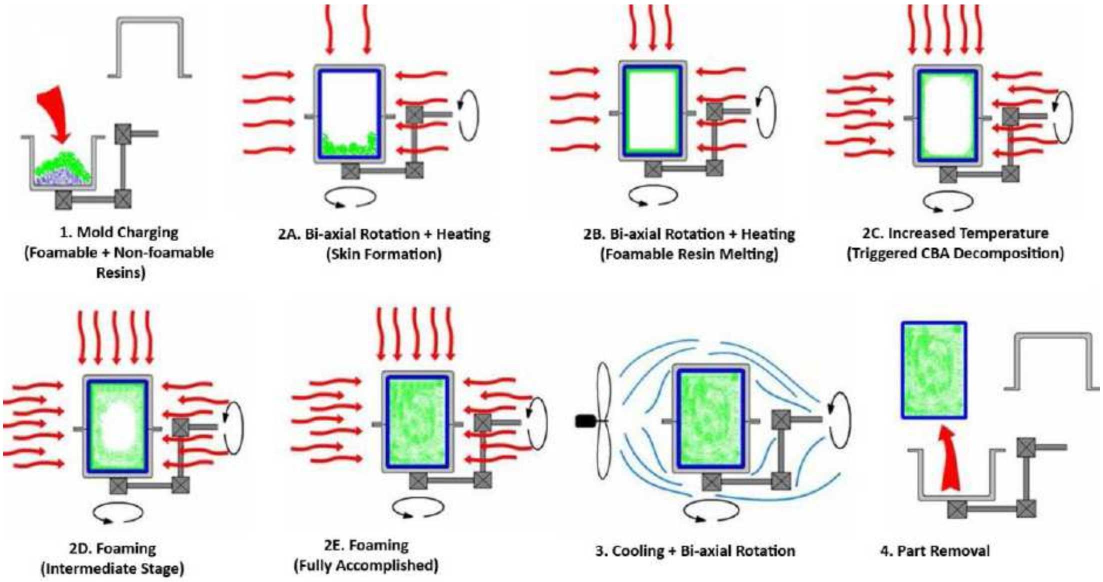


Figure 2.11 : Single-charge rotational foam molding processing steps.

In case of the experimental trials could involve a variety of thermoplastics based on foamable formulations with a chemical blowing agent (CBA) that are compounded and processed by utilizing an extruder, and are foamed and injected as a foamed core, instantly, into the cavity of a suitable non-chilled rotationally molded hollow shell made of non-foamed pulverized thermoplastic polymers.

The investigated mold shapes included a cylindrical shaped mold and a rectangular flat shaped mold. The obtained moldings are examined for the quality of the skin surface, the skin-foam interface, and the achieved foam morphologies that are characterized in terms of foam density, average cell size, and average cell density.

2.4 Properties of Polymer Foams

2.4.1 Foam geometry

When gas bubbles grow in a liquid, the foam goes through a number of stages. Figure 2.12 shows a two-dimensional view in which the regularly spaced bubbles are all the same size. As the density of the foam decreases, the bubbles come into contact, forming a closed cell foam. Finally the cell faces burst and liquid drains to the cell edges leaving an open cell foam. Beyond this the foam collapses back to a liquid. When plastic foams are examined by scanning electron microscopy (SEM) two main types are found. If the gas bubbles have grown in highly viscous thermoplastic melt, the thinning of the cell walls is a slow process, and solidification can stabilise the closed cell foam.

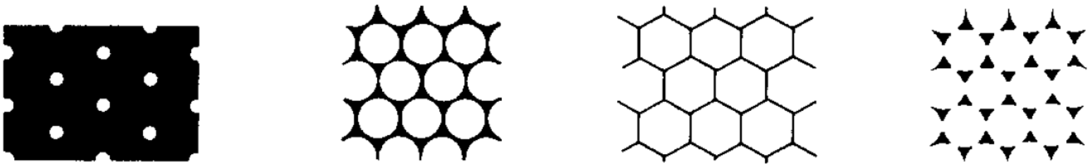


Figure 2.12: Change in the structure of a foam containing a regular array of bubbles as the volume fraction of gas increases.

A section through the cell walls of a similar PVC foam shows that the cell faces are uniformly thick. The faces, rather than the edges, contain most of the polymer. It is easier to form such foams using glassy polymers, but recently the melt rheology of polypropylene has been modified to allow stable foams to be formed in the narrow process temperature window above the melting point of the crystalline phase. It is also possible to crosslink polyolefins before foaming, which makes the cells more stable.

When a low viscosity thermoset prepolymer is foamed the polymer can eaily drain from the cell walls before the crosslinking reaction stabilises the foam cell edges. Figure 2.2.a shows a polyurethane open cell foam in which only the cell edges remain. These have three concave sides, the shape being fixed by the surface tension of the liquid prepolymer.

Microcellular foams differ from classical foams, because of their cell structure, higher density of the foams, which is typically 200 kg/m^3, and the structure of the matrix. Microcellular foams are foamed segmented elastomers with smaller number of round cells, unlike polygonal cells with ribs in standard foams. Because of their superior mechanical properties they are used for shoe soles, car bumpers, etc. [32].

The geometrical parameters are interrelated for a family of polymer foams made by the same process. For polystyrene bead foam, where the density is determined by the initial mass of beads placed in the mould, the cells become larger and the cell walls thinner as the density of the foam decreases [13].

2.4.2 Foam density

Cell Density, defined as the number of cells per unit volume with respect to the nonfoamed composite was determined by (2.4) [119]:

$$N = [nM^2/A]^{3/2} \text{ x } \psi \qquad \textbf{(2.4)}$$

Where, N = Cell density (cells/cm^3), n = Number of cells, M = Magnification factor, A = Area of the micrograph (cm^2), and Ψ = Expansion factor of foamed sample.

2.4.3 Foam structure

The next parameter used to describe a foam is the fraction of open and closed cells it contains. The latter are generally measured by comparing the external volume of a foam specimen to the pressurized gas volume differential measured when the foam is put in a hermetic chamber. If both volumes are equivalent, the foam has a 100 % closed cell structure. If these volumes are different, their difference is attributed to the open-cell fraction, which permits the penetration of the gas into the foam. This study deals with industrial foams in which a closed-cell morphology predominates.

2.4.4 Cell size distribution

Another very important microstructural parameter required to describe a foam is the cell size distribution, from which different statistical parameters can be derived. The cell size distribution is obtained from quantitative observations of foams cells. These cells are observed on the microtomed or fractured surface of the foam. By image analysis, the surface area of individual cells, A_i, is measured and the corresponding cell size, d_i, is calculated from the equivalent diameter of a circle of area A_i ($d_i = 2\sqrt{Ai/\pi}$). To reflect the foam microstructure with a good statistical representation, the number of cells to be measured should be reasonably high, e.g., 200–300.

By plotting the cell size in a histogram, the cell size distribution curve can be obtained. From such a distribution, the number-average diameter d_n and the volume-average diameter d_v can be calculated using (2.5) and (2.6):

$$\overline{d}_n = \frac{\sum n_i d_i}{\sum n_i} \quad \textbf{(2.5)} \qquad \overline{d}_v = \frac{\sum n_i^4 d_i^4}{\sum n_i^4 d_i^3} \quad \textbf{(2.6)}$$

where d_i and n_i are a measured diameter i and the number of such diameters measured, respectively.

A cell size distribution that is close to perfectly normal will show very close values of d_n and d_v, while other distributions, a bimodal distribution for example, will show very different values of d_n and d_v. Thus, the ratio of d_v / d_n represents a useful tool for evaluating cell size dispersity, similar to the molecular weight polydispersity used in polymer chemistry to characterize molecular weight distribution. It is generally believed that a cell size dispersity ratio close to 1 (e.g., below 1.25) indicates a statistically normal distribution or a monodisperse distribution. According to the Schwartz–Saltikov statistical method for the correction of measured diameters [120], the diameter correction for a monodisperse distribution is given by a constant equal to $4/\pi$ (≈ 1.27). Since the correction factor is a constant for all foams with cell size dispersity ratios close to 1, it will not be considered in the morphological characterization of the foams.

2.4.5 Foam anisotropy

Foams produced as extruded panels generally exhibit morphological anisotropy, which affects their mechanical behavior. Depending on the application, it could be necessary to obtain their cell size distribution, average aspect ratio, and orientation in three orthogonal directions, i.e., in the extrusion or machine direction, in the direction normal to the machine direction, and in the direction normal to the thickness of the panels. These three microstructural parameters account for their morphological anisotropy, which will be reflected in their mechanical anisotropy. The principal microstructural parameters are summarized in Table 2.5.

2.4.6 Melt Rheology Suitable For Foaming

When low-density foams are produced, the polymer melt undergoes high biaxial extension to form cell faces. Its flow properties (rheology) must suit the process. High molecular weight polymer melts are highly viscous, with part of the deformation being elastic. The melt must sustain high tensile stresses without cell face fracture which would cause neighbouring cells to join. Repeated fracture leads to very large cells, and eventually to foam collapse. PS melts of high molecular weight have a relatively low entanglement density [118], so can undergo high biaxial extensions without fracture. Consequently linear PS can be used for foams. Various techniques have been used to characterise the rheological differences between these polymers. Characterisation of melt elasticity using a small oscillatory shear strain to evaluate the complex shear modulus G^* is inappropriate, since it cannot characterise the high strain response. Consequently, tests subject melt extrudates to large tensile deformations.

Table 2.5 : Useful microstructural parameters to describe foams.

Foam Characteristics	Microstructural Parameters
Amount of material	Density, relative density, void fraction
Foam structure	Fraction of open and closed cells
Cell size distribution	Number-average and volume-average diameters, cell size dispersity
Anisotropy	Cell size in orthogonal directions, cell aspect ratio, and cell orientation*

* Orientation of the maximum cell diameter with respect to a reference direction.

Ruinaard [122] was the latest of many researchers who measured the tensile viscosity of polyolefin melts. When a PP melt extrudate was stretched at a constant ε the tensile viscosity η increased with time, as the tensile strain increased, due to the entanglement network in the melt becoming significantly extended.

Figure 2.13 shows the behavior of a polymer under variations of pressure and temperature. For example, if the temperature is increased in the system, the velocity of the molecular movement and the kinetic energy will be increased as well. As a consequence of this energy increase, the number and frequency of collisions between molecules will rise, resulting in an increase of the residence volume of the molecules. On the other hand, the volume of the system will decline due to its compressibility if the pressure is increased in the fluid phase [63].

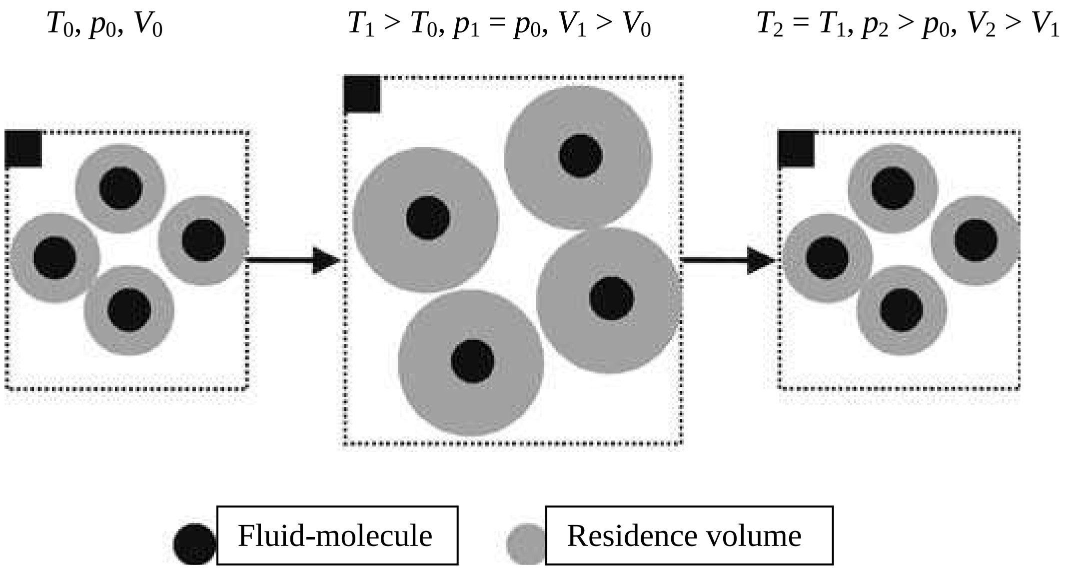


Figure 2.13 : Impact of temperature and pressure on the blowing agent.

2.5 Characterization Methods of Polymer Foams

Polymeric foams are generally characterized in terms of mechanical performance by means of different conventional mechanical testing methods. The most popular of these methods are summarized in Table 2.6.

Table 2.6 : Summary of the most popular mechanical testing methods used for foams.

Testing Method Designation	Test Method Description
Compression	Constant section (square or circular) specimen compressed at constant nominal strain rate until specimen failure or until the deformation reaches the nominal void fraction.
Flexural	Constant rectangular section beam specimen in three- or four- bending until specimen failure or load plateau.
Falling dart impact	Clamped plate specimen with a circular rig impacted by a falling dart equipped with a load cell and a displacement transducer (impact should generate failure of the specimen).
Dynamic shock cushioning (flat sheet impact)	Constant section (square or circular) specimen impacted by a plateau at high speed until specimen failure or the deformation reaches the nominal void fraction (test may be repeated to obtain maximum compression or densification).

While these mechanical characterization techniques can help to produce a foam that will perform according to certain functional requirements, additional work still needs to be done in order to understand the origin of their performance. To achieve this, the relationship between the morphology of engineering foams and their functional behavior needs to be defined. Until now, the relationship between morphology and performance has been discussed according to the approach proposed by Gibson and Ashby [124], which relates foams’ mechanical properties to their density. However, this approach, based exclusively on the foam density, does not take into account the detailed morphological characteristics of foams, such as their cell size distribution and anisotropy.

In recent years, some attempts at considering detailed morphological foam characteristics in mechanical behavior analysis have been reported.

Table 2.7 : Characterization methods and standards of rigid cellular plastics [100], [125].

Subject	Standard
Test methods	ISO 9054, ISO 7214
Tensile properties	ISO 1926, ASTM D 1623,DIN 53430
Flexural properties	ISO 1209-1/-2, JIS K 7221
Shear strength	ISO 1922, DIN 53427
Compression properties	ISO 844, ASTM D 1621, EN 826
Compression creep test	ISO 7616, ISO 7850
Thickness measurement	EN 12431
Pendulum impact strength	ISO 179
Density	ISO 845, ASTM D 1622
Dimensions	DIN 53570
Tensile strength perpendicular to faces	EN 1607, DIN 53292
Dielectric constant and dissipation factor	ASTM D-1673
Dielectric breakdown and dielectric strength	ASTM D-149
Electrical resistance	ASTM D-257

However, this is not intended to provide an exhaustive survey of foam properties, nor a comparison of the performance of different foams or foamed structures. The textbook of Gibson and Ashby [124], which provides a very wide survey of foam structures and properties. A microstructural description of foam materials that takes into account their detailed morphological characteristics and that can be employed as a single microstructural parameter to report mechanical properties will be provided.

The foam samples could be characterized by the volume expansion ratio and the cell-population density. The expansion ratio of the foam is determined by measuring the weight and volume expansion of the sample. The volume of foam sample is determined by the water displacement method (ASTM D792). The volume expansion ratio (Φ) is calculated on the basis of the ratio of bulk density of pure material (ρ_p) to the bulk density of foam sample (ρ_f) as follows [126]:

$$\Phi = \frac{\rho_p}{\rho_f} \quad or \quad \rho_f = \frac{\rho_p}{\Phi} \tag{2.7}$$

The cell-population density is calculated from the microstructure obtained from the scanning electron microscope (SEM). SEM pictures are used to investigate morphology, number and shape of foamed cells/bubbles/voids and whether a cellular structure is being achieved or not. The foam samples are fractured in liquid nitrogen and the fractured surface is coated with gold before SEM. The cell density (n) is defined as the number of cells per unit volume with respect to the unfoamed polymer. A certain area is chosen in the SEM photograph. The number of cells per unit volume (3D) is estimated from 2D information, assuming that the cells are in a spherical shape. It may be noted that it is used the cell-population density defined with respect to the unfoamed polymer and the volume expansion ratio to better describe the processing-to-structure relationships. These parameters indicates how well cell nucleation and expansion are controlled during foam processing [126].

The most popular mechanical testing method used for foams is the compression test. This testing method [127] consists of compressing a foam specimen and recording the load reaction as the specimen reduces in thickness as a result of the imposed displacement. The compressive stress–strain curve is obtained by dividing the load at any moment during the test by the nominal area and the imposed reduction in thickness by the initial thickness of the specimen. An illustration of this compressive stress–strain curve is shown in Figure 2.14. This compressive stress–strain curve typically shows three stages. The first stage is characterized by a linear elastic or Hookean behavior where the stress is proportional to the strain, following Hooke's law. The compressive modulus of elasticity E^* is obtained from the slope of this initial linear portion of the compressive stress–strain curve. The compressive strength σ_y^* is obtained from the compressive stress at the yield point if a yield point occurs before 10 % deformation or, in the absence of such a behavior, from the compressive stress at 10 % deformation. The compressive yield point is defined as the first point on the compressive stress–strain curve at which an increase in strain occurs without an increase in stress.

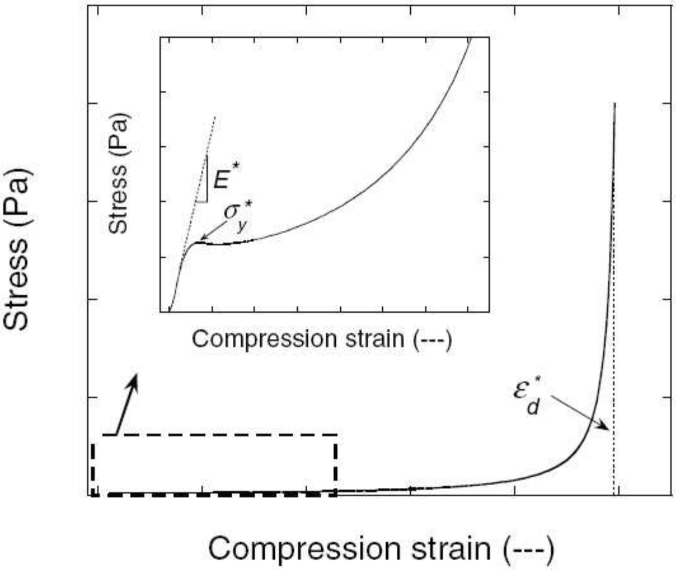


Figure 2.14 : Typical compression stress–strain curve of a low-density elasto-plastic foam, with compressive modulus of elasticity *E**, compressive strength σ_y^*, and strain at densification ε_d^*.

Starting from the yield point, the second stage of the compressive stress–strain curve is characterized by an approximately constant compressive stress rate (plateau) during which the foam undergoes plastic deformation, either by elastic buckling, plastic yielding, or brittle crushing, depending on the foam behavior. This constant compressive stress rate stage extends over a certain amount of compressive deformation and ends at the onset of densification, which defines the third and last stage of the compressive stress–strain curve. The densification stage is a progressive one, during which the foam cells collapse completely, resulting in a rapid increase of the compressive stress as a result of the densification of the foam. The limit of this densification stage in terms of deformation is set by the amount of material in the foam, i.e., its density. As a first approximation, this deformation at densification ε_d^* may be obtained from the void fraction in the foam, given by 1 – ρ*r* (where ρ*r* is the relative foam density). As the foam is collapsing, the compressive stress–strain curve progressively tends towards the bulk modulus of the material in the foam.

Other testing methods have also been used to characterize the mechanical performance of foams. Flexural tests [128], either in three-point or four-point bending configurations, can be performed. The advantage of the latter is that it permits the researcher to obtain the flexural modulus and the flexural strength, which are of prime interest in the production of foam cores in sandwich panels, for example. It also allows one to obtain the mechanical performance of foams under a positive tensile stress, which is very difficult to obtain for polymeric foams in tensile testing due to stress concentration effects at the grips used to hold the tensile specimens. Variations of impact testing, either with a falling dart [129] or a flat sheet impact (dynamic shock cushioning) [130] are also of interest for quantifying the foam's ability to resist high velocity puncture by an object or to absorb dynamic compressive shocks and retain its properties.

2.6 Application Areas of Polymer Foams

Foams, as engineering materials, are now used in all industrial sectors and represent an extraordinary class of materials. They are intended for packaging, thermal and electrical insulation, buoyancy, and structural applications such as decks, road pavements, sandwich panels, and so on. This extraordinary character comes from their diverse functionalities — stiffness, strength, impact resistance, dielectric and thermal resistance, and permeability, among others — which can be customized to obtain properties ranging beyond the limits of all other classes of engineering materials. A great challenge in engineering foams is to address parameters such as specific weight and cost while answering functional requirements.

Lower density plastic foams, i.e., up to ≈ 300 [kg/cm^3], are used in a variety of applications; these include: comfort cushioning (automotive, transportation, and furniture); floatation (in-place floatation for small vessels, marine life vests, pool accessories, child toys); shock mitigation (food packaging, construction and transportation crash barriers); and thermal shielding (industrial coolants, appliances, insulative packaging) [131].

Higher density plastic foams, i.e., above ≈ 300 [kg/cm^3], in o*ppo*sition, are used to serve the following applications: furniture (frames, tables); materials handling (pallets, milk and soda cases, containers); industrial (battery cases, trash containers, electrical housings); automotive (decorative paneling, glove box door, instrument panels, fender liners, vehicle crash barriers); and marine (seats, fish boxes, cabin structures) [131].

Table 2.8 : Typical markets for low-density foams [131].

Market	Application
Comfort Cushioning	Automotive, transportation, and furniture seating, mattresses, bedding and carpet underlay
Flotation	Marine buffers, marine life vests, pool accessories, toys
Shock Mitigation	Package protection for light bulbs, eggs, fruit, electronics, furniture, and machinery, surface protection as overwrap
Thermal Barrier	Sidewall and roofing insulation, industrial insulation for coolers, tanks, and reservoirs, appliance and hot water insulation

Table 2.9 : Typical markets for high-density foams [131].

Market	Application
Furniture	Panels, frames, tables, seating, bed structures
Cabinetry	Stereo components, equipment housings
Material Handling	Pallets, milk and soda cases, containers
Industrial	Battery cases, underground conduits, transformer housings
Consumer	Toys, coolers, totes, mirror and picture frames
Construction	Shutters, shingles, windows, doors
Appliances	Washer tops and doors, tubs and bases
Automotive	Decorative paneling, glove box door, seat frames
Marine	Fascia, seating, fish boxes, cabin structure

Composite sandwich structures consisting of thermoplastic skins and foamed core are finding increasing use in a variety of applications such as mass transit and automotive structures [132], [134 - 137]. In many cases, thermoplastic sandwiches offer many advantages compared to traditional materials, such as steel, aluminum, and thermoset composites, due to their high-specific strength, good damping capacity, corrosion resistance, superior impact resistance, and ease of shaping and recycling [138]. Moreover thermoplastic sandwiches are characterized by other physical properties, such as thermal and acoustic insulating properties, making these structures an attractive alternative to more traditional solutions. The design of such structures requires the knowledge of different mechanical parameters due to their intrinsic nonhomogeneity. Among other requirements, skin and core stiffness and also skin–core adhesion characteristics are important. An example for composite structure of a thermoplastic sandwich panel used in insulating walls of containers for food transportation [139] is that foamed poly(ethylene terephtalate) (PET) core (100 mm thick) with polypropylene (PP)/glass fiber skin sandwich (4 mm thick).

2.7 Literature Review of PET Foams

R. G. (Dick) Angell, Jr. [140], of Union Carbide Corporation described the structural foam process. The article in its introduction stated; *"With the structural foam molding process a product with a cellular core and integral solid skins is molded in a single operation. Almost any thermoplastic resin can be used. This structure is tough, rigid, light in weight, and impervious to gases and liquids at moderate pressures."*

Xanthos et al. [141] evaluated extrusion foamability of a variety of PET resins with different rheological characteristics using several CBAs and found that an exothermic CBA (Expandex 5-PT) performed better than two other endothermic ones. They produced high to medium density PET foams (> 0.6 g/cc). The foam densities varied with respect to the material variables (type and concentration of CBA) and the operational variables (die set temperature and screw rpm). In order to obtain improved foamability of PET with PBA, they suggested the use of PET with modified viscoelastic characteristics.

Baldwin et al. [142 - 143] performed microcellular foaming with a commercial PET. They used cell density as a representative variable to describe the foam characteristics, and the higher cell densities of $10^{10} \sim 10^{12}$ cells/cc were obtained with the semi-crystalline PET rather than APET (amorphous PET) or CPET (nucleated PET).

The published information on foaming of aromatic polyesters is mostly about PET foaming rather than PBT. This may also be related to the lower cost of the PET resin vs. PBT and the recent penetration of PET foams in competitive packaging markets that are currently served by low cost commodity resins [144].

There exist many technical and scientific articles on chain extension/branching used to modify its structure as well as applications of the modified PET in extrusion foaming. PET modifiers and examples of their use have been reviewed [145 - 146]. By its versatility, the reactive modification of PET has been applied to recycled post-consumer PET with the intent of producing extrusion foamed products. Xanthos et. al. [147 - 148] showed the improvement of foamability of the recycled PET by rheological modification with pyromellitic dianhydride (PMDA) in a comparative study of unmodified and modified (post-consumer) PET using physical blowing agents. They delineated the rheological characteristics of the modified PET as higher MFI, higher melt viscosity, early shear thinning with high shear sensitivity, and higher extrudate swell ratio as compared to the unmodified PET. They could obtain low density foams (< 0.5 g/cc) with the modified PET, while foams with density below 0.7 g/cc could not be achieved with the unmodified polymer.

Japon et al. [149] used a tetraepoxide to reactively modify recycled PET. They obtained branched structures with broadened MWD, and highly increased elongational viscosity. Their application of the modified PET to extrusion foaming with PBA resulted in foams with high density of 0.85 ~ 1.0 g/cc.

Xanthos et. al. [150] showed that glycidyl functionalized additives such as a diepoxide and an ethylene-glycidyl methacrylate (E-GMA) copolymer reacted readily with the functional groups of PET, acting as chain extending/branching agents. The modified product showed promising rheological characteristics for low density foaming. They also found that the diepoxide had higher reactivity than E-GMA and could be used at much lower concentrations to produce resins with the desired characteristics.

Dhavalikar and Xanthos [151] performed a comparative study of four different multi-epoxides, N,N’-bis[3(carbo-2’,3’ epoxypropoxy)phenyl] pyromellitimide (BGPM), glycidyl ether of bisphenol-A (DGEBA), triglycidyl isocyanurate (TGIC) and triglycidyl glycerol (TGG), as PET rheology modifiers. They found that TGIC and BGPM were most efficient in the modification reactions; however, a limitation of BGPM was that it was not commercially available. As shown in their subsequent work [116], the melt modified PET by TGIC showed an increase in relaxation time and broadening of relaxation times distribution with corresponding effects on MW and MWD.

A compherensive comparison study was published by Xanthos et. al. [94]. Low molecular weight multifunctional anhydrides and epoxides were evaluated as rheological modifiers for PET by reactive extrusion under controlled conditions. The dianhydrides, used in the study, were: PMDA and 3,3’,4,4’-benzophenone tetracarboxylic anhydride (BTDA). The multi-epoxides were BGPM, TGIC and tetraglycidyl diamino diphenyl methane (TGDDM). Correlations of die pressure with extrudate swell and melt flow index with melt strength by off-line testing showed that the most reactive modifiers were PMDA, TGDDM, and TGIC.

Crystallinity in MCFs of semicrystalline polymers also plays a role and should be considered [114]. It thus appears that the specific morphological characteristics of MCFs have a great influence on their mechanical properties, both at low and high strain rates, and that the cell size, among other microstructural parameters, plays an important role in the determination of these properties.

Solubility of CO_2, Ar and N_2 in different polymer systems has been obtained using the in-line method developed in a single screw extruder. Carbon dioxide has the highest solubility in PET, nitrogen has the lowest, and argon somewhere in between [115]. This trend is consistent with literature results obtained for the same systems under temperatures below the polymer T_g [33]. Solubility decreases with increasing temperature for both CO_2 and Ar.

Hirai et al., produced modified PET foam with density as low as 0.3 g/cm^3 by extrusion using a saturated hydrocarbon foaming agent. The modified PET had increased the viscosity and the tensile strength of the PET melt. The modified PET foams showed higher glass transition temperature and the thermal cracking temperature compared with those with the unmodified PET [34]. Baldwin et al. investigated the effects of four major processing variables (gas saturation time, gas saturation pressure, foaming time, and foaming temperature) on the microcell nucleation processes of amorphous and semicrystalline PET. They found that the cell density of PET increased with increasing gas saturation time and pressure, the foaming time had a relatively weak effect on the cell nucleation, and the foaming temperature near the glass transition influenced the density of the amorphous PET [142 - 143].

Guan et al. developed a new method to microcellularly process a PET sheet with a general hydraulic press above PET’s crystallization temperature and below its melting temperature within the time of a few minutes [6]. The low melt strength, low shear and elongational viscosities of conventional PET prevents from being easily foaming. Sorrentino et al. produced high-molecular-weight PET foams, where chain extension of polymers was used, by the pressure quench method with N_2, CO_2, and their 80/20 mixture as blowing agents and correlated to the thermal, rheological, volumetric, and gas sorption properties [7].

2.8 Polycaprolactone–poly(dimethylsiloxane) Block Copolymers

Copolymers containing poly(dimethylsiloxane) (PDMS) have received considerable attention due to their unique properties, such as very low glass transition temperature, low surface energy, low solubility parameter, and physiological inertness [76 - 77]. Some of their specialty applications are in the fields of biomaterials [85] and surfactants [72]. Though a variety of synthetic routes have been used to prepare PDMS containing copolymers, less work has been done preparing block copolymers of dimethyl siloxane and α,β-unsaturated esters [121]. This is mainly attributed to the limited copolymerizabilities of both monomers in anionic polymerization [21].

Polysiloxane possesses a unique combination of many interesting properties, especially a high surface activity and an extremely low solubility parameter. These properties lead to the thermodynamic incompatibility of polysiloxanes with almost all other organic polymer systems. One method to overcome this difficulty is by blending the siloxane-containing copolymers with organic polymers since siloxane homopolymers can only provide a temporary surface modification to the blend. In siloxane-containing multiphase, block, segmented, or graft copolymers, siloxane segments migrate to the air–polymer surface; but the organic segments in the copolymers act as an ‘‘anchoring group’’ for the siloxane blocks, and then the permanent surface modification can be achieved. For this purpose, the syntheses of siloxane-containing copolymers have been studied for about 30 years. In 1964, Jarvis Fox, and Zisman reported first that the siloxane-containing copolymers were blended with the base resin to modify the surface [73]. After that, the siloxane copolymers are used as surface-modifying agents in some important applications, such as paints, coatings, and textile fiber.

Polydimethylsiloxane (PDMS) containing copolymers display an unusual combination of properties. These include extremely low glass-transition temperatures of -120 °C; very low surface energies; good thermal, UV, and flame resistance; water repellancy; hydrolytic stability; and biocompatibility. If the organic blocks and PDMS segments are properly designed it is possible to use silicone copolymers as surface-modifying additives for organic polymers. In such systems organic blocks interact with the base resin through entanglements, cocrystallization, or electrostatic interaction, such as hydrogen bonding, whereas silicone segments provide the surface modification.

When such additives are used in small amounts, the change in surface properties is achieved without influencing the bulk morphology or properties of the base resin. In view of the preceding observations, it is possible to optimize the application-specific surface properties of a polymeric system by proper choice of a base resin with the desired bulk properties and a surface modifying silicone copolymer and blending them before processing.

Their large molar volumes and low cohesive energy densities result at exceptionally low surface tensions, surface energies, and solubility parameters. Although PDMS is a good candidate for modification of other polymer surfaces and interfaces, it is highly immiscible with almost all other organic polymer systems; and if PDMS is used by blending, it does not function properly. An effective way to increase compatibilities is certainly to form their copolymer systems; different block, segmented, and graft copolymers of siloxanes are already known. ABA-type siloxane-containing block copolymer, α,ω-dihydroxy polycaprolactone–poly(dimethylsiloxane), (PCL-PDMS-PCL) triblock copolymer were used in this work.

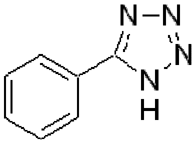
3. EXPERIMENTAL PART

3.1 Chemicals Used

3.1.1 Poly(ethylene terephthalate) (PET)

Poly(ethylene terephthalate) was obtained from AKSOY Plastik Company (Octal GP01). Its intrinsic viscosity is 0.81 dL/g at 30 °C in Ph/TCE 60:40 (ASTM D4603-03). Weight of 100 pieces chips are 1.63 g. Melting point of PET is 247 °C.

3.1.2 5-Phenyl-1H-tetrazole (5-PT)



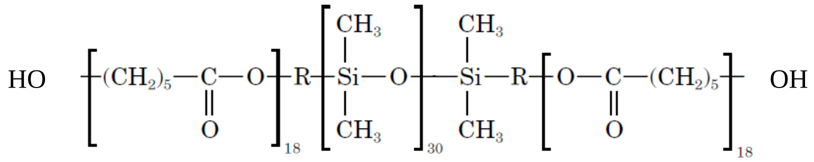
5-Phenyltetrazole was used as an exothermic non-ammonia foaming agent for the engineering plastic, PET. It has the appearance of white to off-white crystalline powder. Melting point of 5-PT is 216 °C, and 5-PT decomposes around 250 °C. Tetrazole is one of a class of organic heterocyclic compounds containing a five-membered diunsaturated ring structure composed of four nitrogen atoms and one carbon atom. Its molecular formula is $C_7H_6N_4$.

Decomposition of 5-PT occurs in 2 first order steps; tale pink intermediate then decomposition. Blowing gas yield is 200 cm^3/g (98 % N_2 and 2 % NH_3), molecular weight of 5-PT is 146.15, heat of combustion of 5-PT is -3907 kJ/mol.

5-PT is the product of Sigma Aldrich company with a 99 % purification, was used without any purification procedure in this study.

3.1.3 Polycaprolactone–poly(dimethylsiloxane), (PCL-PDMS-PCL)

TEGOMER® H-Si 6440 P is a wax type siloxane co-polyester which is in pellet form. It is the product of Evonik Goldschmidt GmbH with a 99 % purification, was used without any purification procedure in this study.



$$HO-\left[(CH_2)_5-\overset{O}{\overset{\|}{C}}-O\right]_{18}-R-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_{30}-\underset{CH_3}{\overset{CH_3}{Si}}-R-\left[O-\overset{O}{\overset{\|}{C}}-(CH_2)_5\right]_{18}-OH$$

The α,ω-dihydroxy polycaprolactone–poly(dimethylsiloxane) (PCL-PDMS-PCL) triblock copolymer used was a commercial product of Evonik (Tegomer H-Si 6440) with Mn = 6500 (+/- 600); $Mw_{(PDMS)}$ = 3000; and PCL endblocks = 2000 g/mol. It was dried at 70 °C in a vacuum oven for 48 h before use. This copolymer shortened as PDMS in results and discussion section.

3.1.4 Paraffin liquid (medium)

Paraffin Liquid (Medium) or mineral oil, is a mixture of heavier alkanes. It has a density of around 0.8 g/cm^3. It was used to wet the surface of the polyester granules and to occur mixing with dust form of ingredients of the process.

3.2 Equipments Used

3.2.1 Vacuum Oven

In vacuum oven, the heat-treating process takes place inside a vessel that is airtight. The entire heat-treating process can take place under vacuum with the help of vacuum pump. The direct contact between the load and the heatable and removable thermoshelves in the chamber of the vacuum oven ensures rapid and uniform temperature control without the loss of heat.

Figure 3.1: Vacuum oven instrument and vacuum desiccator.

Digital electronic vacuum, temperature, pressure control. Memmert VO 500 model vacuum oven was used at 130 °C, five hours according to ISO 1133-1 to remove the moisture from polyester raw material.

3.2.2 Melt flow index device (MFI)

Melt flow index (MFI) is a value that consists of melt flow rate (MFR) and melt volume rate (MVR) values. It is a measure of the ease of flow of the melt of a thermoplastic polymer. MFR is the weight of flowed sample in a certain time (g / 10 min) MVR is the volume of flowed sample in a certain time (cm^3 / 10 min) under 2.16 kg load. HAAKE Melt Flow MT was used to measure MFR and MVR values of sample (Figure 3.2).

Figure 3.2: “Melt flow index” MFI device.

3.2.3 Hydraulic hot press

Qualitest MHM100 model Hydraulic Molding Test Press was used for compression molding of PET foam samples. This instrument has a maximum temperature of 300 °C, and maximum pressure of 250 bar. It has the capacity of 10 tons.

Figure 3.3: Temperature control panel and pressure gauge of hydraulic hot press instrument.

The machine is convenient for preparing samples as they ensure uniform process and save time.

Figure 3.4: Hydraulic hot press machine.

3.2.4 Hydraulic cold press

Qualitest MPM100 model Hydraulic Molding Test Press was used for compression molding of PET foam samples. This instrument has a water cooling system, and maximum pressure of 250 bar. The press works under hydraulic system, working fast and steadily.

3.2.5 Mechanical test device

To obtain flexural properties of polyester foams, mechanical test was made by using Zwick Roell ProLine testing machine. Three-point bending flexural tests of samples were measured using ASTM D790-10 and ISO 178 represent classical characterization methods for rigid and semi-rigid plastics. Maximum weight capacity, pre-load is 2 N, and maximum speed of the device is 1mm/min.

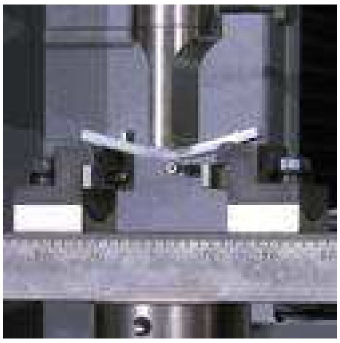


Figure 3.5 : Three-point bending mode flexural test instrument.

Typical test results include the flexural E-modulus, stress at 3.5 % elongation and strains at yield point and at specimen break. The results of the flexure test show in particular material behavior near the surface of the specimen. The deflections measured are approximately four times greater than the extensions recorded in the tensile test.

3.2.6 Contact Angle Measurement Instrument

CAM 200 (KSV) model Attension THETA Optical Tensiometer with a video camera based fully computer controlled contact angle meter was used for contact angle measurements of PET foam samples at room temperature. Digital video camera 60 fps (frames per second) including zoom and camera stage. One touch manual dispenser movement (OTD), and software trigger to enable automatic contact angle measurement versus time or versus location with only one push of the dispenser level per drop. Software trigger takes measurement after predefined time delay after push of the dispenser lever. Operation sequence: create drop - push - move sample - create. Automatic single liquid dispenser for dynamic contact angle and surface tension measurements by pendant drop method. PC control of dispensing operation.

Hamilton 1 mL syringe C205A with tubing and dispensing gauge 22 needle C209-30. Dispensing resolution 0.1 µL manual single liquid dispenser syringe.

Basic frame with back light and control electronics and an interface for extra light source and temperature control options. Software for determination of: 1) Contact angle by sessile/raising drop method with automatic base line detection, 2) Surface/interfacial tension by pendant/raising drop method, surface tension and contact angle by liquid meniscus method, 3) Image fittings, polynomial, tangent, circular fit, Young-Laplace, including autobaseline algorithm, 4) Surface free energy.

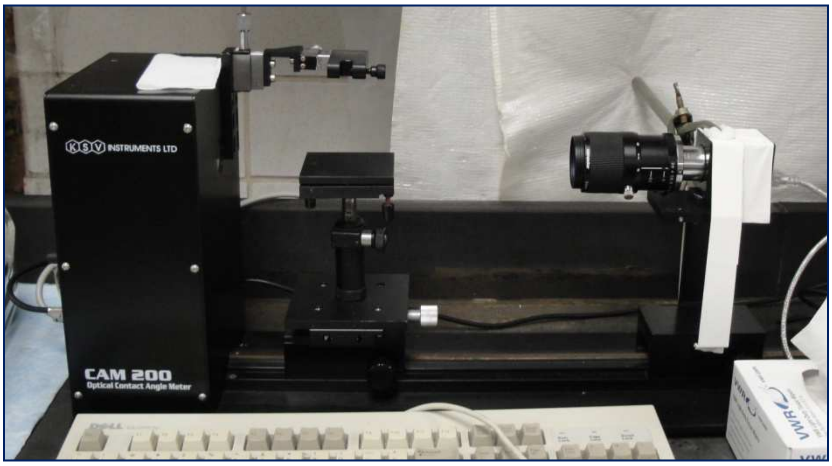


Figure 3.6 : Contact angle measurement instrument.

The contact angle is the angle at which a liquid/vapor interface meets a solid surface. The equilibrium contact angle is specific for any given system and is determined by the interactions across the three interfaces. A single system of drop/medium (air/surface) has a spectrum of contact angles ranging from the so-called advancing (maximal) contact angle to the receding (minimal) contact angle.

3.2.7 Calliper

The precision of length measurements may be increased by using a device that uses a sliding vernier scale. The instrument has a main scale (in millimetres) and a sliding vernier scale. This instrument may be used to measure outer dimensions of objects (using the main jaws), inside dimensions (using the smaller jaws at the top), and depths (using the stem).

Vernier callipers can be used to determine dimensions of ≥30 mm on plastics and rubbers (ISO 178, ISO 4648, ASTM D 3767, DIN 53534), and dimensions ≥10 mm of rigid cellular plastics (DIN 53570).

3.2.8 Thermogravimetric (TGA) and differential thermal (DTA) analysis instrument

Thermogravimetric analysis (TGA) is a thermal analysis technique which measures the weight change in a material as a function of temperature and time, in a controlled environment.

Figure 3.7 : Linseis STA PT 1750 model TGA/DTA combined instrument.

This can be very useful to investigate the thermal stability of a material, or to investigate its behavior in different atmospheres (e.g. inert or oxidizing). It is suitable for use with all types of solid materials, including organic or inorganic materials [118].

Differential thermal analysis (DTA) is a calorimetric technique, recording the temperature and heat flow associated with thermal transitions in a material. This enables phase transitions to be determined (e.g. melting point, glass transition temperature, crystallization etc.).

Linseis STA PT 1750 model TGA/DTA combined instrument was used for the thermal characterization. (Figure 3.7) The measurements were applied via aluminum crucibles within 20 mg sample weight, at the speed of 10 °C/min in nitrogen atmosphere. The instrument measurement temperature range starts from -150 up to 1750 °C.

3.3 Experimental Procedure

3.3.1 Preparation of the mixture

All PET pellets were dried in vacuum oven at 130 °C for 5 hours, after they have taken out from there, they were put into vacuum desiccator.

In all experiments, approximately 0.1 g Paraffin were used because of the size differences between granules of PET and powders of CBA. 5-phenyl tetrazole powder was stuck on the surface of PET granules, but sometimes they were cumulated when exposed to paraffin.

Figure 3.8 : Charging of the mold within PET mixture into hot press instrument.

A commercial-grade PET granules were mixed with 5-PT and PDMS, and were placed in a 120 X 120 X 2 mm^3 mold between Teflon sheets in 1.0 mm thicknesses, and were loaded into a hydraulic hot press in which the experimental conditions had adjusted before. Under heating and pressure, the foaming reagent 5-PT decomposes to produce nitrogen gas at elevated temperatures.

3.3.2 Production of cellular structure

Compression molding was used for processing of thermoplastic material, PET. Initially, PET was mixed with weighed amounts of CBA and PDMS filler. Then, the process was ready for the four main stages of compression molding process:

1) mold charging, 2) compressing, 3) cooling, and 4) part removal.

First, between the preheated hot platens in a hydraulic press was put the mold which was charged with material. Second, the mold was compressed to melt the material and flow to fill the cavity of the mold. Some of CBA may start decomposing during this process. Certain residence time is required to get homogeneous bubble size distribution. Third, the mold was cooled down to solidify the product. Fourth, the mold was decompressed, and the product was released. Amorphous structures of the products were observed owing to fast cooling procedure by Cold Press instrument.

3.3.2.1 Heating process in hydraulic hot press

Polymer foams were prepared by using hydraulic hot press instrument with the processing temperature and pressure in the ranges of 255 - 275 ^{o}C and 10 - 100 bar, respectively. The amount of 5-PT was around 0.10 % and 0.20 % (wt). The PCL-PDMS-PCL was added in between 0.050 % and 0.300 % (wt). Foaming time were taken from 6 to 22 minutes.

3.3.2.2 Cooling process in hydraulic cold press

Cooling period of molten product was maintained in hydraulic cold press instrument. Cold press instrument pressure adjustment was 50 Bar, and the total processing time was 5 minutes. Amorphous structure of product because of fast cooling by cold press instrument.

3.4 Tests and Analysis

The prepared closed cell PET foams were characterized morphologically, physically and mechanically in terms of contact angle measurement (ASTM D5946, ASTM D5725), apparent density calculation (ASTM D1622-08), cell density measurement and 3-point bending test (ASTM D790-10).

3.4.1 Melt flow index

The melt flow properties of the PET samples were determined by calculating the values of MFR and MVR. PET samples were dried at 130 ^{o}C, 5 hours in vacuum oven according to ASTM D1238 standard before the tests. The determination of the melt flow rate, MFR, measurements followed ISO 1133-1 with MVR test temperature at 280 °C under 2.16 kg load. The MFR and MVR measurements were done, and the MFR value was found as 86.29 g/10 min for PET.

3.4.2 Mechanical test

The three point bending mode flexural test provides values for the modulus of elasticity in bending E_f, flexural stress σ_f, flexural strain ε_f and the flexural stress-strain response of the material.

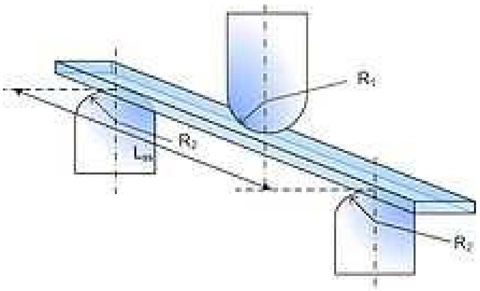


Figure 3.9 : The three point bending flexural test layout, loading.

The main advantage of a three point flexural test is the ease of the specimen preparation and testing. However, this method has also some disadvantages: the results of the testing method are sensitive to specimen and loading geometry and strain rate. From the measured stress, strain values; elastic modulus, maximum stress, and stress at break were calculated from the average of at least four (4) specimens tested.

To make a comparison for the mechanical improvements of PET foam samples, flexural properties of PET foams were considered, measured, and calculations were done. 1 mm/min test speed were used for the measurements.

A brittle material will deform reversibly to a small amount and then fracture. A ductile material will also deform reversibly up to a certain amount and then yield and flow under the applied force until it begins to harden under load and then fail. Up to the elastic limit, the material will return to its former shape and size when the force is removed. Beyond this point deformation is irreversible i.e. creep has occurred.

3.4.3 Contact angle analysis

If the molecules of a liquid are strongly attracted to the molecules of a solid (for example water on a strongly hydrophilic solid) then a drop of the liquid will completely spread out on the solid surface, corresponding to a contact angle of 0°. Less strongly hydrophilic solids will have a contact angle up to 90°. On many highly hydrophilic surfaces, water droplets will exhibit contact angles of 0° to 30°. If the solid surface is hydrophobic, the contact angle will be larger than 90°. On highly hydrophobic surfaces the surfaces have water contact angles as high as ~120° on low energy materials e.g. fluorinated surfaces (Figure 3.10).

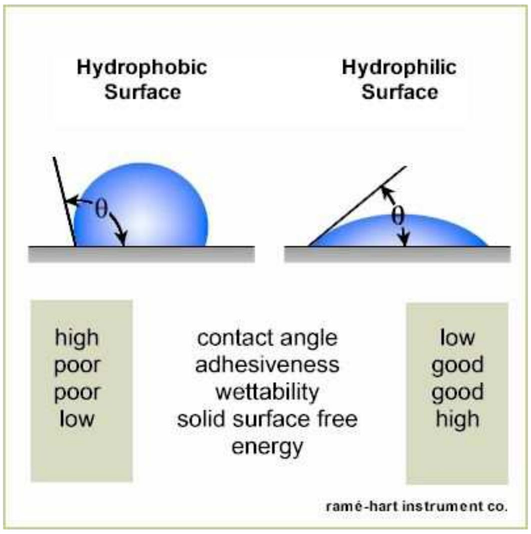


Figure 3.10 : Contact angle, hydrophobic and hydrophilic surfaces.

3.4.4 Bulk density analysis

Dimensional analysis(dimensions and volumes of samples) of PET foam samples were made with the Calliper. Vernier callipers was used to determine dimensions ≥10 mm of rigid cellular plastics (DIN 53570). Density measurements were achied with Calipper and Balance (mass of samples).

3.4.5 Cell density analysis

The pictures of PET foam samples were taken from Digital video camera 60 fps (frames per second) including zoom and camera stage. The diameters of bubbles measured with perfect screen ruler software programme. Conversation factors from the x and y scale (512 x 480) pixel to (5.883 x 5.506) mm are that x-scale factor is 0.01149, and y-scale factor is 0.01147 used.

The cell density analysis results were evaluated for the cell size distribution, and the number-average diameter d_n and the volume-average diameter d_v were calculated due to the equations 2.5 and 2.6 which are stated in section 2.4 properties of polymer foams.

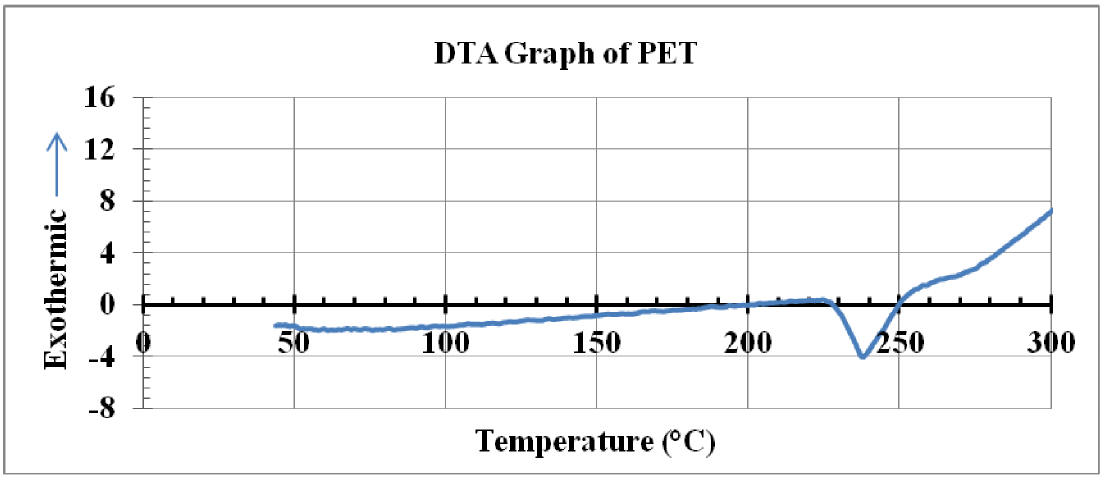
3.4.6 Thermogravimetric (TGA) and differential thermal (DTA) analysis

Linseis STA PT 1750 model TGA/DTA combined instrument was used for the thermal characterization. (Figure 3.7) The measurements were applied via aluminum crucibles within 20 mg sample weight, at the speed of 10 °/min in nitrogen or oxygen atmosphere. The instrument measurement temperature starts from room temperature to 300 ^{o}C.

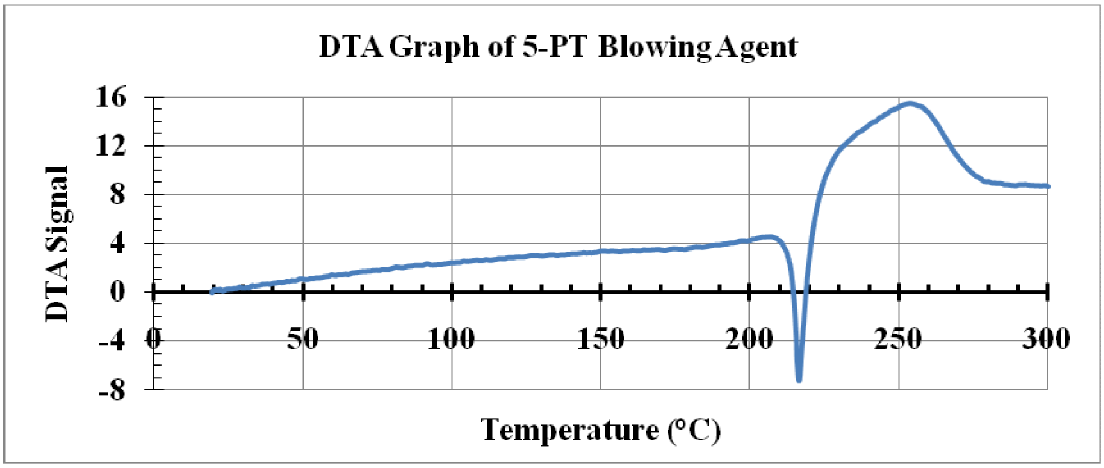
5-Phenyl tetrazole shows melting temperature at around 215 °C, and decomposes at around 250 °C. Nitrogen gas is liberated within the mass by thermal decomposition of 5-PT, the chemical blowing agent. Poly(ethylene terephthalate) shows melting range between 230 °C and 260 °C (Figure 3.11).

The measurements via thermogravimetric (TGA) and differential thermal (DTA) analyses showed that the temperature ranges of 5-PT and PET are overlapping with each other at around 250 °C (Figure 3.11). Therefore, 5-PT is suitable to work with PET.

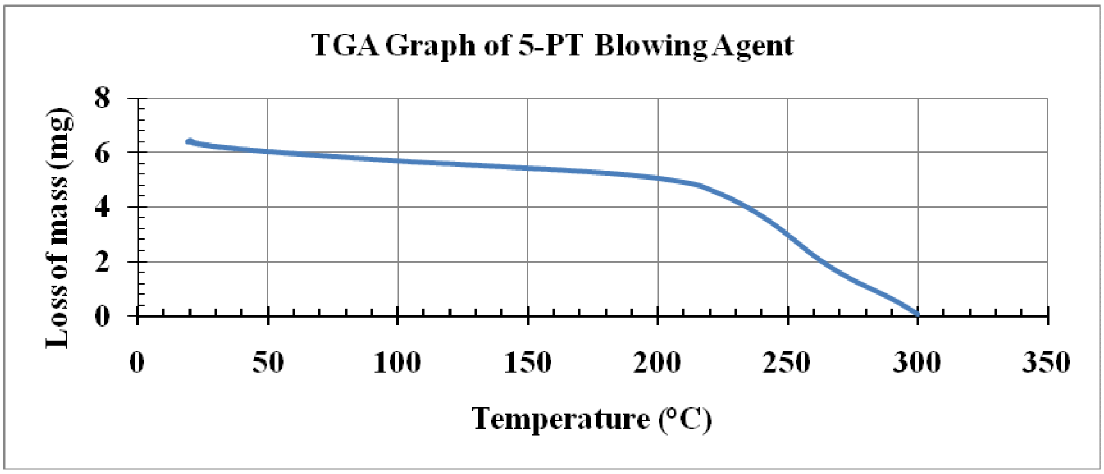
The thermal behaviour of 5-PT with increasing temperature was observed using a lab scale oven, with ranging temperatures between 200 °C and 300 °C. As stated in literature, decomposition occurs in two (2) first order steps; telltale pink intermediate then decomposition (Figure 3.12).



(a)



(b)



(c)

Figure 3.11 : Thermal analysis (TGA and DTA) graphs: (a)DTA graph of PET. (b)DTA graph of 5-PT blowing agent. (c)TGA graph of 5-PT blowing agent.

Figure 3.12 : Decomposition behaviour of 5-PT with increasing temperature.

Intermediate decomposition products (typical pink coloured) and residues of 5-PT are shown in Figure 3.12 at different temperature scales (220 °C, 230 °C, 240 °C, 250 °C, 260 °C, 270 °C, 280 °C).

The most commonly reported solid decomposition product of 5-PT is 3,5-diphenyl-1,2,4-triazole and the other solid decomposition products claimed are aminodiphenyltriazole and triphenyl-s-triazine.

4. RESULTS AND DISCUSSION

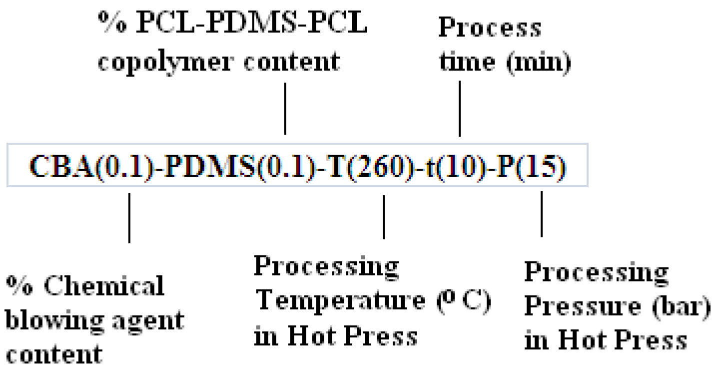
In this work, twenty samples with PCL-PDMS-PCL additive and seven samples without PCL-PDMS-PCL additive, totally twenty seven poly(ethylene terephthalate) (PET) foam samples were prepared with a chemical blowing agent and a poly(dimethyl siloxane) additive. The polymer foams were produced by compression molding, and they were structurally, morphologically, and mechanically characterized, respectively. During the production of PET foams, hydraulic hot and cold press instruments were used with respect to the compression molding process.

PET foam samples were produced based on process parameters that are processing temperature, processing pressure and foaming time in the ranges of 255 - 275 ^{o}C, 10 - 100 bar, and 6 - 22 minutes, respectively. The amount of 5-PT additive as chemical blowing agent was changed between 0.05 % and 0.25 % (wt) during the preparation of PET foam mixtures. PCL-PDMS-PCL copolymer as surface modifying agent was mixed with PET at low concentrations (0.050 % – 0.300 % by weight).

In the first stage of foaming process in hydraulic hot press, PET-additive mixture was kept for a period of time at certain temperature and pressure. Melt form of PET was obtained and PET foam samples were produced by decomposition of chemical blowing agent. In the second stage, the foamed products were cooled in hydraulic cold press under 50 bar pressure with constant cooling time of 5 minutes to produce PET foams in amorphous structure with the help of rapid cooling.

The prepared closed cell PET foams were characterized morphologically, physically and mechanically. The methods used in the characterization were given in ASTM standards as ASTM D5946 and ASTM D5725 for contact angle measurements, ASTM D1622-08 for foam density calculations, and ASTM D790-10 for three-point bending mode flexural tests.

Each sample description refers to a specific composition involving the components used in the preparation of the samples. An example of sample description is given below:



Where CBA: Chemical blowing agent content (wt %), PDMS: PCL-PDMS-PCL copolymer content (wt %), T: Processing Temperature in hot press (^{o}C), t: Processing time (min), P: Processing Pressure in hot press (bar).

Pre-works were done in order to determine the optimum compression molding conditions in hydraulic hot and cold presses.

4.1 The Optimization of Processing Conditions

Optimization experiments for PET foaming were carried out by using different temperatures, CBA and PDMS weight percentages, processing times and pressures to determine optimum conditions in hydraulic hot press for compression molding method. Homogeneous cell distribution was considered as a main driver for determining of the optimization conditions during the investigation of polyester foaming.

The weight optimization was one of the most challenging points. Decomposition of 5-PT at high temperatures generates nitrogen gase which causes volume expansion of the system inside of the mold. The amount of PET should be determined according to 5-PT decomposition effect and the size of the mold. In ordered to define the right amount of PET needs to be filled in the mold, several trials were performed. Finally, the weight of PET was optimized as 35 grams.

The surface deformation of Teflon sheets were another issue needs to be optimized. The quick closing of the hot press plates generates deformation on the Teflon sheets closing the bottom and upper surfaces of the mold. To eliminate this negative effect of the pressure on PET granules and having flat surfaces on the both end of the product, several different types of Teflon sheets with different thicknesses were used.

In addition, Teflon material does not have enough heat conductivity. During the initial experiments, 240 °C was used and it was not proper temperature. After having several trials, the optimum process temperature was optimized as 260 °C and the Teflon sheets thickness was selected as 1 mm to have flat surfaces and to provide convenient heat conduction into the sample.

The process time period optimization was another major issue. After having melted form of PET foam samples, a big cavity (center upwards) and a heterogeneous bubble distribution were observed inside of the product. To eliminate these obstacles, several different processing time periods were tried and finally, the process time period was optimized as 10 minutes.

At high temperatures, because of its residues (aminodiphenyl-triazole; 3,5-diphenyl-1,2,4-triazole; triphenyl-5-triazine), the chemical blowing agent, 5-PT, dark yellow colour to products. At low temperatures, because of inhomogenious heating and cooling period of the mold, mixed product structure morphology (crystallize and amorphous structures) was occurred. PET melted in mold but pink colour on the middle of the surfaces (up and down) of the product was observed. There were unmelted PET granules in the inner center of the mold, however all outer surfaces were in melted form. In the structure of the product, the bubbles were formed with big cell sizes at higher temperatures and longer processing times.

Consequently, the optimized conditions were determined as 260 °C processing temperature, under 15 bar pressure, 0.10 % CBA and 0.075 % PDMS with 10 minutes processing time in order to have homogeneous bubble size and distribution.

4.2 Density Analysis Results

4.2.1 Bulk density analysis results

The bulk density measurements of PET foam samples were done according to ASTM D1622-08 standard. The measurement of dimensions of the samples to calculate their volumes, a calliper compass was used. The mass of the samples was measured with the laboratory balance. The bulk densities of the samples were calculated with the mass of the sample divided by its volume.

The bulk density values of PET foam samples are changing between 0.945 g/cm^3 and 1.190 g/cm^3 with the average of +/- 0.06 standard deviation. These results show that high density foams were obtained.

The bulk density is changed with the certain parameters. The bulk density of PET foam samples were decreased with increasing processing time, increasing processing temperature, decreasing processing pressure and increasing amount of chemical blowing agent. The effect of foaming time on the bulk density of the PET foam samples can be seen in Table 4.1.

Table 4.1 : The average cell diameter and the bulk density analysis results of PET foam samples that are changing with processing time.

Time * (min)	Average cell diameter (mm)	Bulk density (g/cm^3)
6	0.24	1.165
10	0.27	1.115
12	0.36	1.100
14	0.39	0.990
22	0.44	0.945

* Constants: T = 260 °C, P =15 Bar, 5-PT = 0.10 %, PDMS = 0.075 %.

When the foaming time is more than 6 minutes, the bulk density decreases. This was because the longer the gas was allowed to diffuse into the cells, the larger the cell size was. When the foaming time increases, the average cell diameter also increases (Figure 4.1).

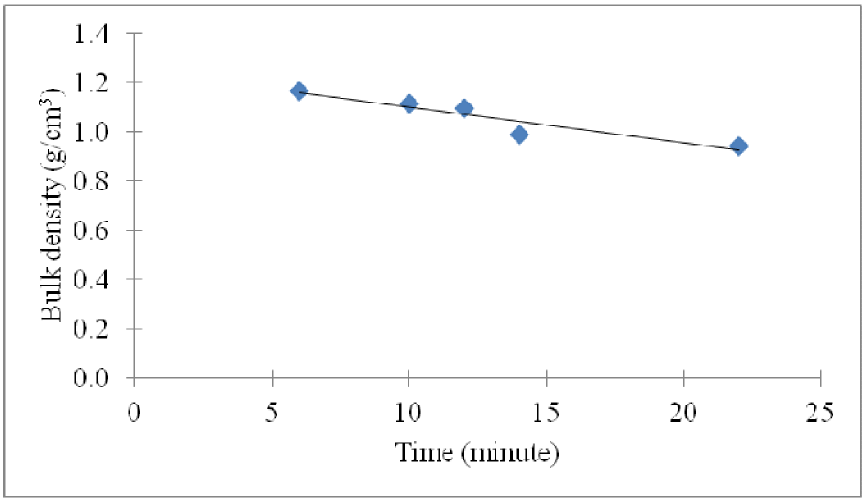


Figure 4.1 : Time versus bulk density graph of PET foam samples.

4.2.2 Cell density analysis results

The process variables of gas saturation time, gas saturation pressure, foaming time, and foaming temperature are important parameters for the explanation of cell nucleations in polymer foams. In this study, one of the results is having the transparent PET foam products with amorphous structure due to they were obtained by rapid cooling of the mold of the foam in cold press instrument. This result is in compliance with the result of the transparent foamed samples that are considered to be amorphous if they have less than 10 % crystallinity by mass, and semicrystalline if they have crystallinities greater than 10 %, when the crystallinities were measured using differential scanning calorimeter (DSC) analysis with a heat of fusion of 125.6 J/g at a scan rate of 20 °C/min [8].

Cell density measurements were carried out with magnified photos of the PET foam samples. Conversation factors that are used for the dimensional calculation of the photos are from x and y scale (512 x 480) pixel to (5.883 x 5.506) mm are that x-scale factor is 0.0114905, and y-scale factor is 0.0114714, which were used to calculate the cell size and the cell density of the PET foam samples.

Cell density analysis graphs of PET foam samples are also presented on the basis with 0.2 mm diameter range versus number of cells with the sample codes (Appendix A.4).

Table 4.2 : The cell density and cell size dispersity ratio analysis of PET foam samples.

Sample ID	Cell density (cells/cm^3)	Cell size dispersity ratio (d_v/d_n)
CBA(0.10)-PDMS(0)-T(260)-t(10)-P(15)	4350	0.99
CBA(0.10)-PDMS(0.050)-T(260)-t(10)-P(15)	3280	1.03
CBA(0.10)-PDMS(0.075)-T(260)-t(10)-P(15)	3270	1.12
CBA(0.10)-PDMS(0.100)-T(260)-t(10)-P(15)	2660	0.90
CBA(0.10)-PDMS(0.125)-T(260)-t(10)-P(15)	2640	1.02
CBA(0.10)-PDMS(0.150)-T(260)-t(10)-P(15)	2590	0.96
CBA(0.20)-PDMS(0)-T(260)-t(10)-P(15)	5960	0.96
CBA(0.20)-PDMS(0.075)-T(260)-t(10)-P(15)	3950	1.01
CBA(0.20)-PDMS(0.100)-T(260)-t(10)-P(15)	2930	0.92
CBA(0.20)-PDMS(0.200)-T(260)-t(10)-P(15)	2160	0.90
CBA(0.20)-PDMS(0.300)-T(260)-t(10)-P(15)	1820	0.91

Cell density analysis results were used to calculate the number average diameter and the volume average diameters by using the equations 2.5 and 2.6 given in section 2.4.4, respectively. The cell density and the cell size dispersity ratio (d_v / d_n) of PET foam samples were given in Table 4.2. The cell density analysis were resulted in between 1740 cells/cm^3 and 6220 cells/cm^3 having +/-25 cells/cm^3 deviations and, these results prove that conventional foams, in which foam structures with a cell density less than 10^6 cells/cm^3, were produced.

The ratio of d_v / d_n represents a useful tool for evaluating cell size dispersity, similar to the molecular weight polydispersity used in polymer chemistry to characterize molecular weight distribution. The cell size dispersity ratios of PET foam samples are calculated, and found to be between 0.90 and 1.12 (Table 4.2). When a cell size dispersity ratio close to 1 (e.g., below 1.25) indicates a statistically normal distribution or a monodisperse distribution.

Table 4.3 : The average cell size and density analysis results of cellular PET samples changing with process variables in terms of temperature and 5-PT % content.

Temperature * (°C)	Avg. cell diameter (mm)	Bulk density (g/cm^3)	Cell density (cells/cm^3)
250	0	1.310	0
260	0.27	1.115	3270
265	0.30	1.110	2440
270	0.37	1.050	2130
275	0.48	0.950	1740

* Constants: P = 15 Bar, t = 10 min, 5-PT = 0.10 %, PDMS = 0.075 %.

5-PT * (%)	Avg. cell diameter (mm)	Bulk density (g/cm^3)	Cell density (cells/cm^3)
0.05	0	1.310	0
0.10	0.27	1.115	3270
0.15	0.32	1.010	3310
0.20	0.46	0.965	3950

* Constants: T = 260 °C, P =15 Bar, t = 10 min, PDMS = 0.075 %.

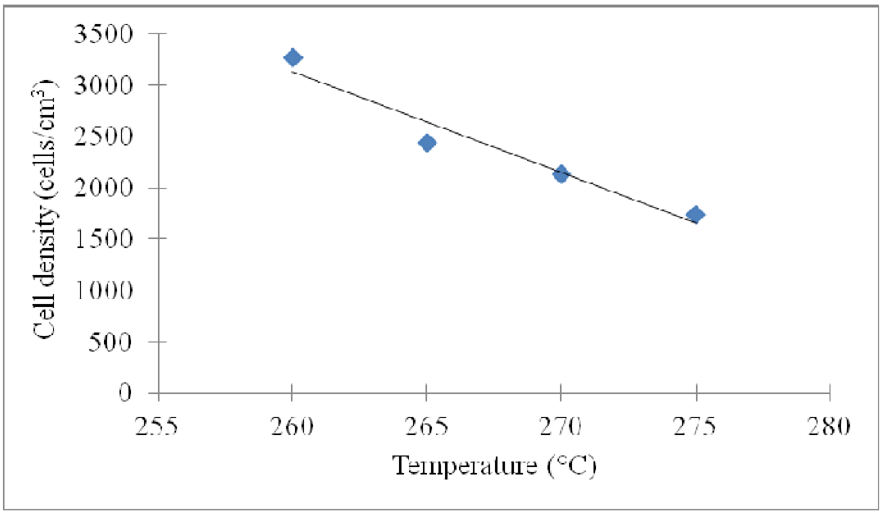


Figure 4.2 : Temperature versus cell density graph of PET foam samples.

The effect of foaming temperature on the mechanical properties occurred in the temperature range between 250 and 275 °C, as shown in Figure 4.2. When the foaming temperature was lower than 250 °C, there was no detectable cell structure.

One of the reasons was that the foaming reagent 5-PT could not decompose completely at lower temperature; hence, there was probably not enough gas necessary to form cellular PET.

Another reason was that at lower foaming temperatures, the PET matrix stiffness might have been sufficiently large enough to prevent nucleated cells from growing to detectable size, even though the allotted foaming time should have allowed all of the available gas to diffuse into the cells.

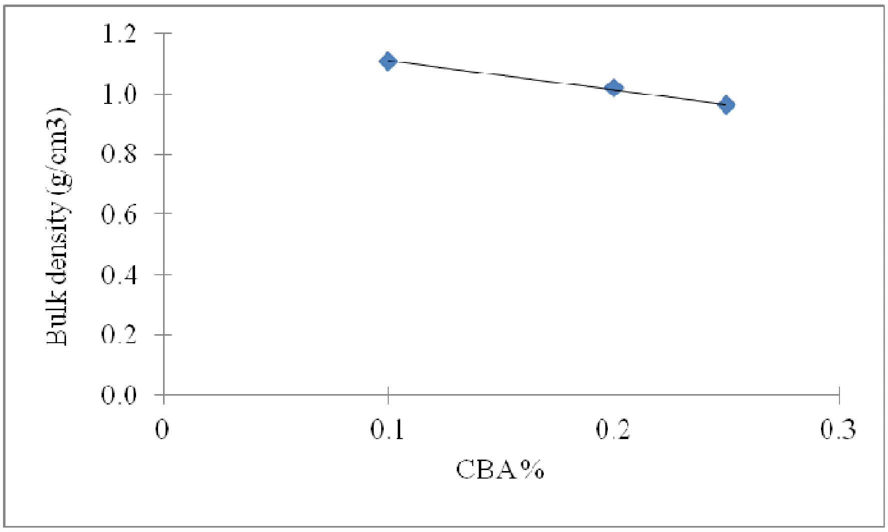


Figure 4.3 : CBA percentage versus bulk density graph of PET foam samples with 0.075 % PCL-PDMS-PCL.

The morphologies of the cells were strongly dependent on the foaming temperature, solubilization pressure and chemical blowing agent content.

Table 4.4 : The average cell size and density analysis results of cellular PET samples changing with process variable in terms of PCL-PDMS-PCL % content.

PDMS * (%)	Avg. cell diameter (mm)	Bulk density (g/cm^3)	Cell density (cells/cm^3)
0.050	0.25	1.120	3280
0.075	0.27	1.115	3270
0.100	0.28	1.100	2860
0.125	0.30	1.090	2640
0.150	0.32	0.965	2590

* Constants: T = 260 °C, P = 15 Bar, t = 10 min and 5-PT = 0.10 %

PDMS * (%)	Avg. cell diameter (mm)	Bulk density (g/cm^3)	Cell density (cells/cm^3)
0.100	0.32	1.070	2930
0.200	0.35	1.020	2160
0.300	0.38	0.980	1820

* Constants: T = 260 °C, P = 15 Bar, t = 10 min and 5-PT = 0.20 %

The experimental results of polycaprolactone block poly(dimethyl siloxane) (PCL-PDMS-PCL) additive on rigid PET foams are presented in Table 4.4. It was observed that when the PCL-PDMS-PCL additive was increased in the production of PET foams, the average cell size of the PET foams were increased.

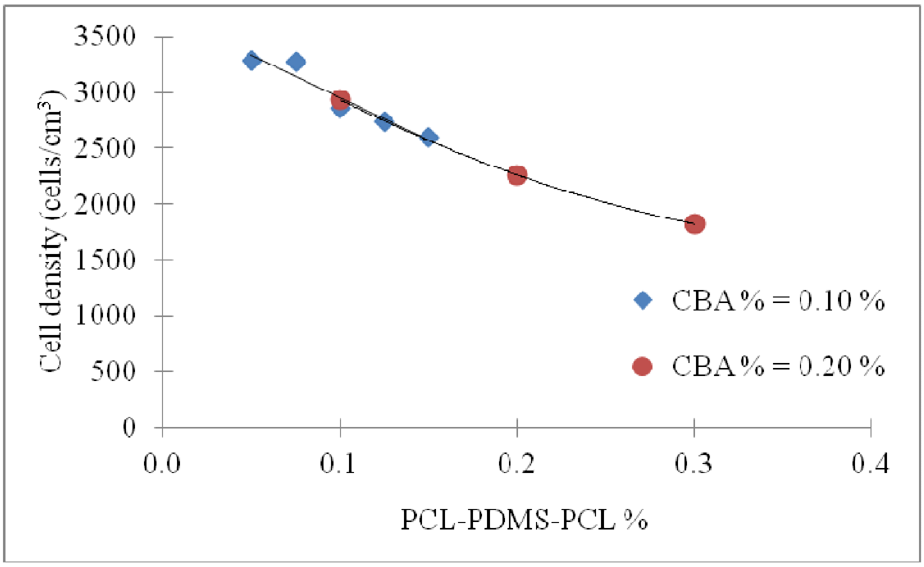


Figure 4.4 : PCL-PDMS-PCL weight percentage versus cell density graph of PET foam samples.

Table 4.5 : The average cell size and density analysis of PET foam samples without PCL-PDMS-PCL additive content.

Pressure * (Bar)	Avg. cell diameter (mm)	Bulk density (g/cm^3)	Cell density ($cells/cm^3$)
10	0.29	1.165	2650
15	0.27	1.115	4350
20	0.21	1.095	4980
100	Vague cell structure	0.960	Vague cell structure

* Constants: T = 260 °C, t = 10 min and 5-PT = 0.10 %.

5-PT (%) *	Avg. cell diameter (mm)	Density (g/cm^3)	Cell density ($cells/cm^3$)
0.10	0.18	1.110	4350
0.20	0.24	1.020	5960
0.25	0.27	0.965	6220

* Constants: T = 260 °C, P = 15 Bar, t = 10 min.

According to the Sanchez–Lacombe equation of state and experimental data from Sato et al., the solubility of nitrogen in polymers increases linearly with pressure up to about 25 MPa [16], [46]. Therefore, increasing foaming pressure actually increased the foaming gas concentration inside of PET, and the net result was a cell-size decrease (Table 4.5) and a cell density increase.

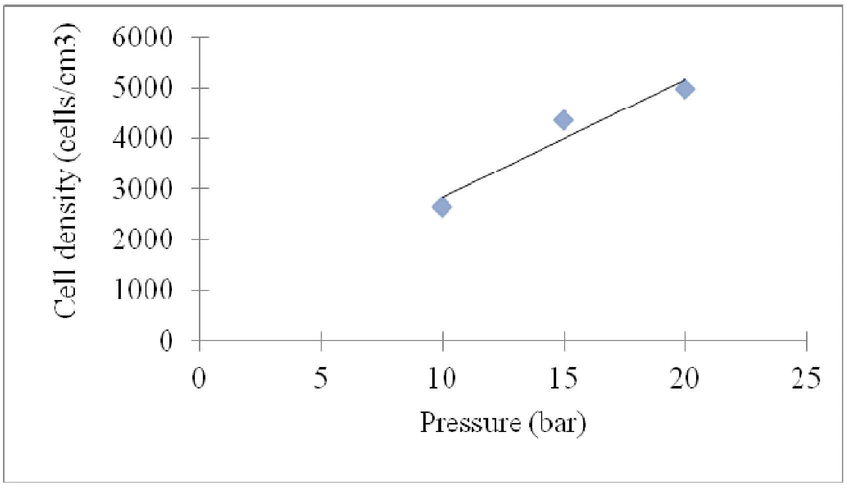


Figure 4.5 : Pressure versus cell density graph of PET foam samples.

Figure 4.5 shows the effect of foaming pressure on the mechanical properties of PET foam samples. The tensile strength first increased and then decreased with increasing foaming pressure, whereas the breaking extension increased all the way.

The larger the cell density was, the larger the breaking extension was. This explains why the breaking extension increased with increasing foaming pressure under our foaming pressure scope.

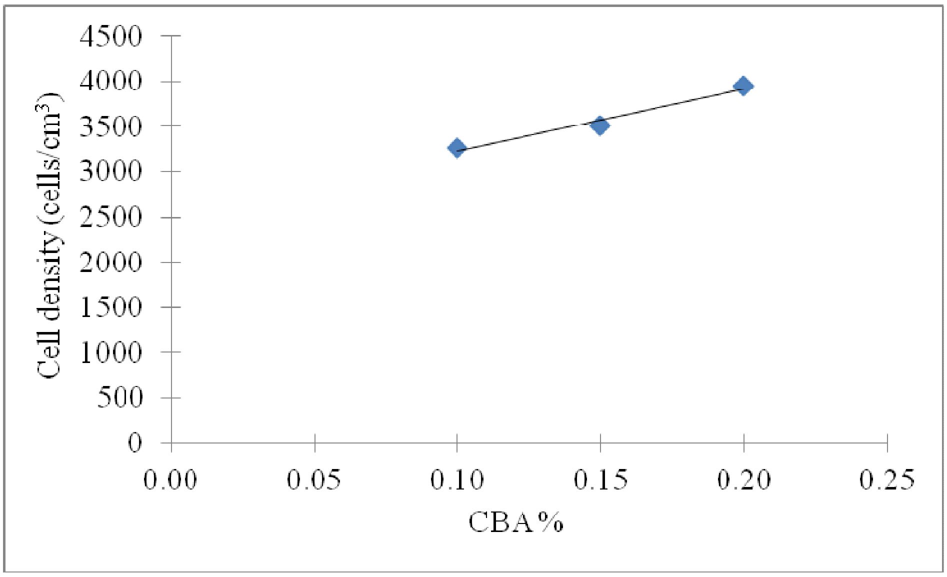


Figure 4.6 : CBA % versus cell density graph of PET foam samples.

We know that when the foaming pressure was smaller than 10 MPa, the PET sample showed no detectable cell structure. This means that the foaming pressure should exceed 10 MPa if one hopes to obtain microcellular PET foam.

4.3 Contact Angle Analysis Results

The contact angle measurements were done with CAM 200 KSV model Attension THETA Optical Tensiometer.

The results are presented as right angle and left angle in Table 4.6 according to whether its upper surface or lower surface.

Due to their outstanding properties, polysiloxanes have low surface energy (i.e. high surface activity), low glass transition temperature, high chain flexibility, and thermal and UV stability). These properties lead to the thermodynamic incompatibility of polysiloxanes with almost all other organic polymers. Using poly(dimethylsiloxane) (PDMS) copolymer systems overcome their incompatibility. In siloxane containing copolymers, siloxane segments migrate to the air-polymer surface, whilst the organic segments in the copolymer act as anchoring groups for the siloxane blocks, which can result in permanent surface modifications being achieved. The effects of polycaprolactone block poly(dimethyl siloxane) (PCL-PDMS-PCL) additive content on rigid PET foams were investigated mainly. In Table 4.6, there is an increase in contact angle values with increase of PCL-PDMS-PCL percentage because of the migration of PCL-PDMS-PCL molecules to air-polymer surface in PET foam samples.

Considering PET foam samples, the cell densities change with PCL-PDMS-PCL weight percentages which is given in Figure 4.4. PCL-PDMS-PCL addition to the PET foam samples gave increased toughness and better surface properties than those of the PET foam samples without PCL-PDMS-PCL additive under the same conditions. The brittleness of the PET foams was also decreased although PCL-PDMS-PCL was added at very low weight percentages during the preparation of the PET foam mixture.

Table 4.6 : Contact Angle measurement results of PET foam samples with the average of +/- 0.19 standard deviation.

Sample ID	Contact Angle (°)							
	Surface (Up)				Surface (Down)			
	0 (sec)		20 (sec)		0 (sec)		20 (sec)	
	R.A.[*]	L.A.[**]	R.A.	L.A.	R.A.	L.A.	R.A.	L.A.
CBA(0.10)-PDMS(0)-T(265)-t(10)-P(15)	93.4	93.0	87.7	88.8	80.3	80.5	74.4	74.8
CBA(0.20)-PDMS(0)-T(265)-t(10)-P(15)	92.9	92.2	75.6	74.5	84.1	82.4	60.5	60.2
CBA(0.10)-PDMS(0.050)-T(260)-t(10)-P(15)	95.6	94.7	84.5	85.5	91.4	93.7	89.3	89.4
CBA(0.10)-PDMS(0.075)-T(260)-t(10)-P(15)	96.2	96.7	92.7	92.5	90.4	90.6	88.0	87.3
CBA(0.10)-PDMS(0.100)-T(260)-t(10)-P(15)	96.8	97.2	91.8	92.3	95.8	94.6	83.7	84.9
CBA(0.10)-PDMS(0.125)-T(260)-t(10)-P(15)	99.7	99.9	93.7	95.3	96.9	96.2	85.9	86.8
CBA(0.10)-PDMS(0.150)-T(275)-t(10)-P(15)	97.3	96.1	92.3	92.0	88.1	87.2	86.4	86.3
CBA(0.20)-PDMS(0.200)-T(265)-t(10)-P(15)	102.2	100.5	97.0	97.0	99.4	96.7	90.2	90.3
CBA(0.20)-PDMS(0.300)-T(265)-t(10)-P(15)	107.4	106.6	99.8	100.4	98.03	98.9	91.4	92.3

[*]: R.A. = right angle, [**]: L.A. = left angle.

The experimental results show that the elastic modulus of PET foam increased as PCL-PDMS-PCL additive increased. Besides, as the foam density increased the elasticity of the foam was also increased. In general, crystallized products are more brittle than amorphous products. PCL-PDMS-PCL addition to the PET foam samples gave increased toughness and better surface properties than those of the PET foam samples without PCL-PDMS-PCL additive under the same conditions. The weight reduction of PET was achieved without sacrificing much of the mechanical properties by introducing cellular structure in thermoplastic materials. It was observed that the elastic modulus increased nonlinearly as the relative foam density and PCL-PDMS-PCL additive content increased.

There is an increase in contact angle measurement results with certain amount of PDMS percentage increasement because of the migration of PDMS molecules to air-polymer surface in PET foam samples. According to the calculated results, for the samples, which do not include PCL-PDMS-PCL, showed decrease in elongation at break. It was observed that when the PCL-PDMS-PCL additive content was increased, the elastic modulus of PET foams increased, and the elastic modulus was also increased as the relative foam density was increased.

4.4 Three-Point Bending Mode Flexural Test Results

To obtain flexural properties of polyester foams, mechanical test was made by using Zwick Roell ProLine testing machine. Because the effects of PCL-PDMS-PCL additive give remarkable results in three-point bending mode flexural test, this test was applied to PET foam samples with the reference of ASTM D790-10 and ISO 178 standards. Elastic modulus, yield strength, tensile strength, breaking strength, strain of break, and toughness at break of PET foam samples were obtained from the four (4) samples averaged. The calculated results were given in Table 4.7. According to these values, for the samples which do not include PDMS, decrease in elongation at break.

When the foaming time was more than 6 minutes, the tensile strength and elongation at break of cellular PET started to decrease. This was because the longer the gas was allowed to diffuse into the cells, the larger the cell size was. Therefore, the larger cell size (larger to some extent) decreased the tensile strength and breaking extension. In contrast to Baldwin et al. who found that the foaming time had a relatively weak influence on cell nucleation and cell growth for the amorphous and semicrystalline polyester because the gas in their samples was constant (meaning there was no effect on the mechanical properties), the foaming time in our experiment did have effects on the mechanical properties.

Table 4.7 : Three-point bending mechanical test results of PET foam samples with the average of +/- 0.09 standard deviation.

Sample ID	Elastic Modulus (MPa)	Yield Strength (MPa)	Tensile Strength (MPa)
CBA(0.10)-PDMS(0)-T(265)-t(10)-P(15)	2240	70.5	112.0
CBA(0.10)-PDMS(0.050)-T(260)-t(10)-P(15)	2370	76.2	116.4
CBA(0.10)-PDMS(0.075)-T(260)-t(10)-P(15)	2390	70.6	85.2
CBA(0.10)-PDMS(0.100)-T(260)-t(10)-P(15)	2560	77.1	102.1
CBA(0.10)-PDMS(0.125)-T(260)-t(10)-P(15)	2720	83.4	106.6
CBA(0.10)-PDMS(0.150)-T(265)-t(10)-P(15)	2830	79.5	79.7
CBA(0.20)-PDMS(0)-T(265)-t(10)-P(15)	2070	73.9	106.4
CBA(0.20)-PDMS(0.100)-T(260)-t(10)-P(15)	2140	70.5	75.1
CBA(0.20)-PDMS(0.200)-T(260)-t(10)-P(15)	2500	78.2	101.2
CBA(0.20)-PDMS(0.300)-T(260)-t(10)-P(15)	2890	86.3	106.0

Sample ID	Tensile Deflection (mm)	Breaking Strength (MPa)	Breaking Deflect. (mm)
CBA(0.10)-PDMS(0)-T(265)-t(10)-P(15)	10.0	-	-
CBA(0.10)-PDMS(0.050)-T(260)-t(10)-P(15)	8.6	-	-
CBA(0.10)-PDMS(0.075)-T(260)-t(10)-P(15)	5.5	-	-
CBA(0.10)-PDMS(0.100)-T(260)-t(10)-P(15)	7.0	-	-
CBA(0.10)-PDMS(0.125)-T(260)-t(10)-P(15)	6.6	104.0	6.0
CBA(0.10)-PDMS(0.150)-T(265)-t(10)-P(15)	3.5	81.6	4.4
CBA(0.20)-PDMS(0)-T(265)-t(10)-P(15)	8.1	-	-
CBA(0.20)-PDMS(0.100)-T(260)-t(10)-P(15)	4.0	64.4	4.7
CBA(0.20)-PDMS(0.200)-T(260)-t(10)-P(15)	6.6	118.0	7.6
CBA(0.20)-PDMS(0.300)-T(260)-t(10)-P(15)	6.2	-	-

It was observed that the elastic modulus increased as the relative foam density increased (Figure 4.7), and when the PDMS additive content increased (Figure 4.8) the elastic modulus is also increased. The optimum value of the PDMS additive content is 0.075 %.

Moreover, the mechanical properties of polyester foam samples were increased by adding PCL-PDMS-PCL additive. Besides, it was observed that crystallized products (produced with slow cooling of the product to room temperature instead of rapid cooling of the product in cold press) of the PET foam samples are more brittle than amorphous products.

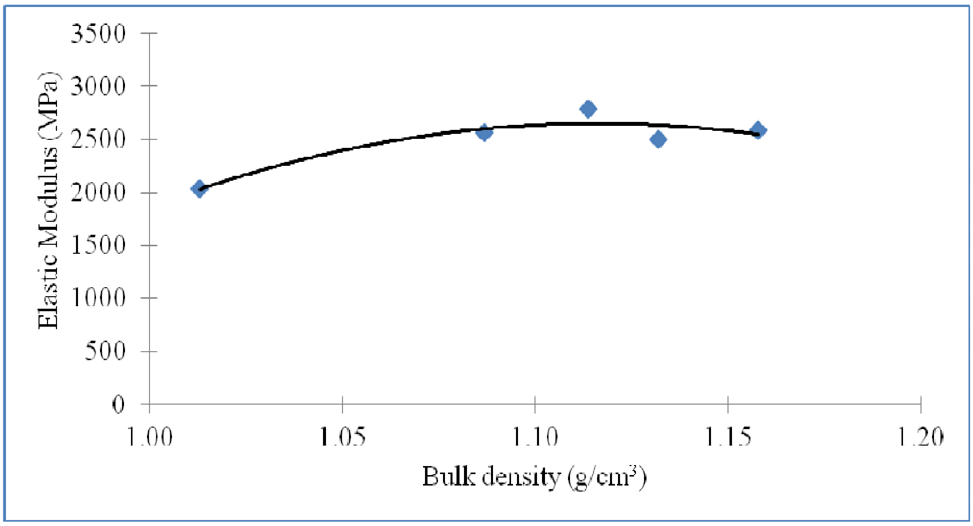


Figure 4.7 : Bulk density versus elastic modulus graph of PET foam samples with 0.075 % PCL-PDMS-PCL.

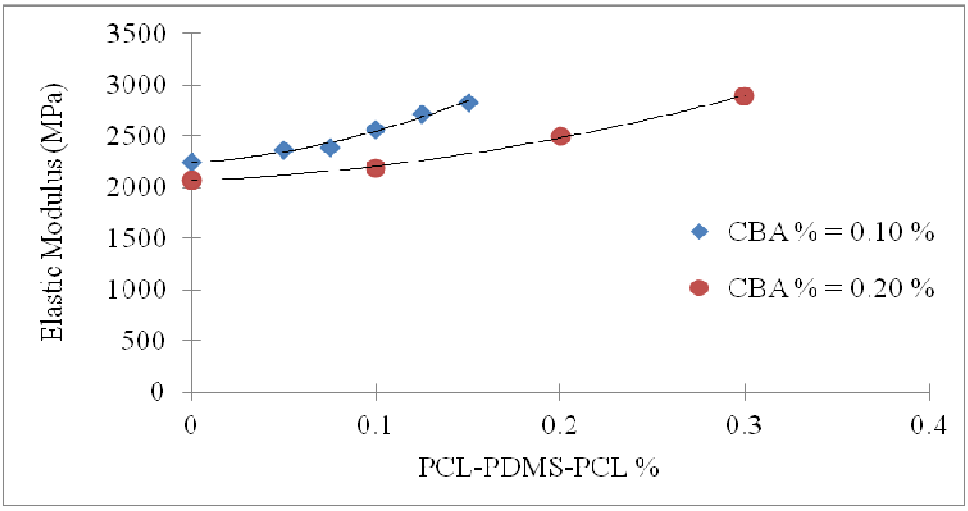


Figure 4.8 : PCL-PDMS-PCL % versus elastic modulus graph of PET foam samples.

Because of good homogeneous dispersion of CBA in polymer matrix, the mechanical properties resulted in meaningful values.

When the three-point bending mode flexural test results of PET foam samples are considered, CBA(0.20)-PDMS(0.300)-T(260)-t(10)-P(15) foam sample indicated the best mechanical properties among others due to its high elastic modulus value and its highest PCL-PDMS-PCL content.

5. CONCLUSION

In this study, closed cell PET foams were produced by compression molding technique. The effects of altering processing parameters and PCL-PDMS-PCL addition of PET foams were investigated with measurements of density, contact angle, cell density measurements and three-point bending mode flexural tests after the optimization trials for the production of a homogeneous foam was achieved.

The foaming of thermoplastic polymer was achieved by using a chemical blowing agent in compression molding process. Compression molding provided a convenient method for quick evaluation of material formulations instead of material intensive extrusion processing.

Poly(ethylene terephthalate), as one of the high-temperature-foaming polymers among other thermoplastic polymers, was foamed with an exothermic type of chemical blowing agent that is 5-phenyl-1H-tetrazole (5-PT).

The experimental results showed that the elastic modulus of PET foam increased with the addition of PCL-PDMS-PCL additive. Moreover, the elastic modulus of foam increased also with increasing foam density. In general, crystalline products are more brittle than amorphous products. PCL-PDMS-PCL addition to the foamed PET samples gave increased toughness and better surface properties than those of the foamed PET samples without PCL-PDMS-PCL additive under the same conditions. The weight reduction of PET was achieved without sacrificing much of the mechanical properties by introducing cellular structure in thermoplastic materials. It was observed that the elastic modulus increased nonlinearly as the relative foam density and PCL-PDMS-PCL additive content increased.

Polymer foams were prepared by using hydraulic hot press with the processing temperatures ranging from 250 to 275 ^{o}C and pressures ranging from 10 to 100 bars. The process time for foaming was about 6 to 14 minutes. Although the content of the chemical blowing agent was kept constant as 0.10 % and 0.20 % in PET foam samples. 0.10 % CBA content gave the best results in terms of homogeneous cell distribution and cell density. The PCL-PDMS-PCL was added in between 0.050 % and 0.300 % (wt %).

PET foam samples were prepared by compression molding technique in hot and cold presses in optimum conditions at 260 °C processing temperature, under 15 bar pressure, by adding 0.10 % CBA and 0.075 % PCL-PDMS-PCL with a processing time of 10 minutes. The 27 samples prepared and investigated from structural, morphological, mechanical and processing points of view. The contact angle measurements, density calculations, cell size analysis and three-point bending mode flexural tests were performed on the PET foam samples.

When the foaming time was more than 6 minutes, the tensile strength and elongation at break values of cellular PET started to decrease. When the foaming time was increased as long as possible, the gas diffused into the cells easily, so the cell size got larger. Therefore, the larger cell size (larger to some extent) decreased the tensile strength and elongation at break. The foaming time had a relatively strong influence on cell nucleation and cell growth for the amorphous and semicrystalline polyesters. Similar strong cell-size dependence on foaming time was reported for styrenic resins [123].

The solubility of nitrogen in polymers was increased linearly with pressure. Therefore, increasing foaming pressure actually increased the foaming gas concentration inside the PET. Due to this increment, cell-sizes decreased and cell densities increased. These results enhanced the elongation at break (ε_b %) values. This explains why the elongation at break increased with increasing foaming pressure under our foaming pressure scope. When the foaming pressure was lower than 10 MPa, the PET sample showed no detectable cell structure. This means that the foaming pressure should exceed 10 MPa if one hopes to obtain microcellular PET foam.

The effect of foaming temperature on the mechanical properties occurred in the temperature range between 250 and 275 °C. When the foaming temperature was lower than 250 °C, there was no detectable cell structure. The chosen foaming reagent 5-PT could not decompose completely at lower temperature; hence, there was probably inadequate gas necessary to form cellular PET. On the other hand, this temperature was low for PET foaming production. The PET matrix stiffness might have been sufficiently large enough to prevent nucleated cells from growing to detectable size, even though the allotted foaming time should have allowed all of the available gas to diffuse into the cells.

The cell density analysis results are found between 1740 cells/cm^3 and 6220 cells/cm^3, and these results proved that conventional foams, in which foam structures having cell densities less than 10^6 cells/cm^3, were produced.

The ratio of d_v / d_n represents a useful tool for evaluating cell size dispersity. A cell size dispersity ratio close to 1 (e.g., below 1.25) indicates a statistically normal distribution or a monodisperse distribution. The cell size dispersity ratios of PET foam samples were calculated, and found to be in between 0.90 and 1.12, accordingly.

High-density polymer foams with good mechanical properties were produced as the bulk density values are in between 0.945 g/cm^3 and 1.190 g/cm^3. These results show that high-density foams were formed.

The effects of polycaprolactone block poly(dimethyl siloxane) (PCL-PDMS-PCL) additive content on rigid PET foams were also investigated. There is an increasing trend in contact angle measurements with PDMS addition, due to the migration of PDMS segments to air-polymer surface in PET foam samples. According to the calculated results, the PCL-PDMS-PCL containing samples showed an increase in elongation at break with a decrease in brittleness. It was observed that the elastic modulus of PET foams increased with the PCL-PDMS-PCL addition.

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APPENDICES

APPENDIX A.1 : Exothermic Blowing Agents

APPENDIX A.2 : Properties of PET

APPENDIX A.3 : Bubble Analysis Photos of PET Foam Samples

APPENDIX A.4 : Cell Density Analysis Graphs of PET Foam Samples

APPENDIX A.5 : Water Contact Angle Measurement Photos of PET Foam Samples

APPENDIX A.1

Table A.1 : Processing Conditions for Common Exothermic Blowing Agents [57].

Grade	Chemical Compound	Gas composition	Solid Decomp. Product	Gas Yield (cc gas at STP)	Decomp. Temperature Range (°C)
AZ	Azodicarbonamide	N_2 65%	Urazol	220	205 - 215
		CO 24%	Biurea		
		CO_2 5%	Cyamelide		
		NH_3 5%	Cyanuric Acid		
RA	p-Toluene sulfonyl semicarbazide	N_2 55%	Ditolyl disulfide	140	228 - 235
		CO_2 37%	Ammonium p-toluene sulfonate		
		NH_3 3%			
		CO 2%			
OT	p,p'-Oxybis (benzenesulfonyl hydrazide)	N_2 91%	Nonpolar aromatic sulfur-containing polymer	125	158 - 160
		H_2O 9%			
TSH	p-Toluene sulfonyl hydrazide	N_2 n/a	Ditolyl disulfide	115	10 - 120
		H_2O n/a	p-Tolyl-p-toluene thiosulfinate		
			p-Toluenesulfinic acid hydrazine		
			p-Toluenesulfonyl hydrazide salt of p-toluene-sulfonic acid		

APPENDIX A.2

Table A.2 : Properties of PET

PROPERTY	PET DATA
Molecular formula	$(C_{10}H_8O_4)_n$
Density amorphous	1.370 g/cm^3
Density crystalline	1.455 g/cm^3
Young's modulus (E)	2800–3100 MPa
Tensile strength(σt)	55–75 MPa
Elastic limit	50–150%
Notch test	3.6 kJ/m^2
Glass temperature	75 °C
Melting point	260 °C
Vicat B	170 °C
Thermal conductivity	0.24 W/(m•K)
Linear expansion coefficient (α)	7×10^{-5}/K
Specific heat (c)	1.0 kJ/(kg•K)
Water absorption (ASTM)	0.16
Refractive Index	1.575
Price	0.5–1.25 €/kg

APPENDIX A.3

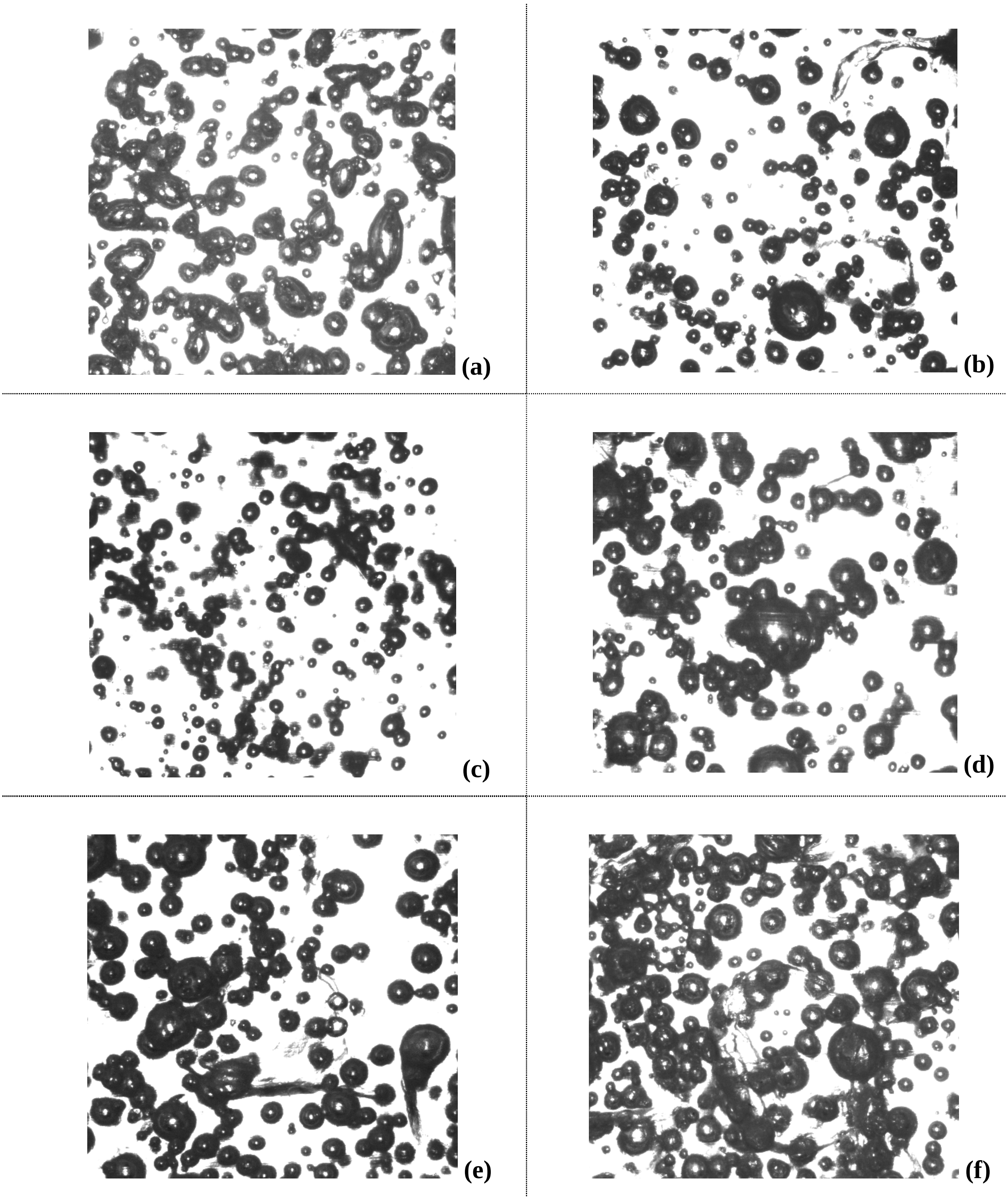

Figure A.3 : Bubble Analysis Photos of PET Foam Samples:
(a)CBA(0.20)-PDMS(0)-T(260)-t(10)-P(15).
(b)CBA(0.10)-PDMS(0)-T(260)-t(10)-P(15).
(c)CBA(0.10)-PDMS(0)-T(260)-t(10)-P(10).
(d)CBA(0.20)-PDMS(0)-T(260)-t(10)-P(10).
(e)CBA(0.15)-PDMS(0.150)-T(260)-t(10)-P(15).
(f)CBA(0.10)-PDMS(0.100)-T(260)-t(10)-P(15).

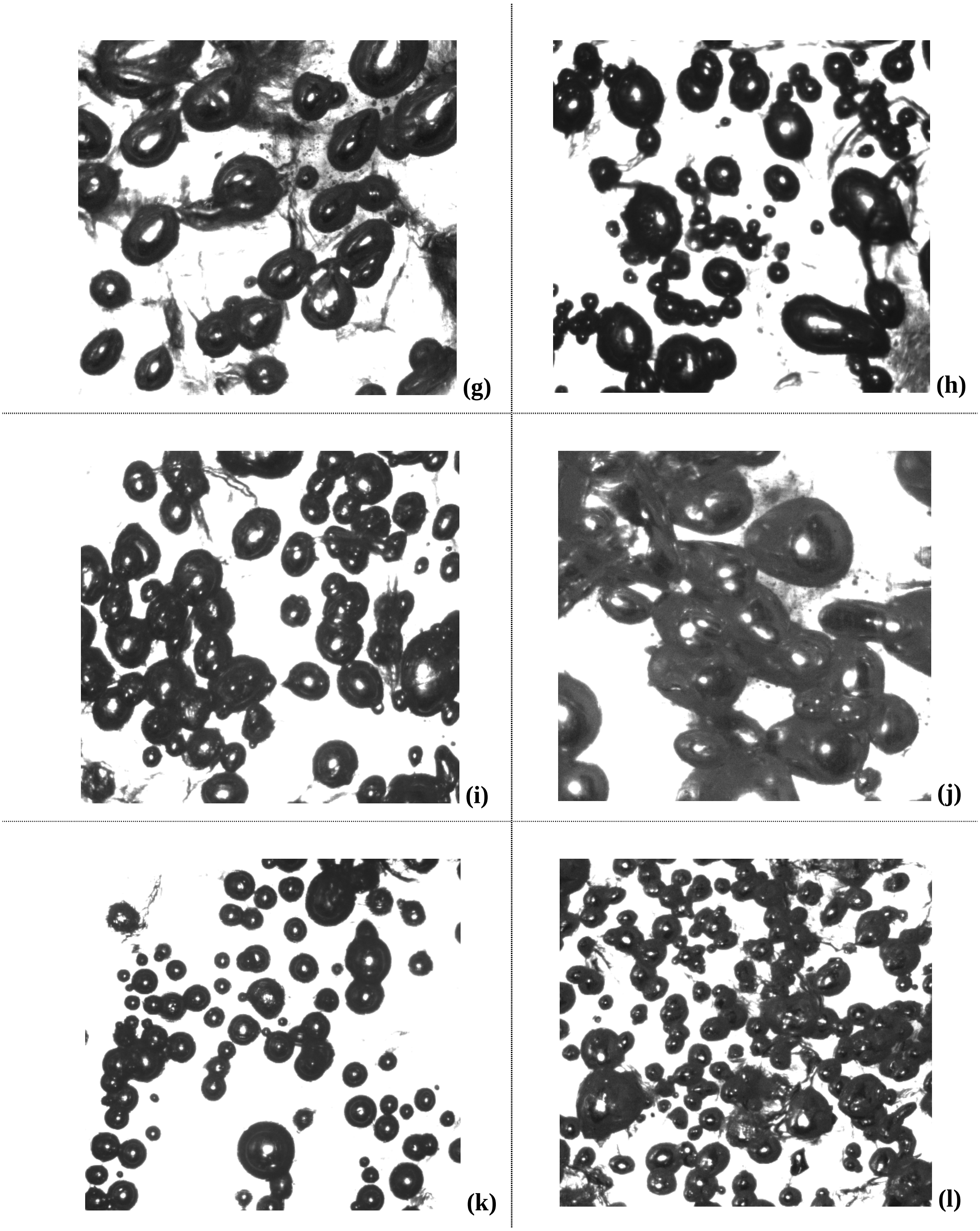

Figure A.3 (contd.) : Bubble Analysis Photos of PET Foam Samples:
(g)CBA(0.20)-PDMS(0.200)-T(265)-t(10)-P(15).
(h)CBA(0.20)-PDMS(0.200)-T(260)-t(10)-P(20).
(i)CBA(0.20)-PDMS(0.100)-T(260)-t(10)-P(20).
(j)CBA(0.20)-PDMS(0.300)-T(260)-t(10)-P(15).
(k)CBA(0.10)-PDMS(0.050)-T(260)-t(10)-P(15).
(l)CBA(0.10)-PDMS(0.050)-T(260)-t(22)-P(15).

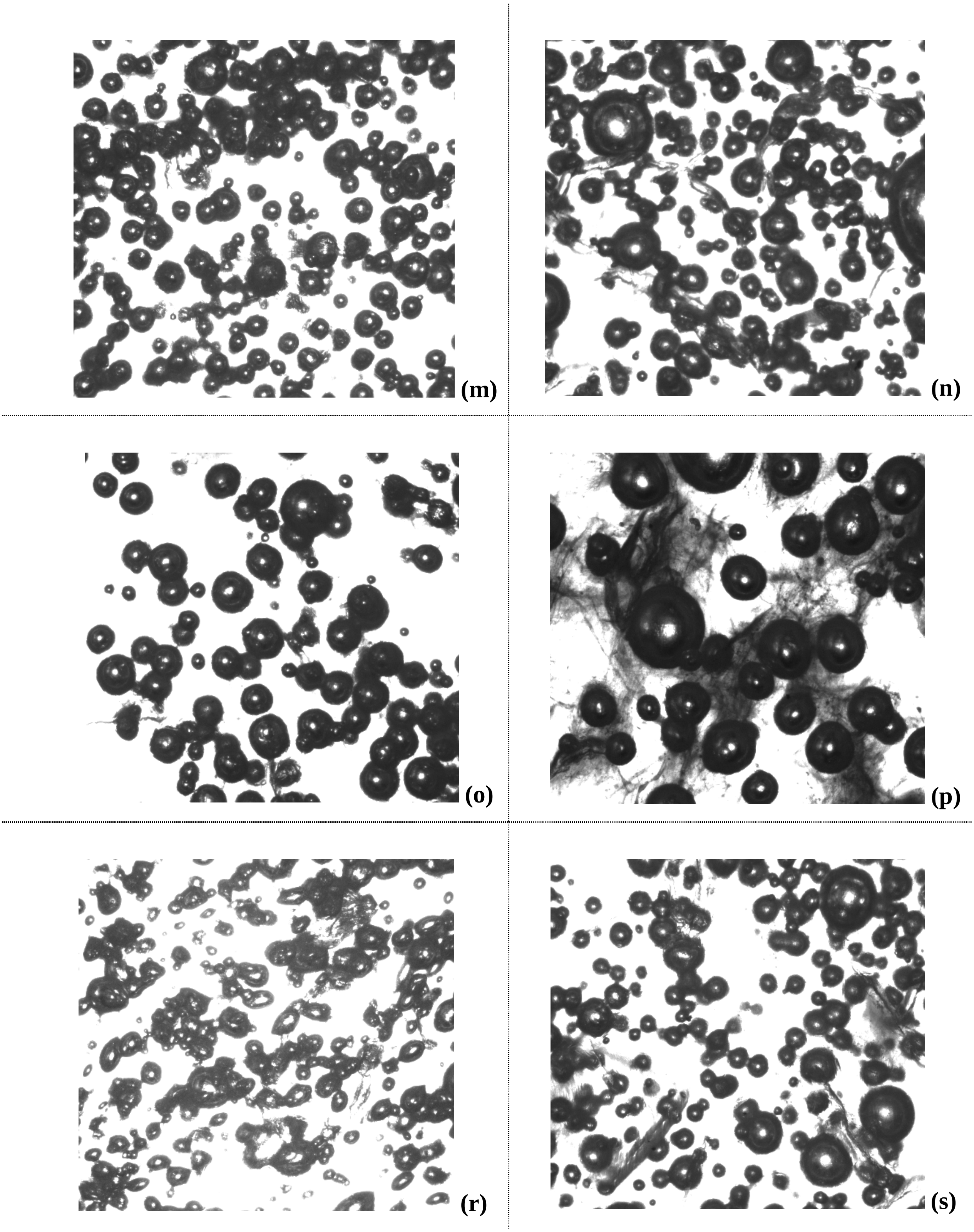

Figure A.3 (contd.) : Bubble Analysis Photos of PET Foam Samples:
(m)CBA(0.10)-PDMS(0.075)-T(260)-t(10)-P(15).
(n)CBA(0.10)-PDMS(0.100)-T(260)-t(10)-P(15).
(o)CBA(0.10)-PDMS(0.125)-T(260)-t(10)-P(15).
(p)CBA(0.10)-PDMS(0.150)-T(260)-t(10)-P(15).
(r)CBA(0.20)-PDMS(0)-T(260)-t(10)-P(15).
(s)CBA(0.10)-PDMS(0.100)-T(260)-t(10)-P(15).

APPENDIX A.4

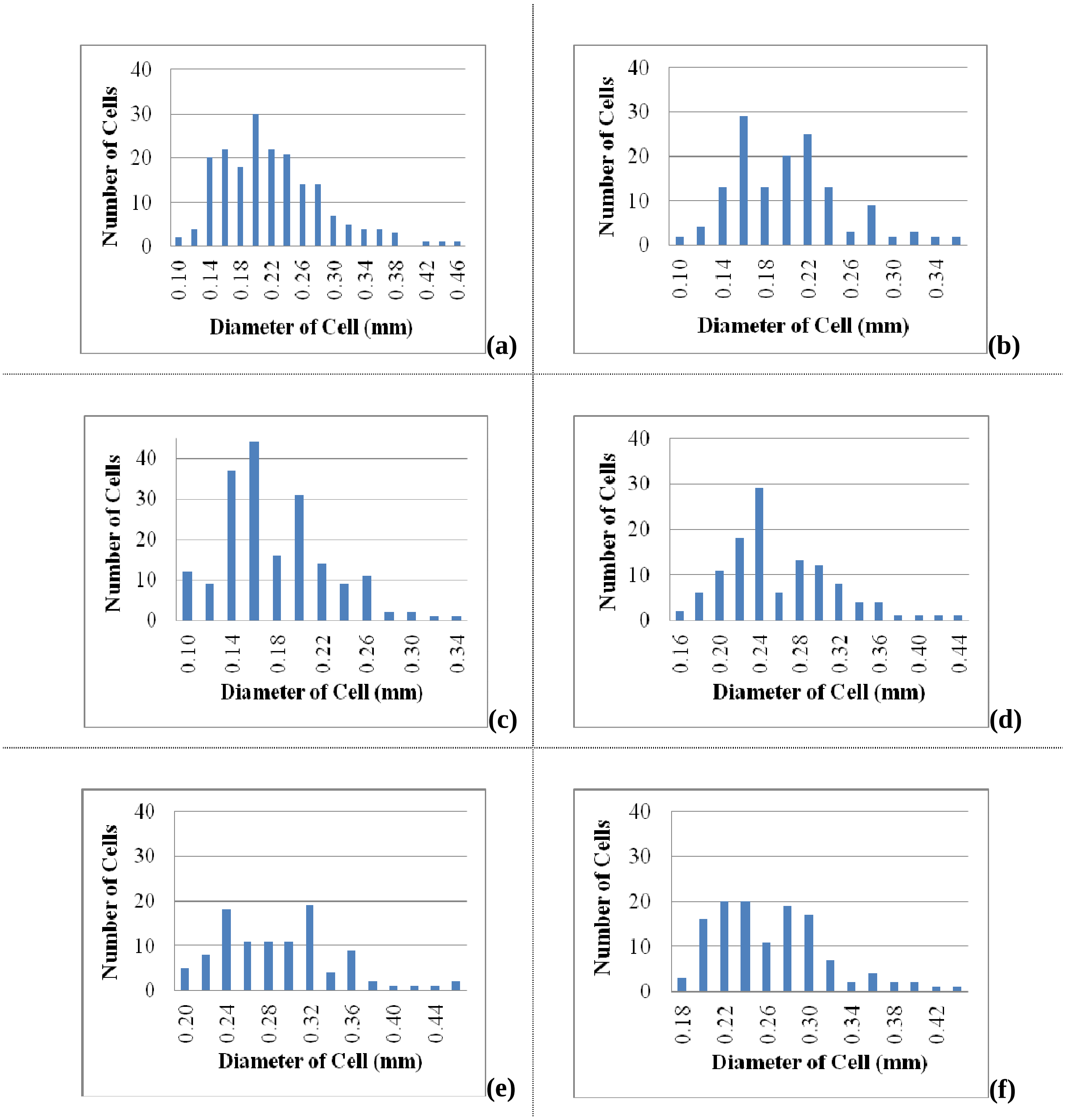

Figure A.4 : Cell density analysis graphs presented on the basis with 0.2 mm diameter range versus number of cells:

(a)CBA(0.20)-PDMS(0)-T(260)-t(10)-P(15).
(b)CBA(0.10)-PDMS(0)-T(260)-t(10)-P(15).
(c)CBA(0.10)-PDMS(0)-T(260)-t(10)-P(10).
(d)CBA(0.20)-PDMS(0)-T(260)-t(10)-P(10).
(e)CBA(0.15)-PDMS(0.150)-T(260)-t(10)-P(15).
(f)CBA(0.10)-PDMS(0.100)-T(260)-t(10)-P(15).

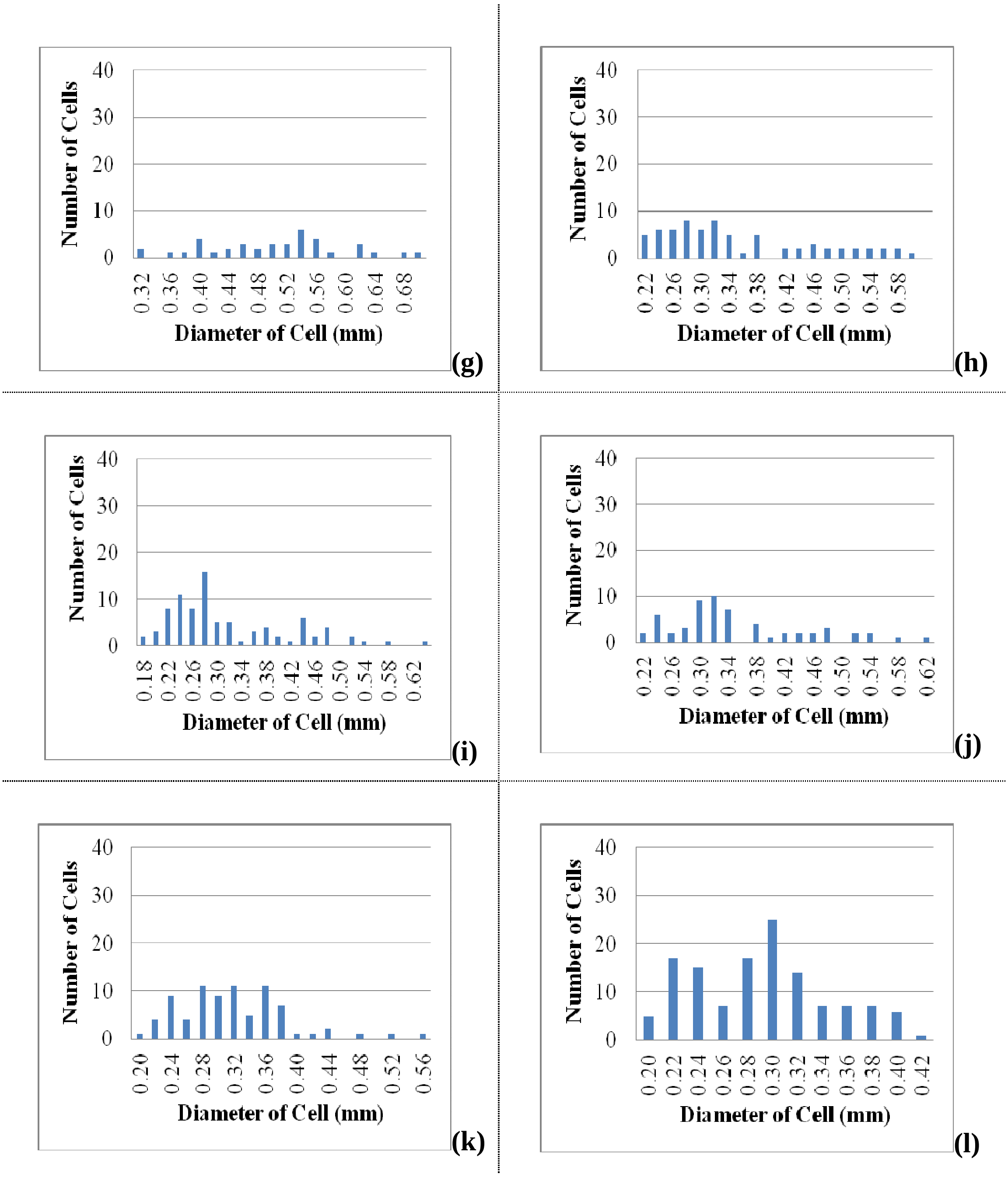

Figure A.4 (contd.) : Cell density analysis graphs presented on the basis with 0.2 mm diameter range versus number of cells:

(g)CBA(0.20)-PDMS(0.200)-T(260)-t(10)-P(15).
(h)CBA(0.20)-PDMS(0.200)-T(260)-t(10)-P(20).
(i)CBA(0.20)-PDMS(0.100)-T(260)-t(10)-P(20).
(j)CBA(0.20)-PDMS(0.300)-T(260)-t(10)-P(20).
(k)CBA(0.10)-PDMS(0.050)-T(260)-t(10)-P(15).
(l)CBA(0.10)-PDMS(0.050)-T(260)-t(22)-P(15).

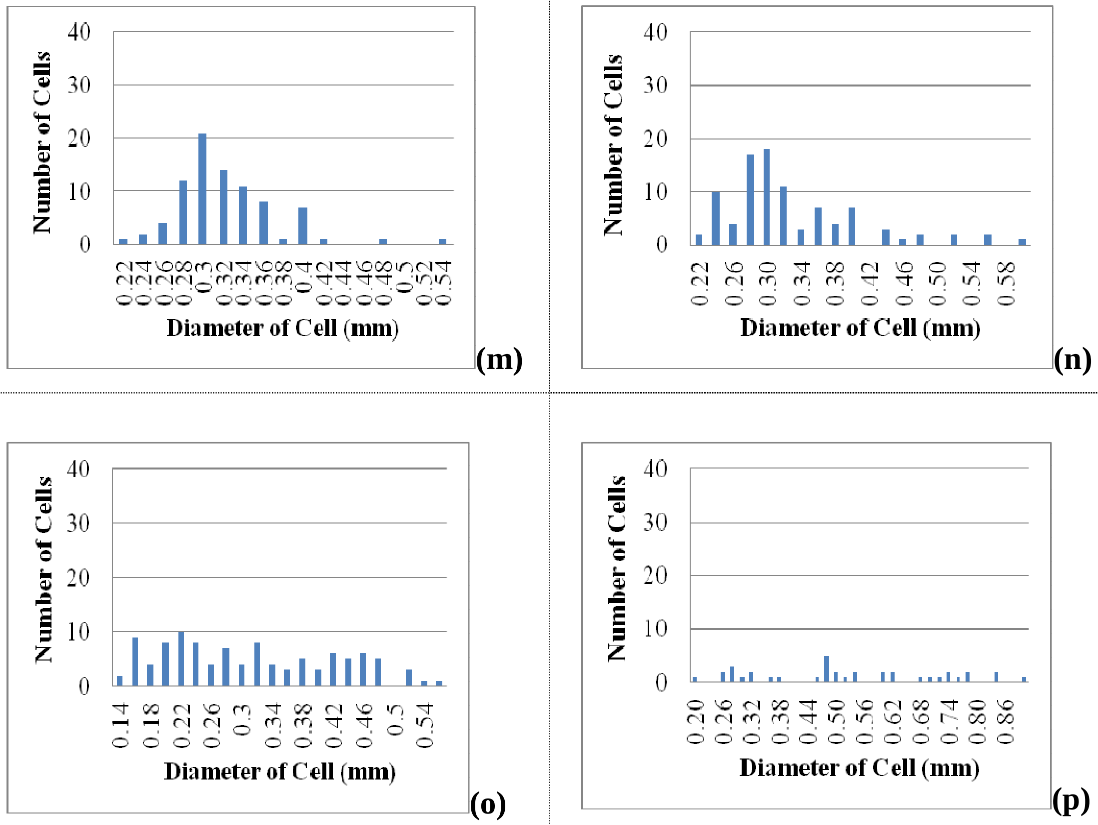

Figure A.4 (contd.) : Cell density analysis graphs presented on the basis with 0.2 mm diameter range versus number of cells:

(m)CBA(0.10)-PDMS(0.075)-T(260)-t(10)-P(15).
(n)CBA(0.10)-PDMS(0.100)-T(260)-t(10)-P(15).
(o)CBA(0.10)-PDMS(0.125)-T(260)-t(10)-P(15).
(p)CBA(0.10)-PDMS(0.150)-T(275)-t(10)-P(15).

APPENDIX A.5

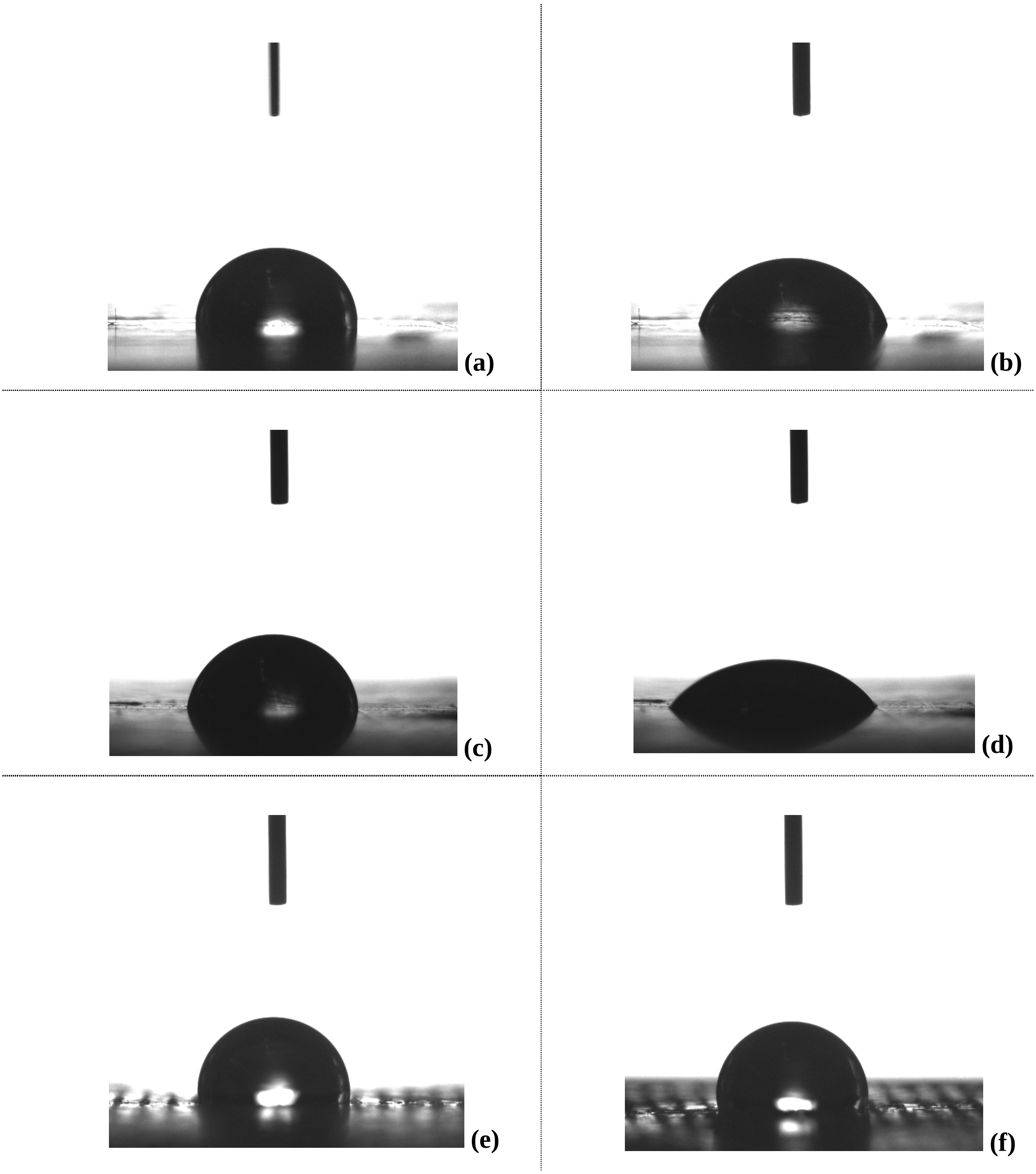

Figure A.5 : Water contact angle measurement photos of PET foam samples:
(a)Upper surface of CBA(0.20)-PDMS(0)-T(265)-t(10)-P(15) initially.
(b)Upper surface of CBA(0.20)-PDMS(0)-T(265)-t(10)-P(15) finally.
(c)Down surface of CBA(0.20)-PDMS(0)-T(265)-t(10)-P(15) initially.
(d)Down surface of CBA(0.20)-PDMS(0)-T(265)-t(10)-P(15) finally.
(e)Upper surface of CBA(0.20)-PDMS(0.200)-T(265)-t(10)-P(15).
(f)Down surface of CBA(0.20)-PDMS(0.200)-T(265)-t(10)-P(15).

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- **Çebişli H.B.**, Yalçınyuva T., Uyanık N., 2011: Production & Characterization of Modified PET Foam. *International Congress* - Eurofillers 2011, August 21-26, 2011 Dresden, Germany.