

CHARACTERIZATION OF BAROPLASTICS

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BAROPLASTİKLERİN KARAKTERİZASYONU

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FOREWORD

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Metallurgical & Material Engineer

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ABBREVIATIONS

TPE	: Thermoplastic elastomers
PS	: Polystyrene
PEHA	: Poly(ethyl hexyl acrylate)
PBA	: Poly(butyl acrylate)
PI	: Polyisoprene
PB	: Polybutadiene
MPG	: Monopropylene Glycol
SANS	: Small angle neutron scattering
UDOT	: Upper disorder-to-order temperature
CRP	: Controlled/'living' radical polymerization
ATRP	: Atom transfer radical polymerization
PDI	: Polydispersity
TEM	: Transmission electron microscopy
SPM	: Scanning probe microscopy
AFM	: Atomic force microscopy
DSC	: Differential scanning calorimeter
UCST	: Upper-critical solution temperature
DMA	: Dynamic mechanical analysis
THF	: Tetrahydrofuran
DCM	: Dichloromethane
NMR	: Nuclear magnetic resonance
GPC	: Gel permeation chromatography
SFE	: Surface Free Energy

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CHARACTERIZATION OF BAROPLASTICS

SUMMARY

Commercial plastics are classified into two common groups; thermoplastics and thermosets. For melt processing of thermoplastics that are more often used in our daily life, they are heated above melting temperature (T_m). This relatively high temperature, as the key factor of thermal processing, causes both high-energy consumption and substantial degradation of polymer. Moreover, it causes limited performance and recyclability of plastics. Recently, many studies were undergone on an alternative polymer that can be solution for the problems cited above. For this purpose specific block copolymers were synthesized using immiscible pair of a high T_g and a low T_g polymer. Although they present microphase separation under ambient conditions, they show pressure-induced miscibility that leads melt like flow at room temperature. Relied to this specification, they are named as “*Baroplastics*”.

As part of researches and developing studies on baroplastic materials, this project has the aim of investigating the behaviors of these well defined block copolymers in various topologies. Thermal, mechanical, morphological and surfacial measurements were performed to baroplastics, before and after processing under the pressure to probe their different properties such as glass transition temperature, elastic and flexural modulus and surface free energy.

As the featuring property of baroplastics is containing both ordered and disordered segments in a single structure after pressure application, observations were focused especially on this original morphological behavior. As immiscible segments of block copolymers, phase separated domains presents glass transition temperatures separately and nearly its constituents. However, mixed domains compose a single T_g relative to the ratio of its constituents likewise miscible segments of block copolymers. Consequently, for unprocessed baroplastic block copolymer, immiscible at room temperature and therefore having microphase separated structure, $T_{g,mix}$, the T_g of the mixed domain, doesn't exist however it appears after processing according to pressure induced miscibility. Thus, $T_{g,mix}$, as an indicator of processability, observed in the light of differential scanning calorimeter, DSC, and dynamic mechanical analyzer, DMA measurements.

Accordingly, effects of processing time and pressure were studied and optimum values were defined. The influences of baroplastics' molecular weight, topology and composition on processing were observed by processing tri-block and star-block copolymers in various compositions. Surface energy measurements were carried out in order to expose the change after processing. In addition, the effect of baroplastic materials' recycle number on morphology and surface were described and 100% recovery was achieved during the recycle of material. Moreover, the idea of infinite recyclable material was raised.

On the other hand, it was demonstrated that baroplastics could be processed at room temperature with standard equipment similarly used for commercial plastics.

BAROPLASTİKLERİN KARAKTERİZASYONU

ÖZET

Ticari plastikler termoplastik ve termoset olarak iki ana sınıfa ayrılırlar. Günlük yaşantımızda daha sık olarak kullandığımız termoplastikler, çoğunlukla eriyik şekillendirme yöntemleri kullanılarak ürün haline getirilirler ve bu amaçla kendilerine özgü erime sıcaklıklarının (T_m) üzerine ısıtılırlar. Sert ve yumuşak fazlardan oluşan termoplastik elastomerlerde bu ısıtma, yapıda fiziksel bir çapraz bağ gibi davranan kristal, sert fazların yumuşayarak malzemenin akmasına neden olur. Böylece madde kolaylıkla bir kalıptan geçirilerek ekstrüzyon yöntemi ile veya kalıp boşluğu doldurularak enjeksiyon yöntemi ile şekillendirilebilir. Bu ısıl şekillendirme yönteminde temel faktör olan yüksek sıcaklık, hem erişilebilmesi için bir enerji sarfiyatı yaratır, hem de malzemenin fiziki veya kimyasal olarak bozulmasına neden olur. Özellikle endüstride plastiklerin özelliklerini iyileştirici olarak kullanılan plastifiyanlar, kaydırıcılar, stabilizatörler ve renklendiriciler gibi birçok yardımcı maddeler yüksek sıcaklığa tekrar ısıtıldığında malzemenin kalitesinin düşmesine yol açar ve bu nedenle malzemenin geri dönüşümünün de sınırlı kalmasına neden olur.

Altmış yıl kadar kısa bir mazisi olmasına rağmen plastik ürünlerin tüketimi hızla artış göstermiş ve günümüzde dünya genelinde 250 milyon tona ulaşmıştır. Bu tüketimin öne çıkan sektörü ambalaj endüstrisi olduğundan genelde tek kullanımlık olan bu ürünlerin bertaraf edilmesi için üç yöntem kullanılmaktadır. Bunlar, yığılarak veya gömülerek doğaya bırakılması, yakılması veya geri dönüşümü. İlk iki yöntemin doğaya ciddi tehditler oluşturması nedeniyle, geri dönüşüm en iyi çözüm olsa da yukarıda belirtilen nedenlerle ancak toplam plastik atıklarının %3 gibi düşük bir oranı geri dönüştürülebilmektedir.

Yakın geçmişte termoplastiklerin eriyik şekillendirme işleminde şart olan yüksek sıcaklığın yarattığı bu geri dönüşümü sınırlama sorununa çözüm olabilecek alternatif bir polimer malzeme üzerinde birçok çalışma yapılmıştır. Bu doğrultuda yapılan araştırmalar kapsamında biri yüksek diğeri düşük camsı geçiş sıcaklığına (T_g) sahip oda sıcaklığında karışmaz ve belli bir sıkıştırma katsayısı aralığındaki polimer çifti kullanılarak özel blok kopolimerler sentezlenmiştir. Ortam koşullarında faz ayrımı göstermelerine rağmen basınç etkisiyle artan karışabilirlik özelliği sayesinde oda sıcaklığında uygulanan basınç ile eriyiğe benzer bir akma göstermişlerdir. Basınç altında soğuk şekillendirilebilen bu özel plastikler “*Baroplastik*” olarak adlandırılmışlardır.

Baroplastik malzemelerin geliştirilmesi üzerine yapılan çalışmalar kapsamında, bu projenin amacı, bu iyi tanımlanmış blok kopolimerlerin davranışlarını incelemektir. Bu amaç doğrultusunda sentezlenmiş olan baroplastik özellik gösteren polimer tozlarının çeşitli kalıplar kullanılarak farklı boyut ve geometrilerde şekillendirilmiş ve şekillendirme öncesi ve sonrası ısıl, mekanik, yapısal ve yüzey ölçümler gerçekleştirilerek örneğin camsı geçiş sıcaklığı, çekme ve bükme mukavemetleri, elastik modülleri, serbest yüzey enerjileri gibi özellikleri ve bu özelliklerin farklı parametreler altında değişimleri incelenmiştir.

Baroplastik özelliğın açıklanmasında karışabilirlik veya faz ayrımı kavramı önemli rol oynamaktadır. Baroplastiklerde, oda sıcaklığında düzenli olan faz yapısı, basınç uygulandıktan sonra yani şekillendirme sonrasında hem karışık hem ayrık faz içeren bir yapı haline gelmesi olduğundan, incelemeler bu yapısal davranış üzerine yoğunlaştırılmıştır. Bu morfolojik davranışın tespiti için ise sıkça kullanılan yöntemler optik ve termal yöntemlerdir.

Birbirleriyle olumsuz etkileşimleri ve düşük karışım entropileri nedeniyle farklı moleküller faz ayrımı göstererek benzer moleküller düzenli şekilde dizilim gösterirler. Bu dizilimlerin geometrisi faz diyagramlarına göre farklılık gösterir ki bu çalışmadaki baroplastiklerde çoğunlukla %50 civarında bir kompozisyon olduğundan faz diyagramına göre beklenen lamelar bir yapı Atomik Kuvvet Mikroskobu (AFM) ile de gözlemlenmiştir. Bu düzgün faz ayrımının basınç uygulanarak yapılan şekillendirme sonrası yapıdaki bazı bölgelerde bozulduğu ve bu bölgelerin karışık hale geldiği, böylece yapıda aynı anda hem düzenli hem karışık fazların varlığı görsel olarak ortaya koyulmuştur.

Bunun yanında ayrık fazlar kendilerini oluşturan polimerlerin camsı geçiş sıcaklıklarını yakın olarak ayrı ayrı korurken, karışık fazlar bu iki polimerin ağırlıksal oranına bağlı olarak yeni tek bir camsı geçiş sıcaklığı oluştururlar. Sonuçta oda sıcaklığında fazları karışamaz olan bir blok kopolimerin davranışı gibi baroplastik bir malzemede de proses edilmeden önce, ayrık faz halinde olduğundan görülmeyen bir karışım T_g si, $T_{g\text{ mix}}$, proses sonrası basıncın etkisiyle kısmi olarak oluşacak karışık faz nedeniyle açıkça gözlemlendiğinden bu durum Diferansiyel Tarama Kalorimetresi (DSC) ölçümleri ışığında değerlendirilmiştir. Bu bağlamda öncelikle DSC ölçümlerinin standardizasyonu için değişik ölçüm parametreleri denenerek optimum değerler tespit edilmiştir. Her ne kadar T_g termal bir davranış olsa da malzeme bu sıcaklığın aşılması durumunda ani olarak mukavemet kaybedeceğinden Dinamik Mekanik Analizör (DMA) T_g ölçümünde kullanılan en hassas yöntemlerdendir. DSC termogramlarında gözlenen ve $T_{g\text{ mix}}$ olarak nitelendirilen endotermik sinyaller, yapılan DMA ölçümlerinde de elde edilen benzer bulgular ile desteklenmiştir.

Bu çalışmada etkisi incelenen diğer parametreler ise baroplastik malzemelerin şekillendirilmesinde kullanılan basınç ve süredir. Aynı baroplastik malzemenin değişik basınçlar altında aynı sürede ve aynı basınç altında değişik sürelerde şekillendirilmesi ile elde edilen numuneler incelenerek uygun değerler tespit edilmiştir.

Ayrıca malzemenin molekül ağırlığı, topolojisi ve kompozisyonunun da şekillendirme üzerinde yarattığı etki, çeşitli kompozisyonlardaki, molekül ağırlığındaki düz ve yıldız blok kopolimerler üzerinde incelenmiştir. Belli sınırlar içindeki yumuşak faz artışının şekillendirme işlemini kolaylaştırarak gerekli basıncı azalttığı fakat bunun yanında mukavemeti de düşürdüğü, bunun yanında star blokların kompakt yapıları nedeniyle düşük viskozitelerinin lineer polimerlere göre kolay şekillendirilmelerini sağladığı gözlemlenmiştir. Yüksek molekül ağırlıklı baroplastiklerde, düşük molekül ağırlıklı zincirlerin oluşturduğu kaydırıcı etkinin aksine kalıp çeperinde tutunmaya neden olacağından, artı olarak basınç altında birbirine dolaşan moleküllerin basınç kalktığında çözümler göstereceğinden, diğer endüstriyel plastiklerde olduğu gibi yüzey hatalarına neden olabileceği ve bunun yumuşak fazı arttırarak çözülebileceği gösterilmiştir.

Diğer bir özellik olarak, çözelti olarak dökülerek hazırlanmış, proses edilmiş ve geri dönüştürülmüş baroplastik filmlerin her biri üzerinde beş farklı çözücü kullanılarak temas açısı ölçümleri yapılmış ve elde edilen bu bulgular yardımı ile Zisman eğrileri çizilerek malzemelerin serbest yüzey enerjileri ölçülmüş, bu değerler karşılaştırılarak şekillendirmeye ve geri dönüşüm sayısı ile oluşan değişime bakılmıştır. Fakat iki metal plaka arasında basınç uygulanarak elde edilen polimer filmlerinin yüzey düzgünsüzlüğü ve nem kontrolsüz test ortamı nedeniyle tutarlı sonuçlar elde edilememiştir.

Ek olarak, bir baroplastik tri-blok kopolimer şerit ekstrüzyon kalıbında proses edildikten sonra mekanik olarak parçalanıp tekrar kalıptan geçirilmiş, bu çevrim ardı ardına tekrar edilerek 20 kez proses edilmiştir. Malzemenin toz hali ve yirminci proses sonrası hali Jel Geçirgenlik Kromatografisi (GPC) de incelenerek bozunma ve madde kaybı gerçekleşmeden %100 geri kazanım sağlandığı tespit edilmiştir. Her 5 çevrimde bir numune alınarak yapılan DSC ölçümlerinde elde edilen $T_{g, mix}$ değerlerinde artan çevrim sayısı ile yumuşak fazın T_g na doğru bir kayma gözlemlenmiş, bu tespit ile bir şekillendirme işlemi sonrası tam karışımın oluşmadığı, fakat adım adım karışık fazın arttığı sonucuna varılmıştır. Bu yaklaşımla, DSC termogramlarından elde edilen $T_{g, mix}$ değerleri Fox eşitliğinde yerine koyularak kendini oluşturan karışık fazın kompozisyonu hesaplanmış ve ardından kullanılan baroplastığın % kompozisyonu da Fox eşitliğinde yerine koyularak tam karışık fazın oluşması durumunda yapının $T_{g, mix}$ değeri de hesaplanmış, tüm bunlar kullanılarak tam karışımın oluşması için gereken çevrim sayısı da grafiksel bir yaklaşımla hesaplanmıştır. Bu yaklaşımda hesaplanan çevrim sayısı sonrası elde edilecek yapıda, baroplastiklerin camsı geçiş sıcaklığı altındaki sıcaklıklarda şekillenebilirliğinin temel faktörü olan ayırık faz hiç kalmayacağından yapı baroplastik özellik göstermeyecektir. Bu nedenle tekrar karışık fazın oluşumu konusunda çalışmalar yapılmış ve baroplastik malzemelerin kendisini oluşturan fazların camsı geçiş sıcaklıklarının üzerinde bir sıcaklıkta yeteri sürede bekletildiklerinde karışık fazın tekrar düzenli hale geldiği ve malzemenin tekrar baroplastik özellik gösterebileceği tespit edilmiştir.

AFM görüntülerinden elde edilen bulgular da geri dönüşüm konusunda yapılan çalışmaları ve DSC ile elde edilen bulguları destekler nitelikte, başta tam düzenli fazdaki yapının şekillendirme sonrası bozulduğu, proses sayısının artışı ile adım adım yapıdaki karışık fazın da arttığı, geri dönüştürülmüş malzemenin şartlandırılmasından sonra malzemenin ilk haline yakın şekilde düzenli bir yapı oluşturduğu görülmüştür.

Bunun yanında, baroplastiklerin oda sıcaklığında yapılan şekillendirme işlemlerinde kullanılan kalıp ve presler endüstride standart olarak kullanılan tipler olduğundan, bu malzemelerin şekillendirilmesinde alışlagelmişin dışında bir teçhizat gerekmediği de göz önüne konmuştur.

1. INTRODUCTION

At the present day, there are thousands of materials available in industry for engineering applications. From the perspective of a materials scientist, each material belongs to one of three major classes; metallic, ceramic and polymeric. Each classification, is under-grouped based on chemical composition or certain physical or mechanical properties. On the other hand, Alloys, for metals; blends, for polymers; and composites for two or more materials from different classes; are the combination and co-existence in a single body to obtain new or hybrid properties for specific applications.

Lightweight, strong, durable, corrosion resistant, biocompatible, easy to process, high thermal and electrical insulator and inexpensive are properties that make polymers preferable in many applications. These materials contains many chemically bonded parts or units which themselves are bonded together to form a solid. Likewise, the polymer molecule is a long chain of covalent-bonded atoms and secondary bonds then hold groups of polymer chains together to form the polymeric material.

Industrially leading polymeric materials are thermoplastics, thermosetting plastics and elastomers, grouped depending on how they are bonded structurally and chemically. Thermoplastics are a large and varied group of synthetic organic materials. The term ‘thermoplastic’ indicates that these materials melt on heating and are melt processed into shape by a variety of forming, molding and extruding techniques. Alternately, ‘thermosetting’ polymers cannot be melted or re-melted. Elastomer or rubbers exhibit large elastic deformation when under an applied force and intend to return to own original shape when the force is released [1].

The mass production of plastics started around half century ago and now most items that humankind use are partly or wholly made of these materials thanks to their known and continuously discovering superior features. Since in some applications, properties of a homopolymer can be insufficient, in that case, blending or copolymerization would have a great importance in plastic industry. These processes

are physical and chemical mixing of polymers respectively that introduce a new material projecting properties of its constituents. Therefore the possibility of blending, copolymerization and even compounding for desired properties, rise the chance of polymer usage from automotive to medicine, over a wild field of industry.

As mentioned above copolymers consist of two or more different type of monomers linked in the same polymer chain. These polymer systems can be in various forms. Linear-block copolymers consist of two or more polymer chains in sequence, whereas star-block copolymers comprise more than two linear block copolymers attached at a common nod point. Another classification is based on the arrangement of units along the block chain, such as Alternating, Random, Block and Graft Copolymer [2, 3].

The ability to control both the length scale and arrangement of chains in block copolymer morphologies makes them attractive for applications requiring controlled distribution of material functionality in two or three ways. Appropriate choices of repeating units and the block sequences render them best fitting material for specific applications.

The morphological prominent behavior of block copolymers is the phase separation for a suitable ratio of the constituent blocks due to their immiscibility. For example, thermoplastic elastomers are block copolymers containing a rubbery matrix (polybutadiene or polyisoprene) with low glass transition temperature (T_g) and containing glassy hard domains (often polystyrene) with high glass transition temperature. The block copolymer, a kind of polymer alloy, behaves as a rubber at ambient conditions, but can be processed by extrusion or injection molding at high temperatures due to the presence of the glassy domains that act as physical crosslinks.

Commercial plastics are heated around their melting temperatures (T_m) in order to manufacture products by molding. In extrusion or injection machines, polymeric material become fluent and then by applied pressure material takes the desired shape of mold.

In the wake of researches on the energy consumption during manufacturing process of plastic products and in the light of foregoing, Mayes *et al.* [4] and Acar *et al.* [5] developed a material called “baroplastics”, processible at room temperature by

pressure application as molecular driving force, unlike melt processing of commercial plastics. The low temperature processing is achieved by choosing a couple of immiscible low T_g and high T_g components having appropriate compressibility coefficient and showing pressure-induced miscibility. Thus, energy consumption decreases and material degradation is hindered.

Polymers are primarily produced from petroleum or natural gas, which cause CO emission. Moreover, during polymer processing, heating around 150 – 250 °C is required for melting the raw material. The high energy consumed to reach these temperatures is another environmental problem. Furthermore, recycling of plastic materials is very low. The sum of recovered plastic is only 2% of total plastic waste. Additionally, these recovered materials can be added only 7% in raw material to reproduce the original product, so the recycling ratio is very low. As a result, this growing plastic waste became an important physical environmental threat day by day.

The main limitation for plastic waste recycling is the low thermal stability, discoloration, and degradation of polymers or additives, besides decreasing of mechanical properties at high temperatures that needed for reprocessing. In spite, the cold processability of baroplastics presents maximum benefit derivation from material by multiple use, 100% and infinite recycle possibility.

The aim of this project is observing effects of material composition and topology, processing parameters, recycling on thermal, morphological, mechanical and surfacial behaviors of baroplastic materials synthesized in our laboratory in various topologies and compositions.

2. THEORETICAL DATA

Macromolecules composed of two or more chemically different polymer chain blocks joined end to end in linear or nonlinear arrangements are called “Block Copolymers” (Figure 2.1) [6]. They are in case when blending is out of point due to the immiscibility of these polymers needed to use. Therefore, the different blocks are mostly incompatible. The rich variety of well-defined self-assembled structures in both bulk and selective solvents is the basis for mainly useful properties and applications ranging from thermoplastic elastomers to information storage, drug delivery, and photonic materials [7].

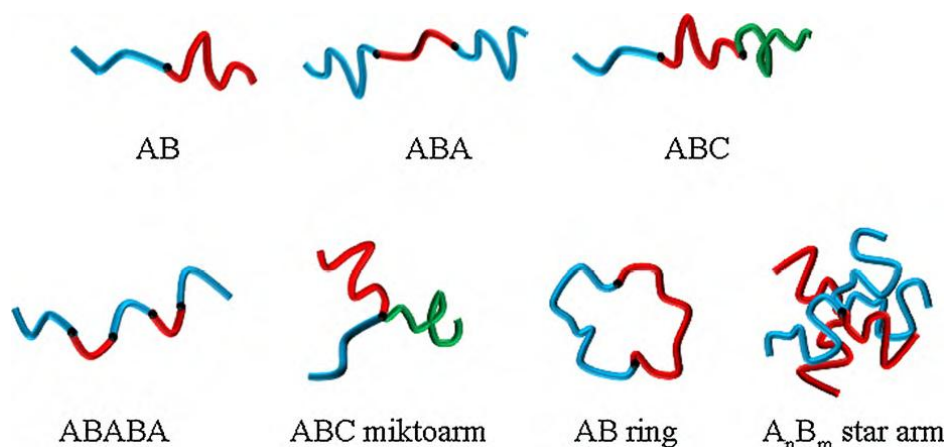


Figure 2.1 : Various molecular architectures of block copolymers.

Block copolymers are useful in many applications since a number of different polymers are connected together to yield a material with hybrid properties. For example, thermoplastic elastomers are block copolymers containing a rubbery matrix (polybutadiene or polyisoprene) containing glassy hard domains (often polystyrene) (Figure2.2).

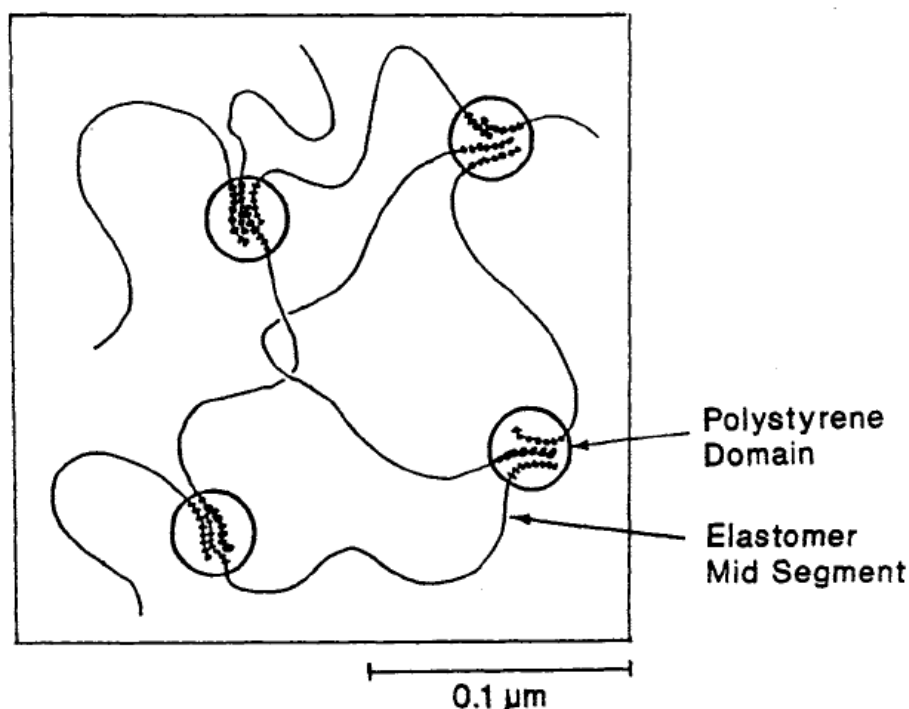


Figure 2.2 : Morphology of styrenic block copolymers.

Thermoplastic elastomers flow when heated or solved with solvent because its domains lose their strength. When the process is reversed, material is cooled down or the solvent is evaporated, the domains harden and the network regains its original integrity [8]. Thus, the block copolymer, kind of polymer alloy, behaves as a rubber at ambient conditions, but can be molded at high temperatures due to the presence of the glassy domains that act as physical crosslink. In solution, attachment of a water-soluble polymer to an insoluble polymer leads to the formation of micelles in amphiphilic block copolymers. The presence of micelles leads to structural and flow characteristics of the polymer in solution that differ from either parent polymer.

The growth of the block copolymer industry has reached a high level of commercial importance, involving many new products and industry participants, as well as a large number of academic research groups. The increasing importance and interest in block copolymers arises mainly from their unique properties in solution and in the solid state, which are a consequence of their molecular structure [9].

As a result, there is a continuous investigation of synthesis processes as well as of the characterization of these materials to external stimuli. Therefore, it is not surprising that these materials play a central role in contemporary macromolecular science covering the full spectrum of polymer chemistry, polymer physics, and applications.

2.1 Miscibility in Block Copolymer Segments

The term compatibility is often assumed to mean the miscibility of polymers with other polymers, plasticizers, or diluents. Decisions on the compatibility of mixture is not always clear-cut, however, it may depend on the particular method of examination and the intended use of the mixture.

Unfavorable interactions between different monomers causes macro phase separation in homopolymer blends. Whereas, block copolymers have chemical bounded individual molecules composed of distinct chemical species and they cannot phase separate into macroscopic regions. Instead, they show microphase separation, forming domains that have limited dimensions by the sizes of the constituent blocks.

A common criterion for miscibility is optical requirements. The mixture must form a transparent film even when the refractive indices of the components differ. In other words, dispersity of polymer molecules must be so well that the dimensions of any segregated regions are smaller than the wavelength of light. Such a fine scale of segregation can be achieved most readily if the components are miscible.

Another criterion is based on thermal behaviors. Thus, miscible polymer mixtures exhibit a single glass transition temperature. When a polymer is mixed with compatible diluents the glass-rubber transition range is broader and the glass transition temperature is shifted to lower temperatures. A homogeneous or equal proportional mixture of polymers exhibit one T_g intermediate between those of the components [10].

2.1.1 Microphase separation in block copolymers

On the microscopic images of block copolymers, periodic structures on a size scale of roughly 10–50 nm are commonly observed. The balance between component immiscibility and chain stretching at the interfacial boundary of a block copolymer give rise materials with characteristic patterns of compositional heterogeneity that is commonly termed microphase separation. Due to the positive enthalpy and small entropy of mixing, dissimilar blocks tend to microphase separate into well-ordered arrays of domains, classically termed microdomains.

Segregation strength, χN , where χ is the Flory–Huggins interaction parameter and N the degree of polymerization, is driving factor for phase separation. Overall morphological behavior of block copolymers are also influenced by the relative volume fraction of the constituent segments. Microdomain arrays can be in spherical, cylindrical, gyroid or lamellar, depending on the volume fractions of the blocks, f , and the degree of microphase separation, χN .

Two-component block copolymers commonly display upper critical solution temperature (UCST) behavior which can be described as formation of ordered, microphase-separated morphologies at lower temperatures and loss of discrete heterogeneity at higher temperatures. Hence, the transition point of this behavior is termed the order-disorder transition temperature (T_{ODT}).

In other words, while cooling of a block copolymer from the melt state, below T_{ODT} , ordered nano-structures (microphase-separated structures) are formed. Above the T_{ODT} , block copolymers phase mix and are disordered [3, 11]

Microphase diagram for conformationally symmetric, diblock copolymers calculated by Matsen and Bates [12] using numerical self-consistent field theory as seen on Figure 2.3. The transition separates the disordered phase (D) from the microphases. The labeled microphases are lamellas (L), gyroid (G), A and B-centered cylinders on a hexagonal lattice (CA and CB, respectively), and A- and B-centered spheres on a body centered cubic lattice, (S_A and S_B , respectively). The narrow regions adjacent to the transition are the close-packed spheres.

While most block copolymers exhibit phase-mixing behavior upon heating due to the increase in the entropy as well as the decrease in the segmental interactions, some block copolymers undergo a transition from the phase-mixed to phase-separated state upon heating. This transition is referred to as the lower disorder-to-order transition (LDOT).

For examination of all these structures, microscopic methods or light scattering methods (SANS) are helpful. Microscopic devices such as transmission electron microscopy (TEM), scanning electron microscopy (SEM) and especially atomic force microscopy (AFM) display better the polymer morphology with unprecedented resolution and accuracy.

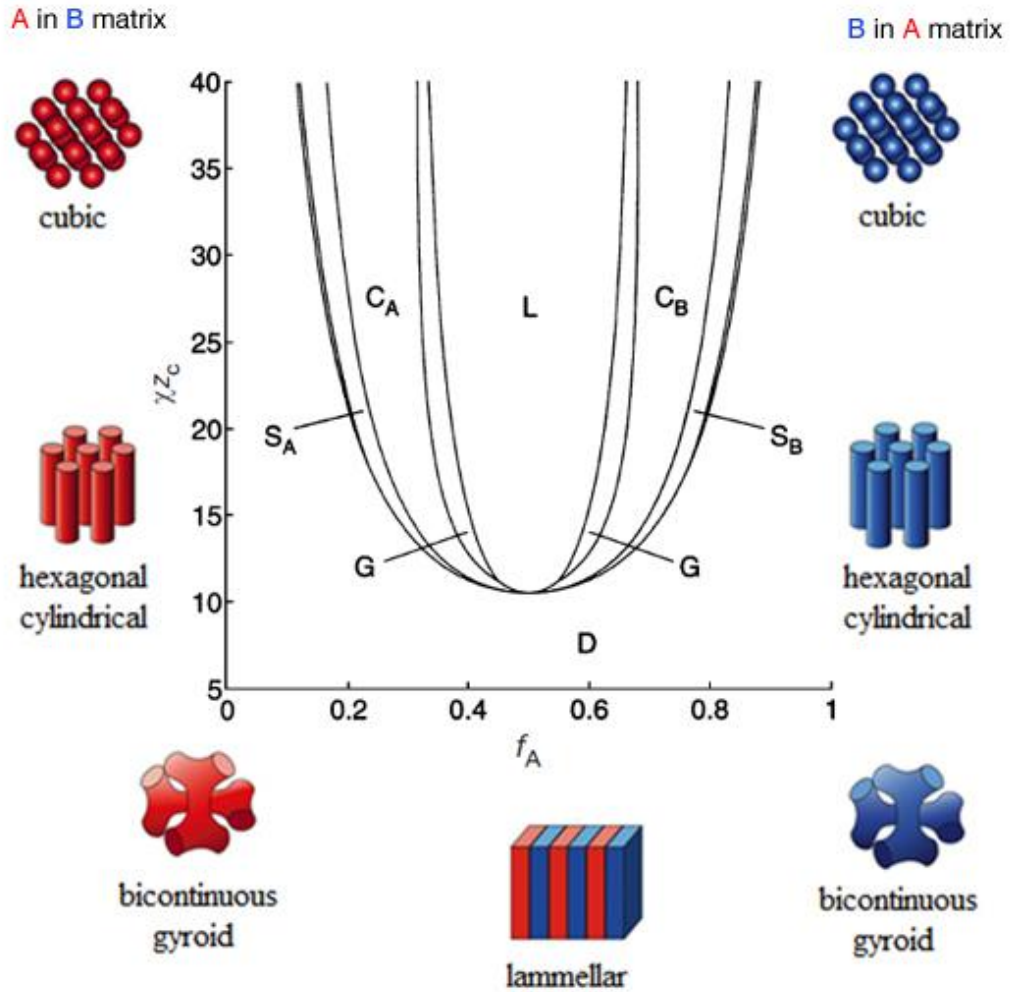


Figure 2.3 : Phase diagram and morphologies of diblock copolymers: cubic packed spheres (S_A , S_B), hexagonal packed cylinders (C_A , C_B), double gyroid (G), and lamellae (L).

An AFM is rather different from other microscopes, because it does not form an image by focusing light or electrons onto a surface, like an optical or electron microscope. An AFM physically ‘feels’ the sample’s surface with a sharp probe, building up a map of the height of the sample’s surface [13].

TappingMode™ method allows high resolution topographic imaging of sample surfaces that are easily damaged, loosely held to their substrate, or otherwise difficult to image by other AFM techniques. This key mode maps topography by tapping the surface with an high frequency oscillating probe tip. Thanks to the cantilever's oscillation amplitude changeability with sample surface topography and to the extremely low tapping force, imaging of the surface is carried out without any damage [14]. A typical image of a phase separated tri-block copolymer is seen in the Figure 2.4 [15].

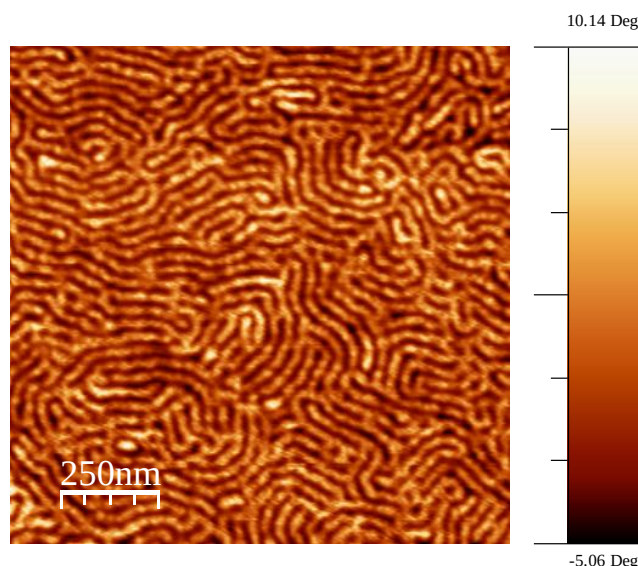


Figure 2.4 : AFM image of phase separated PEHA-*b*-PS-*b*-PEHA tri-block copolymer.

2.1.2 Thermal behavior of block copolymers

One of the most fundamental observations made on polymeric materials is the measurement of the glass transition temperature, T_g which is an important property when objecting polymers for a particular application. T_g is the temperature where the polymer goes from a hard, glass like state to a soft rubber like state. It means below T_g the physical properties are glassy or crystalline state and above T_g they behave like rubbery materials. T_g exist at wholly or partially amorphous plastics. A plastic's properties can be dramatically different above and below its T_g .

Similar to blends, block copolymers consisting of miscible blocks presents a single T_g that is correlated to weight percent of constituent phases. Increasing percentage of high T_g phase, results increased T_g of mixed phase. In practice this increase is linear, but molecular interactions cause a curvature. If self-interactions of constituent's molecules are greater than each other, increase is concave, otherwise it is convex (Figure 2.5).

Block copolymers consisted of immiscible segments show T_g values of its homopolymers on thermogram but closer to each other. If miscible segments are the case, a single T_g is observed upon constituents' T_g . In third state, partially miscible block copolymers show both miscible and immiscible behavior in a single material. The new temperature appeared between T_g values of their homopolymers is called as $T_{g,mix}$ (Figure 2.6).

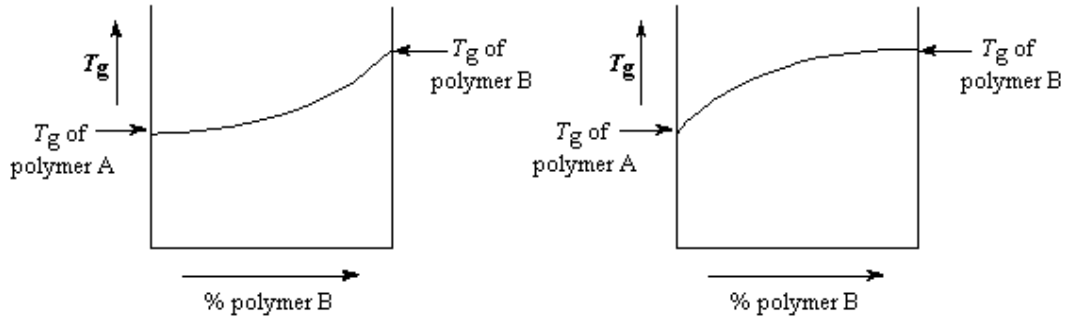


Figure 2.5 : T_g - composition relations in miscible block copolymers.

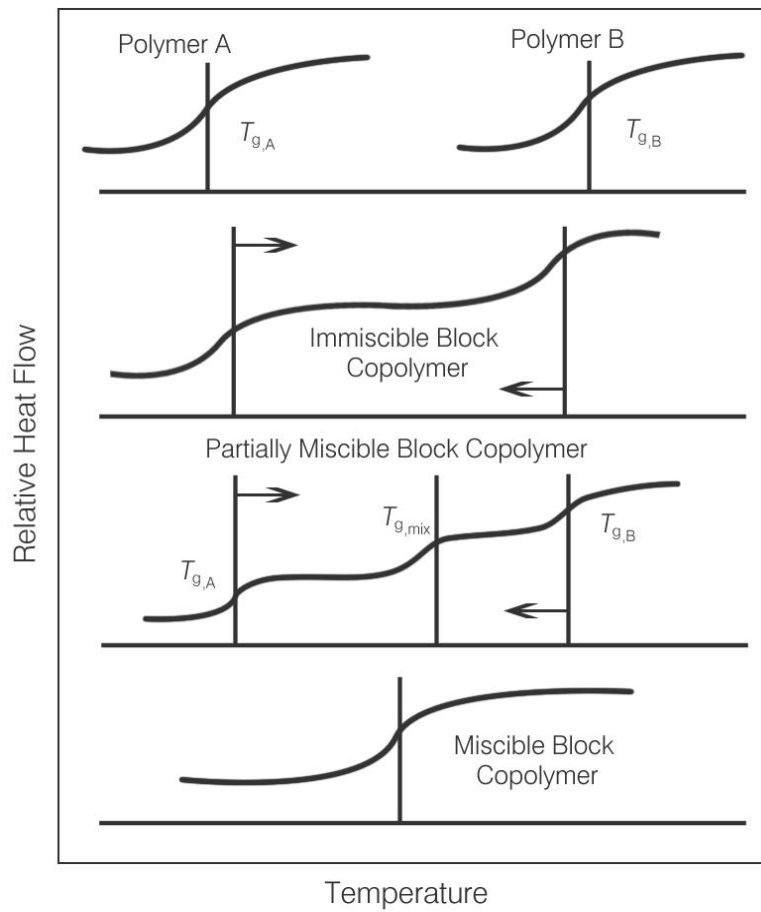


Figure 2.6 : T_g values depending on segment miscibility of block copolymers.

After studies for calculating T_g value of mixed phase formed in miscible systems, from value of pure components, many empirical formulae have been suggested [16, 17] as Fox done [18].

$$\frac{1}{T_{g,mix}} = \frac{\varpi_A}{T_{g,A}} + \frac{\varpi_B}{T_{g,B}} \quad (2.1)$$

where ϖ is the mass fraction of components.

2.1.2.1 Mechanical methods of determining T_g

In general, transitions in materials are associated with different localized or medium- to long-range cooperative motions of molecular segments. Accordingly, T_g is associated with cooperative motion among a large number of chain segments, including those from neighboring polymer chains [19].

Even if, T_g is a thermal property so can be measured by various thermal techniques, by far the most sensitive technique is dynamic mechanical analysis, DMA. DMA measures the viscoelastic moduli, storage and loss modulus, damping properties, and tan delta, of materials as they are deformed under a sinusoidal stress or strain as a function of the temperature. Any of this parameters render to define T_g . An oscillating force is applied to a sample and the resulting displacement of the sample is measured and plotted.

Figure 2.7, shows glass transitions temperatures of same sample using three different parameters [20]:

- *E' Onset*: Occurs at the lowest temperature and relates to mechanical failure.
- *E'' Peak*: Occurs at the middle temperature and is more closely related to the physical property changes attributed to the T_g in plastics. It reflects molecular processes and agrees with the idea of T_g as the temperature at the onset of segmental motion.
- *Tan Delta Peak*: Occurs at the highest temperature and is used historically in literature. It is a good measure of the “leather like” midpoint between the glassy and rubbery states of a polymer. The height and shape of the tan delta peak change systematically with amorphous content [19].

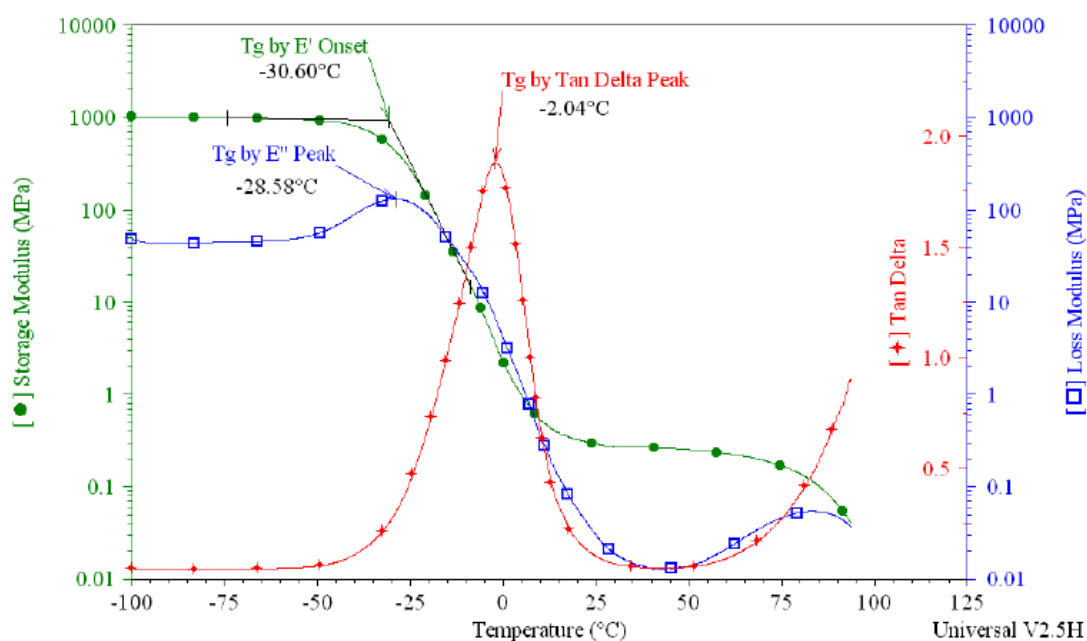


Figure 2.7 : DMA scan of a pressure sensitive adhesive run in tension clamps, at a frequency of 1 Hz, an amplitude of 10 microns, and a ramp rate of 5 °C/min.

2.1.2.2 Thermal methods of determining T_g

Thermal methods of measuring T_g are based on differential scanning calorimeter, DSC. In DSC, the thermal properties of a sample placed in a test pan are compared against a standard reference which is commonly an empty pan (Figure 2.8.).

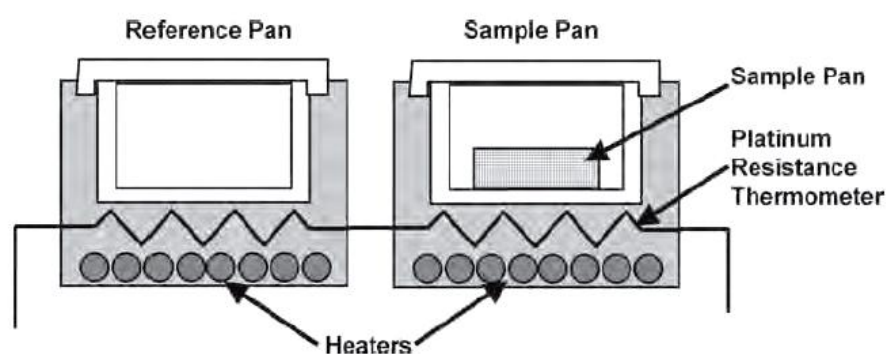


Figure 2.8 : Schematic of a DSC sample and reference cell.

The main principle of DSC is using electrically supplied heat to keep equal the temperature of each holder that are detected by a thermocouple. Thermal transitions occurred in sample cause a difference in heat flow necessary to maintain equal temperature. Thus, heat transfers over a temperature range are recorded as electronic signal and a plot of the difference in energy supplied against the average temperature

is plotted. The glass transition process for a glassy polymer that does not crystallize and is slowly heated from below T_g is seen on Figure 2.9. As the temperature is slowly increased, thermal transitions may be identified.

Here, the drop marked T_g at its midpoint represents the increase in energy supplied to the sample to maintain it at the same temperature as the reference material, due to the relatively rapid increase in the heat capacity of the sample as its temperature is raised through T_g . The addition of heat energy corresponds to this endothermic direction.

The specific heat capacity (C_p) can be also measured using DSC. It can change dramatically at T_g , as shown in Fig. 2.10. The value of T_g depends on the heating or cooling rate of the calorimetric experiment.[2]

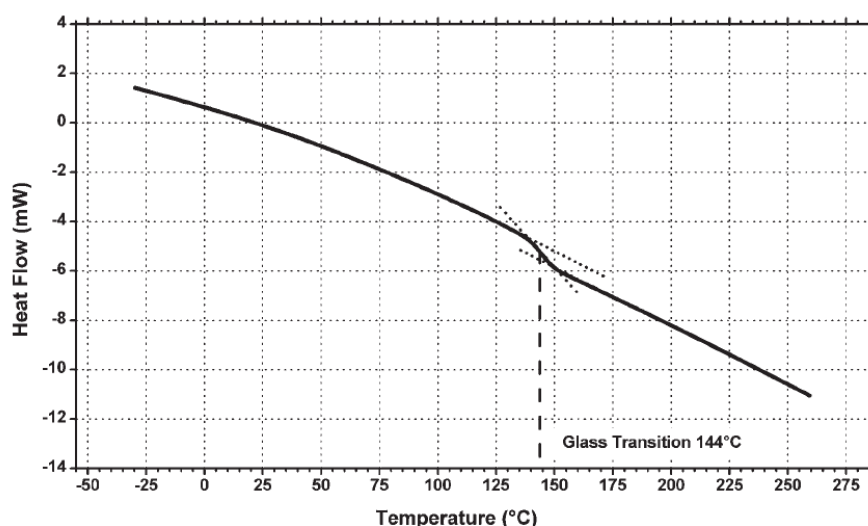


Figure 2.9 : Schematic of a DSC thermogram showing T_g .

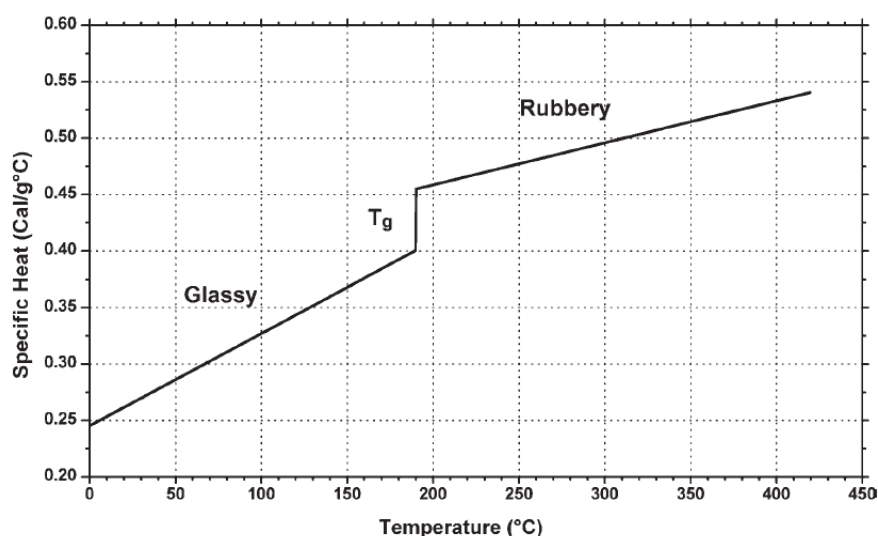


Figure 2.10 : T_g estimate from the change in specific heat capacity vs. temperature for a commercial polysulfone.

Glass transition temperature / melting temperature ratio is also an expressive data for polymers [21, 22]. In some cases quite different values for the T_g / T_m ratio may be observed in copolymers. In this connection, random copolymers and block copolymers should be distinguished. Owing to the irregularity of the structure, crystallization is more difficult in random copolymers than in each of the pure homopolymers. Therefore the melting point is depressed, while the glass transition temperature may have a normal value between those for the homopolymers. This results in a high value for the T_g / T_m ratio.

In block copolymers, on the other hand, long sequences of equal structural units may crystallize in the same way as in the homopolymer. In some cases, a block copolymer may be obtained that combines a high crystalline melting point (corresponding with the value of one component as a homopolymer) with a low glass transition temperature (corresponding with the other pure homopolymer). This results in a low T_g / T_m ratio (Figure 2.11) [23, 24].

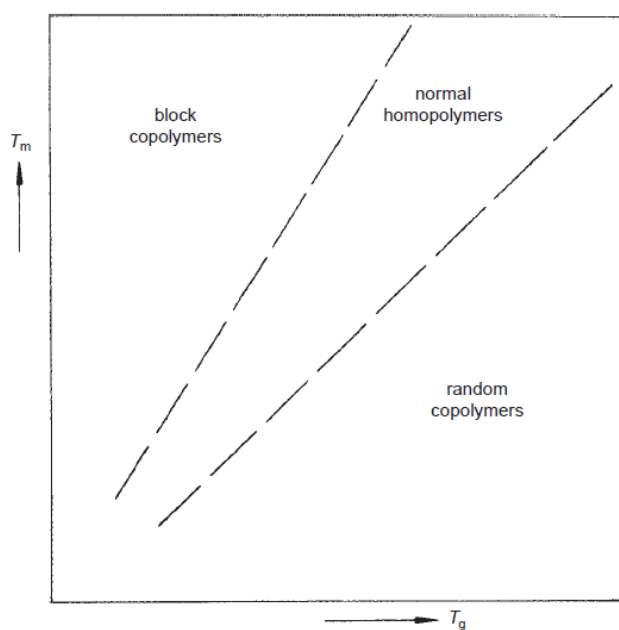


Figure 2.11 : A schematic plot of T_m versus T_g for some types of polymers.

2.1.3 Surface analysis of block copolymers

For estimating the surface energy of solids, Zisman developed a rather simple method based on graphical estimating as represented on Figure 2.12. Zisman proffered that, a series of liquids with known surface tensions provide estimation of critical surface tension, γ_c , by measuring the contact angle on the surface of interest [25].

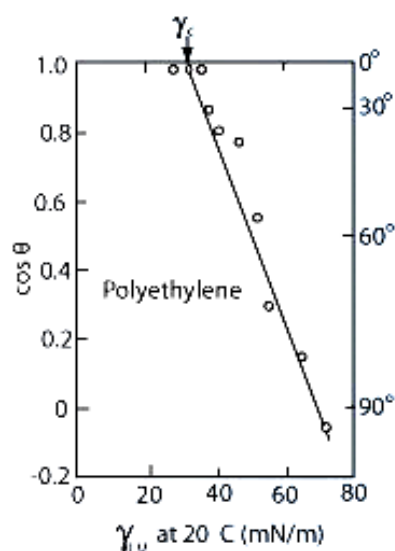


Figure 2.12 : Zisman plot for polyethylene surface with a series of liquid.

He remarked practically that the plot composed by these measured contact angles versus surface tension of test liquids, γ_L , is often linear. The value extrapolated for $\cos \theta = 1$ is named critical surface tension. It means, a liquid having such a γ_L shows complete wetting on substrate and the contact angle measured, θ , is equal to zero. Consequently, a liquid with a surface tension lower or equal to the critical surface tension of a material wets the surface.

2.2 Miscibility of Immiscible Block Segments: Baroplastics

As seen previously, driven by temperature, the relation and compatibility of entropic and enthalpic contributions of different block segments in a block copolymer cause many type of microdomains such as cylinder, sphere or lamellae. When heated, enthalpic repulsive interactions between these microdomains weaken and a transformation occurs from phase-separated to mixed state by resulting in polymer flow. Additionally, the interests on substitution of the heat energy have brought out that hydrostatic pressure also can be another effective driving force for the transition of ordered to disordered state. Thus, the idea to do the pressure as a thermodynamic alternative of heat for polymer flow in processing has been raised and many block copolymer showing pressure induced miscibility have been introduced.

After a series of publication concerning effects of pressure on phase behavior of block copolymers [26, 27], Ruzette *et al.* led the studies of discarding temperature and using pressure in polymer processing. They stated that polystyrene-*b*-poly(hexyl

methacrylate), PS-*b*-PHMA, presents UDOT however polystyrene-*b*-poly(*n*-butyl methacrylate), PS-*b*-PBMA shows LDOT. They proved also the pressure-induced miscibility of these block copolymers that exhibit a flow like behavior during processing which they named “baroplastic behavior” and accordingly the materials as “baroplastic materials”. In addition, they recorded that upper disorder-order transition, UDOT exhibiting block copolymers reveal a high-pressure coefficient that cause the segmental miscibility resulted in melt-like flow [28].

In order to predict baroplastic phase behavior of polymer pairs, Mayes and co-workers developed a mathematical model relevant the free energy of mixture containing compressible blend polymers by adding a third term to Flory–Huggins solution model.

$$\Delta g_{mix} = kT \left[\frac{\phi_A \tilde{\rho}_A}{N_A \nu_A^*} \ln \phi_A + \frac{\phi_B \tilde{\rho}_B}{N_B \nu_B^*} \ln \phi_B \right] + \phi_A \phi_B \tilde{\rho}_A \tilde{\rho}_B (\delta_{A0} - \delta_{B0})^2 + \phi_A \phi_B \left[(\tilde{\rho}_A - \tilde{\rho}_B)(\delta_A^2 - \delta_B^2) \right] \quad (2.2)$$

Where, Φ_i is the pure component volume fraction, ρ_i is the mass density, N_i is the segments of hard core, ν_i^* is the volume of segment of hard core, δ_{i0}^2 is the hardcore cohesive energy density and δ_i^2 is the temperature and pressure dependant cohesive energy density.

In equation 2.2, the first two terms are the entropy (-) and enthalpy (+) of mixing terms in Flory-Huggins model, while the third term arises from compressibility. The third term can either favor (-) or oppose (+) segmental mixing, tending to zero in the incompressible limit [28].

Consequently this research, have described the requirements to show baroplastic properties for a polymer pair which are pressure-induced miscibility, consisting of a high T_g (hard) and a low T_g (soft) component and having a high degree of interfacial surface area.

Contrarily of previous works where the ODT, was observed at temperatures higher than T_g of both components, the demonstration of processing of baroplastic systems containing nanophase domains of one high- T_g and one low- T_g component at room temperature by applying only pressure has been a milestone in 2003. They proved the exhibition of melt-like flow under pressure at ambient temperature through an

apparent semi-solid partial mixing mechanism that substantially preserves the high- T_g phase and molded at room temperature two new baroplastic block copolymers, polystyrene-*b*-polybutylacrylate, PS-*b*-PBA and polystyrene-*b*-poly(2-ethyl hexylacrylate), PS-*b*-PEHA and PEHA/PS, PBA/PS core-shell nanoparticles [5].

Recent studies of Inceoglu and Acar *et al.* on the synthesis of different topologies baroplastic materials and AFM images which sharply demonstrate the pressure induced miscibility are novel developments in baroplastic materials [29]. In addition, works of Acar *et al.* on baroplastic block copolymers as processing aids is another progress on this topic [30].

2.3 Processing of Block Copolymer Under Pressure

There are literally thousands of polymeric materials available for processing, and their number is continuously increasing. In general, they can be classified into two main groups: thermoplastics and thermosets [31].

The highlight feature of polymers is ease of processing even in some cases finished or semi-finished complex articles can be produced by melt processing methods. The most common polymer processing techniques are injection molding, compression molding, transfer molding, extrusion, and extrusion blow molding.

During heating for melting process, amorphous polymers are transformed from brittle to rubbery solids at the glass transition temperature, T_g by a second-order transition. Although T_g is known as a specific temperature value, the transition practically takes place over a temperature range of 5–10 °C. Moreover, increasing heating rate and applied hydrostatic pressure cause a parallel increase of T_g . Amorphous solids gradually become more deformable as they approach T_g , become “rubberlike” at $T_g < T < T_g + 100$ °C, known as the “rubbery plateau” region, and become fluid like at $T > T_g + 100$ °C, called the flow region.

However, the crystalline parts of semicrystalline polymers undergoes a first-order transition from the solid to the liquid state, with a characteristic heat of fusion, at the melting point T_m . Melting of these crystalline parts occurs over a 10–30 °C range, depending on their characters and on the rate of heating. The temperature value at the

end of this process is reported as T_m ; it depends on the polymer structure. Block copolymers exhibit the melting temperature characteristic of each constituent of the homopolymers [32].

At this point baroplastics can be considered as third class materials that don't need undergoing the thermal transitions mentioned above. Baroplastic materials can be processed by similar methods with thermoplastic polymers. Although in both case the pressure applied is around a few hundred bars, the main difference is processing temperature; thermoplastics need melting but baroplastics are processed in solid state at room temperature.

2.4 Recycling of Plastics

With increasing industrialization, production (Figures 2.13, [33]) and consumption (Table 2.1, [34]) of polymeric materials has been on the rise. Plastics do not degrade easily because they are very limited compatible with the nature. The growing environmental impact of plastics makes recovery and recycling more urgent.

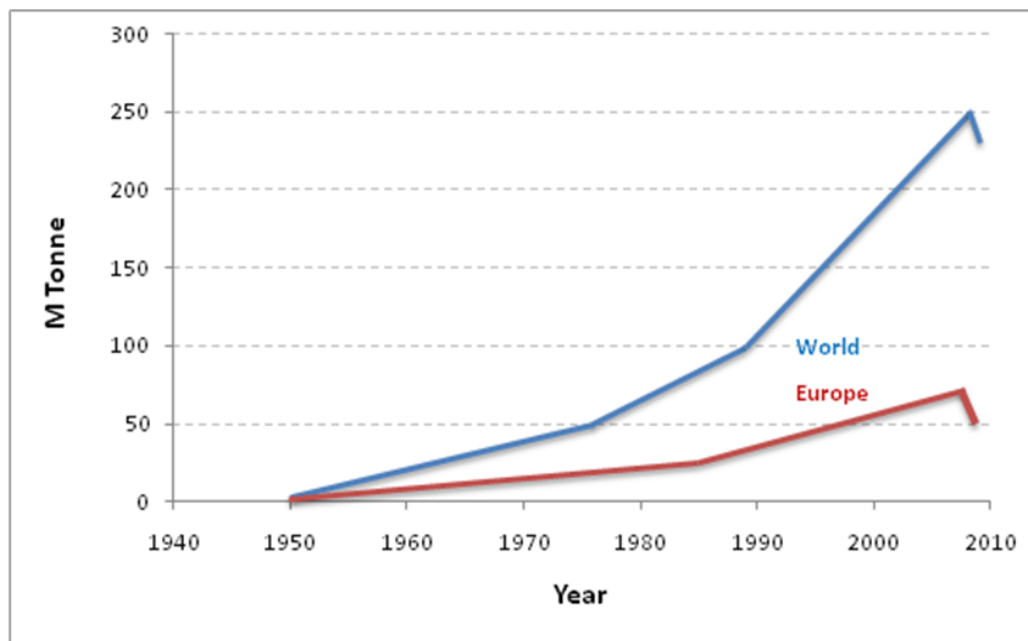


Figure 2.13 : World Plastic Production 1950-2009.

Polyolefins represent the largest groups of plastics and are mainly used as packaging materials. This industry is characterized by the predominance of commodity thermoplastics (Figure 2.14) led by polystyrene and including high-density polyethylene, polypropylene and PVC. Significant consumption is provided also by

the two major clear plastic sheet resins; polyacrylates and polycarbonate. Growth in this market is driven mostly by the increasing use of thermoformed plastics, especially in the rigid packaging market led by the food industry. Even though, after they are used once, they are treated as waste and thrown away [35].

Table 2.1 : 2010 Forecast of plastic material consumption.

	1990	2004	2010
	(%)	(%)	(%)
Western Europe	28.5	28.5	19.0
Africa / Middle East	4.0	6.0	6.0
East-Europe	6.0	4.5	5.0
Latin America	4.0	4.5	5.0
Japan	12.0	6.0	5.0
South and East Asia	16.5	33.5	37.0
North America	29.0	24.5	23.0
Total	86M tons	190M tons	259M tons

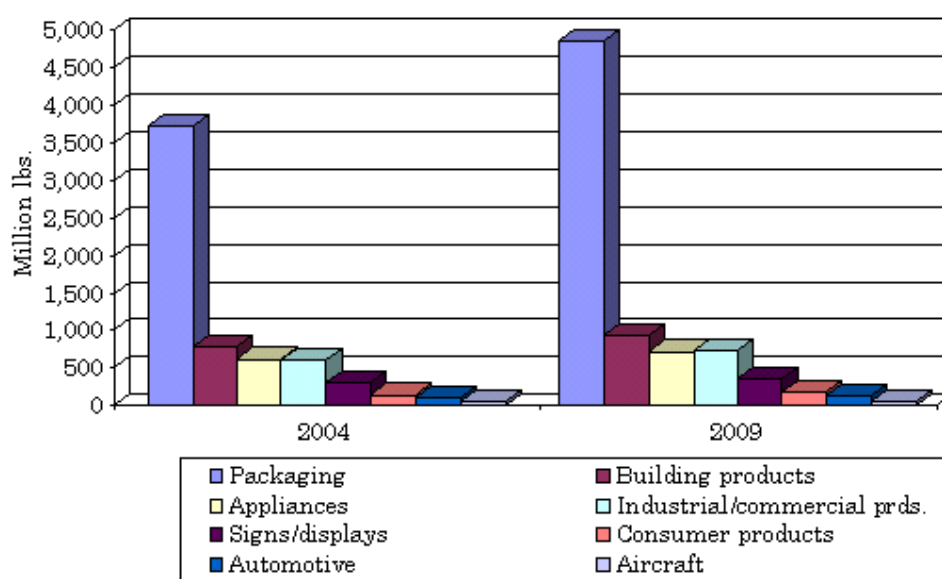


Figure 2.14 : Growth of polymer material by industrial classification (2004-2009).

In recent years, chemical recycling of plastics is being used increasingly and is defined as the breakdown of polymer waste into reusable materials as fuels or chemicals.

Depending on application, plastics are used pure or mixed (e.g. blend or composite). In such cases, separation and purification into industrially pure materials is critical. It is desired to recover plastics waste and reprocess or use the product of the reprocessing as raw material or fuel. Currently, plastic wastes are subjected to any one of the following options [36]:

1. Plastics materials are dumped; however, with the increasing cost of land, this is becoming uneconomical. In addition, there is total wastage of material and energy.
2. Plastics are recycled; but during the recovery stage, the polymers, especially plastics such as composites, lose quality and texture due to partial degradation, which invariably occurs during the recovery stage.
3. The plastics are burned as a municipal waste in incinerators or in steel plants. In this recycle technique, the energy of combustion is recovered and utilized, but the material is lost.

Whereas recycling plastics benefits the environment in various ways;

- Non-renewable fossil fuels conservation.
- Less energy consumption.
- Reduced amounts of solid waste going to landfill.
- Reduced greenhouse gas emissions
- Cleaner planet

However, yet only 2% of plastics are recycled worldwide. Most household plastic is incinerated or land filled, and the larger part of mixed-plastic WEEE (waste electrical and electronic equipment) is exported to Asia and Africa. 10% of household waste and 25% (by weight) of WEEE is made up of mixed plastic [37].

From a waste management perspective, the three “R”; reduce, reuse and recycle are widely efficient to reduce the quantities of plastic. Hopewell *et al.* outlined the benefits and limitations of these strategies. They show that to be effective we need to consider the three ”R”s in combination with each other and together with a fourth “R”, energy recovery. It must be considered also a 5th “R”, the three R’s become five: ‘reduce, reuse, recycle, recover and redesign’. Molecular redesign of plastics (the 5th R) like baroplastics has become an emerging issue in green chemistry [38]. Moreover, since baroplastics are suitable for each “R”, they are perfect green materials.

3. EXPERIMENTAL

3.1 Chemicals

Styrene (S, 99%, extra pure), 2-ethyl hexyl acrylate (EHA, 99%, stabilized), copper (I) chloride (CuCl), copper (I) bromide (CuBr, 98%), ethyl-2-bromo propionate (EBP, 99%), copper (II) bromide, *N,N,N',N'',N''*-Pentamethyldiethylenetriamine (PMDETA, 99%), ethylene glycol (99+ %), ascorbic acid, AA, were purchased from Acros. 2-bromopropionylbromide (BPB, 97%) and glycerol, C₃H₅(OH)₃, anhydrous (99%) were purchased from Aldrich. Sodium sulphate, Na₂SO₄, anhydrous (99%) was purchased from J. T. Baker Co. Tetrahydrofuran (THF), methanol (MeOH), dichloromethane (CH₂Cl₂) were purchased from J.T. Baker. Tris(2-(dimethylamino)ethyl)amine, Me₆TREN, was synthesized by our group members in our laboratory [29].

3.2 Equipment

3.2.1 NMR

To identify the compositions of block copolymers as molar percent of its constituents, they were dissolved in deuterated chloroform (CDCl₃), and the ¹H NMR spectra were measured on a Bruker AC250 (250,133 MHz) NMR spectrometer with the internal reference.

3.2.2 GPC

The molecular weights and polydispersities were measured by a gel permeation chromatography (GPC) system consisting of an Agilent 1200 series pump, three Waters Styragel HR columns (guard, 4, 3) and an Agilent 1100 series RI detector with a THF flow rate of 1 mL/min; poly(methyl methacrylate) or polystyrene were used as calibration standards. The second GPC system with an Agilent 1200 model isocratic pump, four Waters Styragel columns (guard, HR 5E, HR 4, HR 3, and HR 2), and a Viscotek TDA 302 triple detector (RI, dual laser light scattering, λ : 670 nm, 90° and 7°, and differential pressure viscometer) was conducted in THF with a flow

rate of 0.5 mL/min at 35 °C to measure the absolute molecular weights. Three detectors were calibrated with a PS standard having a narrow molecular weight distribution (M_n : 115000 g/mol, M_w/M_n : 1.02, $[\eta]$: 0.519 dL/g at 35 °C in THF, dn/dc : 0.185 mL/g) provided by Viscotek company. The dn/dc value for PEHA is calculated to be 0.058 mL/g at 35 °C in THF using at least three different concentrations of the corresponding polymer.

3.2.3 Hydraulic Presses

3.2.3.1 Manual

For preparation of pellets by compression molding, a Shimadzu manual press (Figure 3.1) was utilized. Its 5 cm piston diameter provides 12 ton force at max 600 kg/cm² pressure.

3.2.3.2 Automated

For late works an heat and pressure automated hydraulic press was got from Hursan Hydraulic Press Company (Figure 3.2). Its piston diameter of 15 cm provides 176.5 kgf for every kg/cm² so, at max 100 kg/cm² hydraulic pressure it generates 17.5 ton force.



Figure 3.1 : Shimadzu Manual Press.



Figure 3.2 : Hürsan Hydraulic Press.

3.2.4 Molds

Both baroplastic materials and commodity polymers are processed by similar molds.

3.2.4.1 Tape (strip) extrusion mold

Strip extruder mold was used for preparation of recycle samples and mechanical analysis samples. Mold piston diameter was 14 mm, applying 65 kg/cm² pressure on the polymer powder for each ton applied by the press. Polymer strips (Figure 3.3.a) and wires (Figure 3.3.b) were obtained in 8 mm width and 1 mm thickness respectively.



Figure 3.3 : a) Primarily designed b) Spring added tape extrusion mold.

During the work, molds were needed some revises and improvements. Especially, pressure application for processes was resulted in jam of piston at the hole. To solve this problem, primarily, a repulsive spring is added to our mold as seen on the Figure 3.3.b. However this conversion was not solved the problem, and gave rise to need of extra force to exceed the spring force. Then it was thought that modular mold body would be the best way to take out the piston (Figure 3.4). Horizontally divided mold body were kept tightly closed by an outer ring.



Figure 3.4 : Modular body tape extrusion mold.

In industry, to avoid mold destructions, some additives and friction decreasing oils or powders are used. However in this study, they were not used in order to prevent penetration of any impurity into the baroplastic material to be characterized and to maintain the sample as pure as possible. Therefore, after performing many process applications with various materials, piston and mold walls were worn off because of friction and pressure. Thus, a new mold were designed (Figure 3.5) and made by STAVAX 2083 stainless steel.

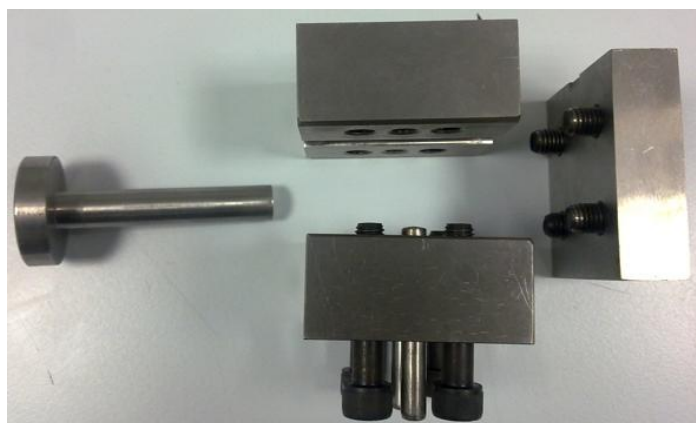


Figure 3.5 : Last design of tape extrusion mold.

3.2.4.2 Wire extrusion mold

Wire extruder mold was used for processability tests and preparation of any mechanical analysis samples. Mold piston diameter was 14 mm, applying 65 kg/cm^2 pressure for each ton on the sample (Figure 3.6) . Polymer wires were obtained in 2 mm diameter.



Figure 3.6 : a) Block body b) Modular body wire extrusion mold.

3.2.4.3 Compression mold

For preparation of polymer pellets, IR pellet mold were used as compression molds.

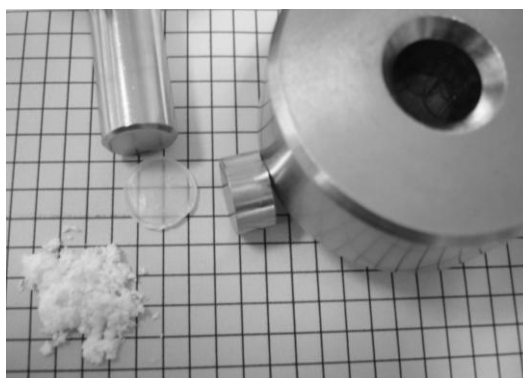


Figure 3.7 : Compression mold.

3.2.5 DSC

Differential scanning calorimetry (DSC) measurements were conducted to find out the glass transition temperatures using auto sampler featured Q1000 (TA Instruments). Thermograms were evaluated from the first heating run in a range of - 90 °C to 150 °C with a ramp rate of 10 °C/min for heating. Cooling ramp is not specified and equilibrate command was used. All tests were carried out under 50 ml/min rate of nitrogen purge. All glass transition temperatures were investigated on TA Universal Analysis software by the inflection of change in the endothermic direction (downwards) of the heat flow of the heating ramp.

3.2.6 DMA

TA Q800 dynamic mechanical analyzer (DMA) was used to measure mechanical properties of baroplastics (stress-strain curve) at room temperature using tensile film clamp and also the glass transition temperature (T_g) was found by examining the

related modulus or tan delta curves. For T_g measurements the material in tension clamps was heated from 30 to 100 °C with a heating rate 5 °C/min while the applied frequency was 0.25 Hz.

3.2.7 Goniometer

Static contact angles for the test liquids were measured using a KSV CAM200 contact angle goniometer system. Droplets of test liquids were placed on the polymer samples surface using a manual 1ml syringe. Side view images were captured with a pre-equipped firewire video camera with 55 mm focus lens at a rate of 60 frames/s. Contact angles were automatically calculated by the instrument's software that is based on fitting of the captured drop shape to the curve calculated from the Young–Laplace equation. Measurements were performed at ambient temperature ($24 \pm 3^\circ\text{C}$) and repeated at least 5 times for each test liquid (25 drops in sum) on fresh surfaces of same sample.

Surface free energy for the tested samples was calculated by Zisman polts drawn using contact angle measurements that were conducted with five liquids (pure water, monopropylene glycol, glycerol, ethylene glycol and methanol) with a range of surface tension.

3.2.8 AFM

The atomic force microscopy (AFM) measurements of the baroplastic films were performed at 25 °C in air. The morphological observation of the samples was conducted on a Nanoscope IIIa scanning probe microscope (Veeco, Digital Instruments, Multimode Model, High Resolution Scanner Serial No: 4683ev, Santa Barbara, CA) in a tapping mode between 2 and 3 Hz scanning rate. The spring constant and the resonance frequency of Olympus silicon tip were 28.81 N/m and 281.4 kHz, respectively. WSxM software was used to process data [39].

3.3 Materials

As mentioned before, block copolymers are composed by the covalent bonding of polymeric chains at their respective ends. The formation of these covalent bonds can be achieved by a variety of chemical following one of suitable polymerization procedures. The diversity in molecular architecture can be further expanded if three

or more macromolecular segments are incorporated into one block copolymer chain. Consequently, in an effort to consist such complex materials, there are many useful polymerization techniques [40]. Controlled/living radical polymerization, CRP, is one of most attractive method because of the possibility to precise the molecular weight and the positions of functional groups within each chain. Therefore Atom Transfer Radical Polymerization, ATRP, which is based on a copper halide/nitrogen based ligand catalyst complex, is one of the most successful CRP method [41].

In this study, for characterization of baroplastics, tri-block and 4 arm star-block copolymers with different compositions were synthesized often by two-pot, rarely by one-pot ATRP method. A typical mechanism for ATRP is represented in Figure 3.8. Homopolymers synthesis are done in our laboratory as well for use as macroinitiators. After polymerization and total conversion of first monomer, block copolymers are obtained by the addition of the second monomer to the flask under nitrogen. During each steps of polymerization, many samples were taken periodically via a syringe and were introduced to GPC to follow the molecular weight and the conversion of the polymer. Detailed information on synthesis of baroplastic block copolymer by ATRP are given in literature [15] and Inceoglu's PhD thesis [29].

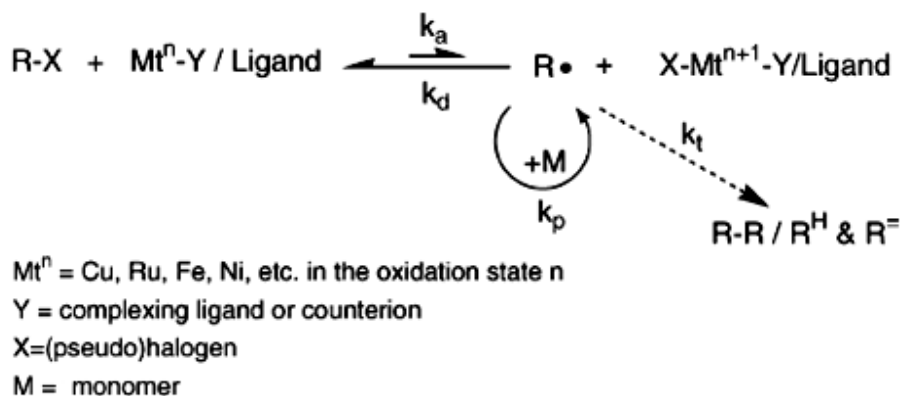


Figure 3.8 : Mechanism for ATRP.

3.4 Sample Preparation

Samples of this research were prepared by several film formation and extrusion methods. For investigating processability of baroplastics samples were prepared by introducing polymer powder into mold and then various applying pressures.

Recycling performance of baroplastics was observed from previously processed samples that were mechanically chopped into little pieces and fed into the mold and then processed again. Each of this chop and process cycle is referred as “1 process cycle”

3.4.1 Film formation

3.4.1.1 Solution cast

Polymer solutions 20% (w/v) were prepared by dissolving 3g polymer powder in 15 ml dichloromethane (CH_2Cl_2). Prior to casting, the Teflon[®] plates were cleaned with methanol and acetone, then were rinsed with water for several times and dried. After casting, plates were covered with a perforated foil paper as a vapor barrier in order to retard evaporation of solvent.

3.4.1.2 Plate

Polymer powder or pieces of previously processed polymer placed and squeezed between two steel plate by applying 6 -10 ton force using press.

3.4.2 Pellet formation

For compression molding 0.1 g polymer in powder form or chopped form is placed into the compression mold (IR pellet mold), which then was closed carefully, placed in the center region of the press and pressed at room temperature (6 ton, 300 kg/cm^2). The amount of polymer is set according to the previously done studies of the effect of sample weight on processability.

3.4.3 Strip and wire extrusion

For compression molding polymer powder or chopped pieces are placed into the strip or wire extrusion mold. Then it was closed carefully, was placed at the center of the press and was pressed at room temperature. Pressure was chosen between 100 to 500 kg/cm^2 , depending on composition of polymer to be processed.

4. RESULTS

4.1 Materials

Block copolymers synthesized in our laboratory are characterized primarily by GPC and NMR measurements. The molecular weights and polydispersities of block copolymers are derived from GPC traces. The retention time of block copolymer is longer compared to the homopolymer used as macroinitiator for ATRP synthesis. Accordingly, in Figure 4.1 PS-*b*-PEHA-*b*-PS tri-block copolymer formation is observed for BP08 by GPC is given as an example.

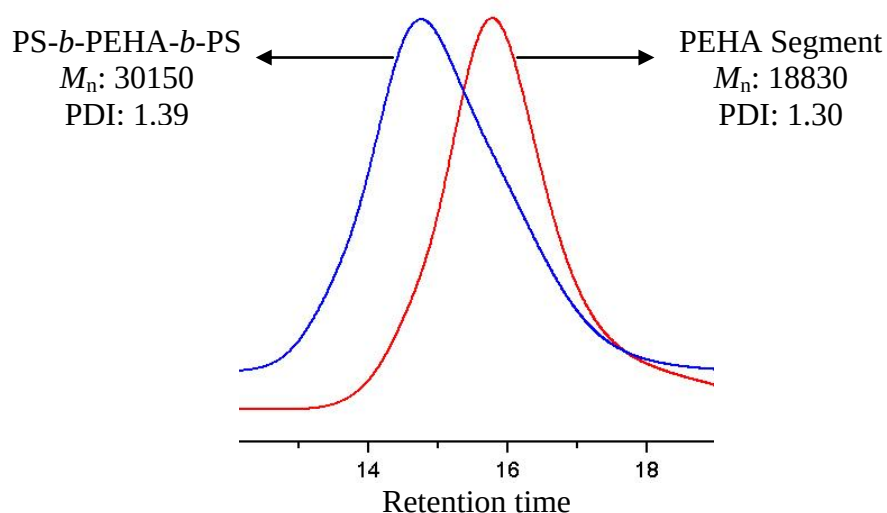


Figure 4.1 : GPC traces of the PEHA segment and PS-*b*-PEHA-*b*-PS tri-block copolymer (50% PEHA, BP08).

The composition of block copolymers was calculated using ^1H NMR measurements by integrating the characteristic peak of the PEHA segment ($-\text{C}(\text{O})\text{OCH}_2-$) at 3.9 ppm versus the aromatic peaks of the PS segment at 6.34-7.06 ppm. In Figure 4.2, ^1H NMR results of PS-*b*-PEHA-*b*-PS tri-block copolymer (49% PEHA, BP07) is given as an example.

Molecular weight and composition values of block copolymers used in this thesis are listed in Table 4.1.

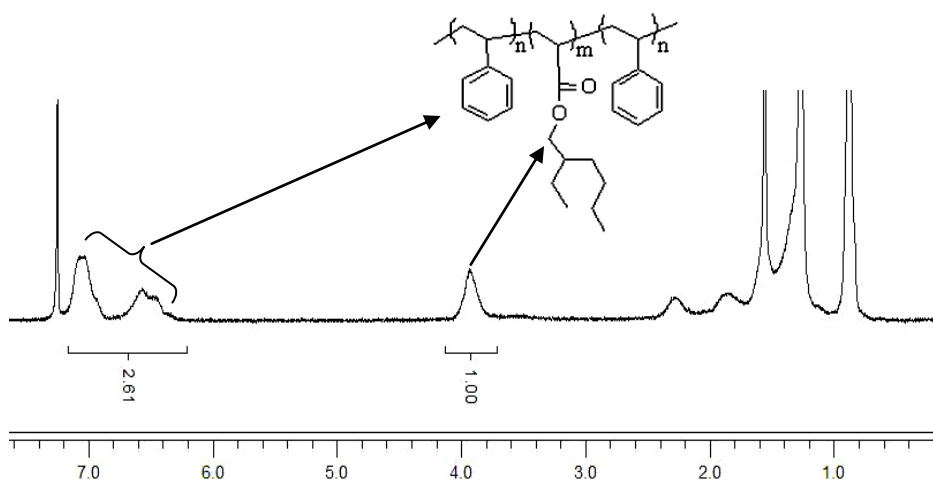


Figure 4.2 : ^1H NMR spectrum of PS-*b*-PEHA-*b*-PS tri-block copolymer (49% PEHA, BP07) in CDCl_3 .

Table 4.1: Characteristics of the block copolymers used in this research.

Code	Topology	$M_{n, \text{GPC}}^a$	M_w/M_n^a	$M_{w, \text{LS}}^b$	Comp. ^c (PEHA, %)
BP01	PS- <i>b</i> -PEHA- <i>b</i> -PS	30290	1.27	33640	40
BP02	PS- <i>b</i> -PEHA- <i>b</i> -PS	124290	1.30	134570	40
BP03	PS- <i>b</i> -PEHA- <i>b</i> -PS	36890	1.49	48090	43
BP04	PS- <i>b</i> -PEHA- <i>b</i> -PS	30780	1.46	40840	45
BP05	PS- <i>b</i> -PEHA- <i>b</i> -PS	41000	1.38	51870	47
BP06	PS- <i>b</i> -PEHA- <i>b</i> -PS	30130	1.44	38730	48
BP07	PS- <i>b</i> -PEHA- <i>b</i> -PS	38540	1.56	59580	49
BP08	PS- <i>b</i> -PEHA- <i>b</i> -PS	30150	1.49	37090	50
BP09	PS- <i>b</i> -PEHA- <i>b</i> -PS	150000	1.16	264450	50
BP10	PEHA- <i>b</i> -PS- <i>b</i> -PEHA	36000	1.35	38220	51
BP11	PEHA- <i>b</i> -PS- <i>b</i> -PEHA	31770	1.54	41160	53
BP12	(PEHA- <i>b</i> -PS) ^{4*}	74150	1.71	155250	48

^a Calculated from GPC calibrated with linear polystyrene standards

^b Absolute molecular weights were calculated with multi angle light scattering in THF and the dn/dc value of blok copolymer= $[X_{\text{PS}}*0.185 \text{ mL/g } (dn/dc \text{ for PS}) + X_{\text{PEHA}}*0.058 \text{ mL/g } (dn/dc \text{ for PEHA})]$.

^c Compositions were calculated by ^1H NMR analysis

4.2 Thermal Measurements (DSC)

As mentioned in theoretical part, baroplastics are block copolymers synthesized using two immiscible homopolymers with suitable properties. These novel materials show pressure-induced miscibility that leads melt like flow. Consequently, as

processing occur under pressure, it result in formation of disordered domains in microphase-separated matrix, which we call partially miscibility. Thus, we can investigate baroplastic behavior by observing mixed domains formed after processing. As expressed before, partially miscibility shows specific $T_{g,mix}$ that is not seen in immiscibility and this is the key difference to pursuit for characterization of baroplastics. In this way DSC measurements play an important role to analyze $T_{g,mix}$ expected only in processed baroplastics possessing mixed and ordered phases in a single structure.

4.2.1 Optimization of DSC measurements

DSC is commonly used to measure the T_g value of polymers which is an important parameter also for baroplastic characterization. A standardized procedure is important for comparisons and necessary to obtain reproducible results. In general, two types of DSC run methods can be used for determination of T_g . One of these is scanning the sample at a specific heating rate from ambient or sub-ambient temperatures to suitable temperature over T_g without pretreatment if thermal history is negligible. The other one involves preheating at over T_g for one minute for erasing thermal history, followed by quick cooling to room temperature before scanning it under the same conditions with first one [42].

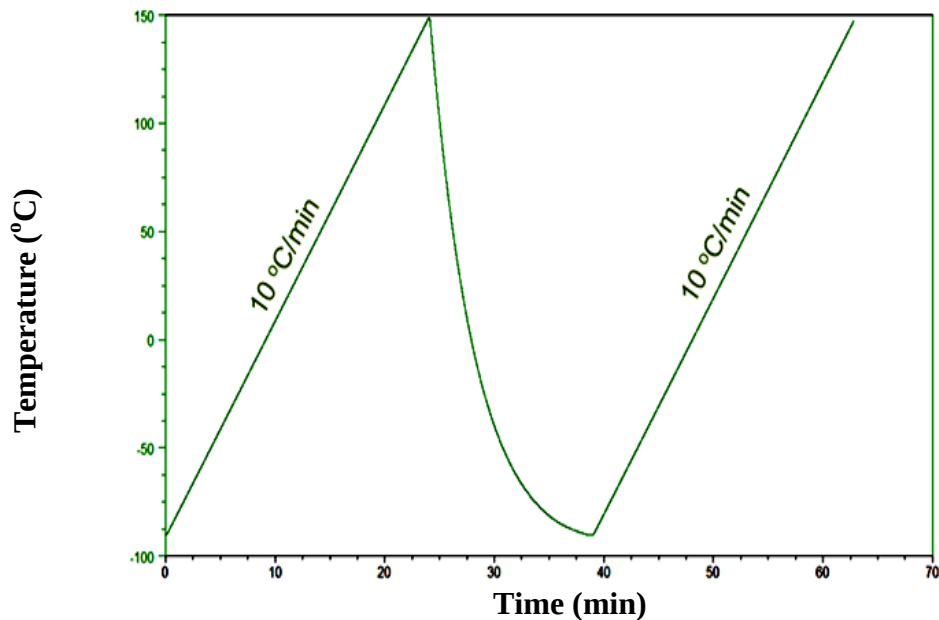


Figure 4.3 : DSC run method.

As the second method cause an annealing effect resulting in clear the thermal history of disordered phases, our DSC measurements were undergone using the first method avoiding preheating. Temperature range was chosen -90 to 150 °C considering T_g values of each segments that are around -70 and 100 °C for PEHA and PS respectively. Second heating is just for checking the disappear of $T_{g,mix}$ that means the polymer reconstruct its initial microphase separated structure due to the annealing effect.

4.2.1.1 Heating rate

Since the beginning of thermal analysis, the most common heating rates used has been 10 and 20 °C/min. Although high heating rates increase the sensitivity, it reduces temperature resolution and accuracy.

While using high heating rates, it must be considered that even after that programmed rate is achieved, the temperature of the sample, the sample container, and parts of the DSC lag behind the furnace control temperature that can be described by Newton's Law of Cooling:

$$T_{lag} = R_o \cdot dq/dt = R_o \cdot (C_p \cdot m + C_{p,pan} \cdot m_{pan}) \cdot dT/dt \quad (4.1)$$

The thermal lag is relevant to heating rate, sample and pan mass, sample and pan specific heat capacity and the thermal resistance between the sensor and the sample. Under identical conditions, thermal lag produced by 100 °C/min heating rate is 10 times greater than 10 °C/min [43].

In order to determine the accurate heating rate to introduce the $T_{g,mix}$ most clearly, equal weight samples are measured at 5, 10, 20, 50 and 100 °C/min heating rate. As shown in Figure 4.4, 50 and 100 °C/min rates presented a great thermal lag at transition region and resulted in a broad endothermic signal. Contrarily, it is observed that the sensitivity of the 5 °C/min is insufficient to detect $T_{g,mix}$. Consequently, 10 °C/min heating rate is chosen as optimum heating rate for $T_{g,mix}$ observations.

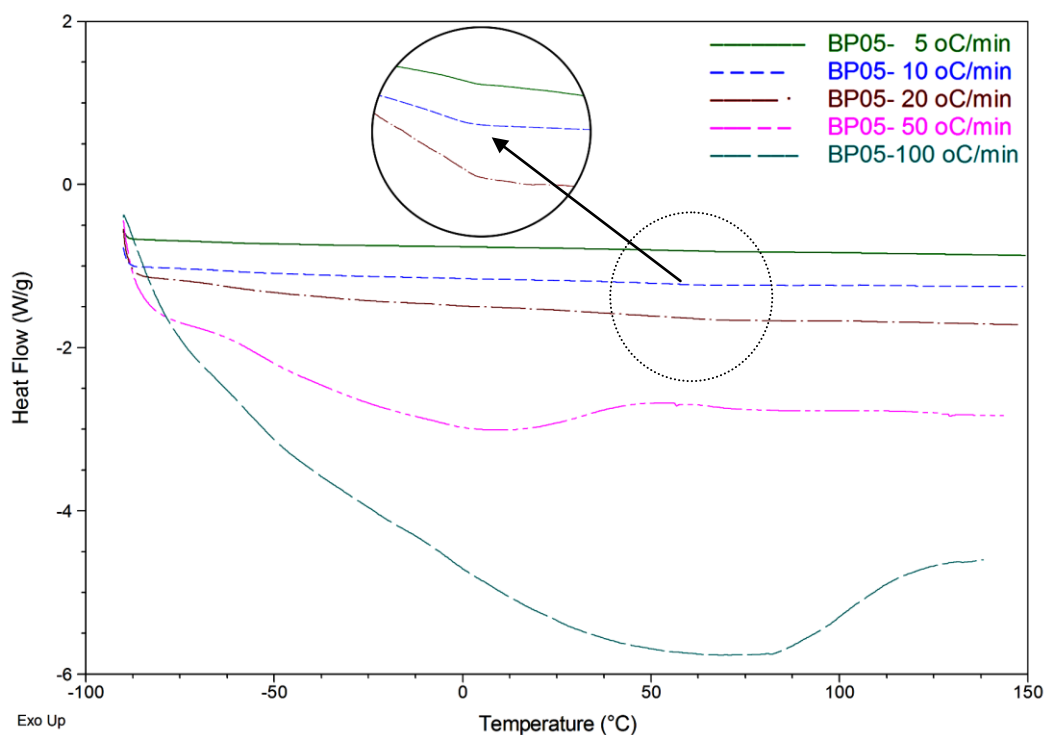


Figure 4.4 : DSC thermograms of a baroplastic sample at different heating rates.

4.2.1.2 Sample mass

In literature, it is reported that the maximum sample weight possible to measure a sample weight independent T_m value depends on heating rate [42].

- 20 °C/min, sample weight ≤ 4 mg,
- 10 °C/min, sample weight ≤ 6 mg,
- 5 °C/min, sample weight ≤ 8 mg.

Accordingly, the sensitivity for the sample weight of the measured $T_{g,mix}$ value is investigated. 3, 7 and 15 mg samples are scanned at 10 °C/min heating rate, which was chosen as optimum previously, and results are illustrated in the Figure 4.5. Parallel to reported in literature for T_m , it is observed that 7 mg is adequate sample weight for $T_{g,mix}$ measurements.

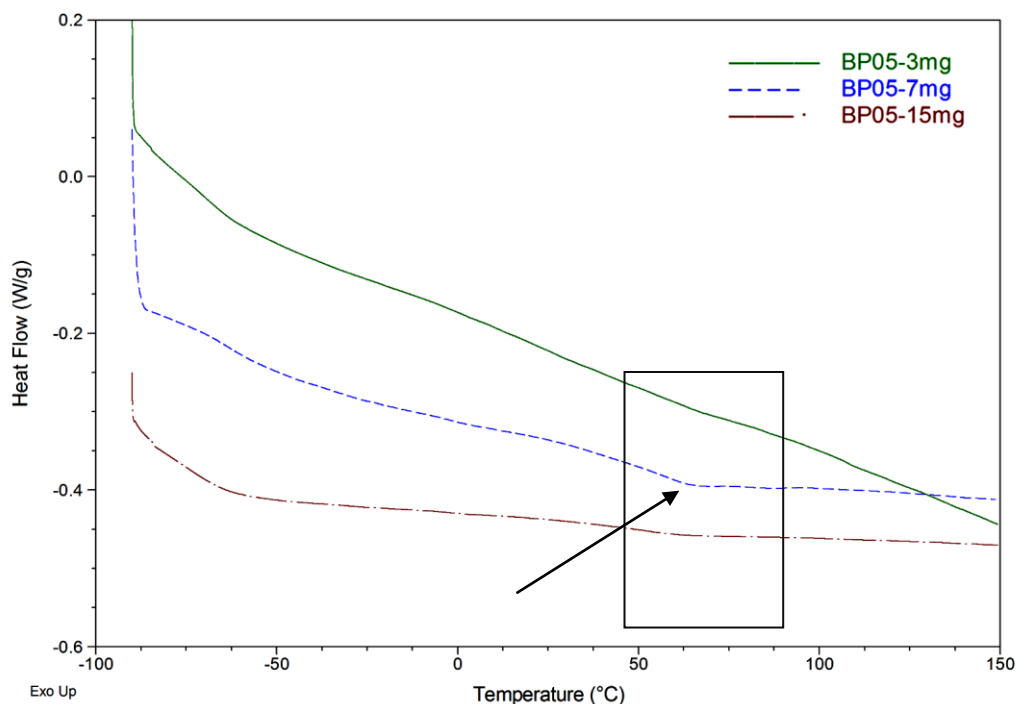


Figure 4.5 : DSC thermograms of a baroplastic with different sample masses.

4.2.2 Effects of processing parameters

Time and pressure effects is studied in order to introduce minimum necessities parameter values and to optimize processing conditions, which are also economically important. Thus, BP06 sample is processed under various pressure and duration values using compression mold.

4.2.2.1 Process pressure effect

Pressure effect is investigated from PS-*b*-PEHA-*b*-PS baroplastic tri-block copolymer (46% PEHA, 30K, BP06) samples processed in compression mold under 50, 100, 200, 300, 350 and 400 kg/cm² pressures (1, 2, 4, 6, 7, 8 tones forces) for 5 minutes. As seen in Figure 4.6, the change in $T_{g,mix}$ is negligible, which is attributed to the mixed phase of block copolymer segments. Consequently, it is understood that baroplastics needs an optimum process pressure to form disordered phase and pressures exceeding this value have any action on miscibility and are wasted.

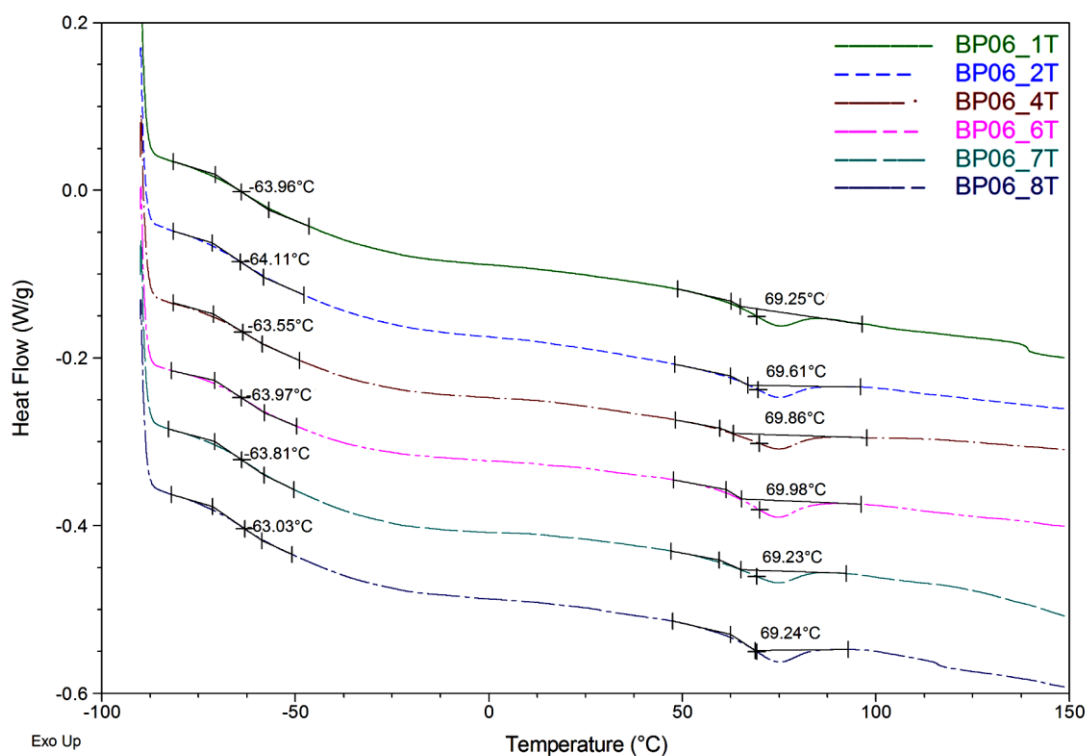


Figure 4.6 : Comparison of DSC thermograms of PS-*b*-PEHA-*b*-PS baroplastic tri-block copolymer (46% PEHA, 30K, BP06) processed in pellet mold at different pressures.

4.2.2.2 Effect of time on processing

Studies concerning time effect of baroplastic processing is carried out to prepare pellets of PS-*b*-PEHA-*b*-PS baroplastic tri-block copolymer (46% PEHA, 30K, BP06) using compression mold applying 300 kg/cm² for 1, 5, 10, 20 and 30 minutes interval.

DSC thermograms (Figure 4.7) of each sample introduce $T_{g,mix}$ value at around 66 °C that prove that the formation and composition of disordered phase is independent of time. Hence, 5 minutes is agreed as process duration and followed compression molding processes of this study has been kept as 5 minute.

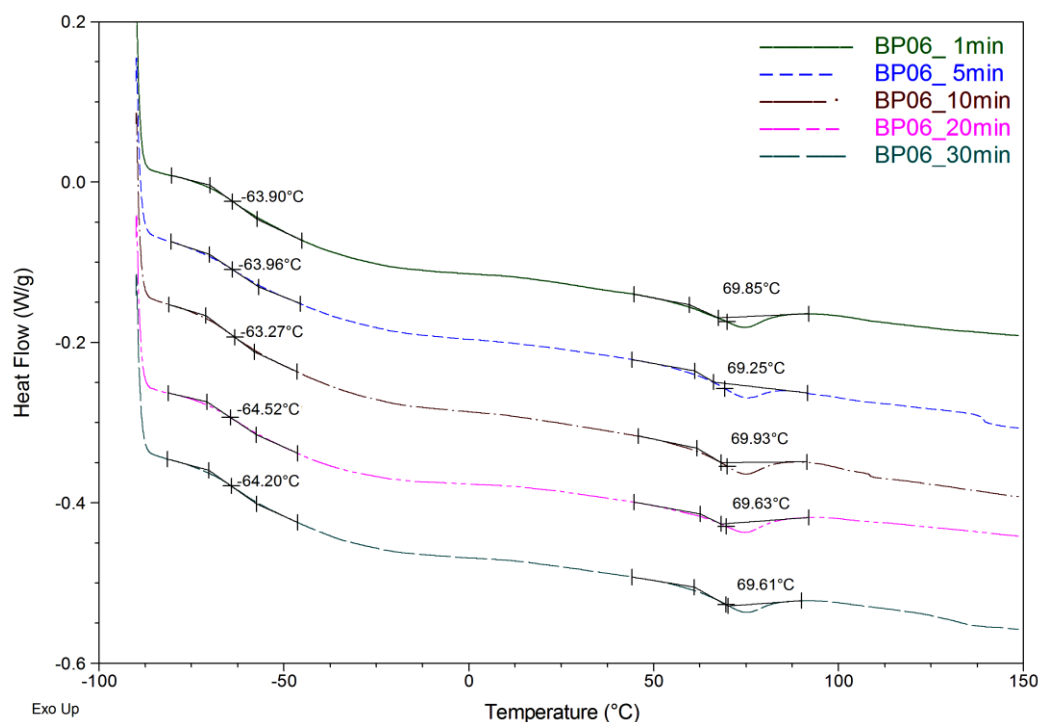


Figure 4.7 : Comparison of DSC thermograms of PS-*b*-PEHA-*b*-PS baroplastic tri-block copolymer (46% PEHA, 30K, BP06) processed in pellet mold at 50 kg/cm² for different times.

4.2.3 Composition / Morphological effects on processing

4.2.3.1 Molecular weight effect

Molecular weight is a restrictive parameter in commodity polymer processing as is in baroplastics. High molecular weight polymer melts are structurally complex fluids in that their macromolecules can assume many conformations, which become more stretched under flow, while gradually recovering into random conformations upon removal of the flow stresses.

One of the main processing parameters that molecular weight effects, is processing pressure. High molecular weight polymers require high pressure, since the viscosity of the system increases with increasing molecular weight. As increase of viscosity is inversely related with molecular mobility, it effects directly pressure ascribed phase mixing of baroplastics that is the driving force of processing.

In a study done by our research group, it was demonstrated that although block segments have favorable properties, block copolymers could not show baroplasticity if they have higher molecular weight value than its composition and topology allow [29].

In this research, further the ability of processing, the effect of high molecular weight on extruded samples was investigated by processing two baroplastics having same topology, PS-*b*-PEHA-*b*-PS tri-block, and composition, 40% PEHA, (30K, BP01 and 124K, BP02). As seen in the Figure 4.8-b, although material shows partially miscibility derived from DSC measurements (Figure 4.10), high molecular weight caused surface distortion on the extruded tape.

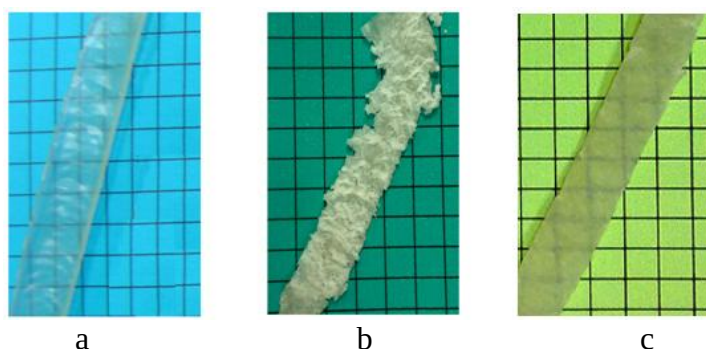


Figure 4.8 : Extruded PS-*b*-PEHA-*b*-PS tri-block samples a) 30K, 40%PEHA, BP01 b) 124K, 40%PEHA, BP02 c) 150K, 50% PEHA, BP09.

Since this phenomena is such like the observations of Denn and coworkers (Figure 4.9), it can be explain with their theories on extrusion instabilities:

- Adhesive failure at the wall,
- Cohesive failure within the material as a result of disentanglement of chains in the bulk and chains absorbed on the wall,
- Creation of a lubricating surface layer at the wall either by a stress-induced transition, or by a lubricating additive. If the polymer contains low molecular weight components or slip-additives, their diffusion to the wall will create a thin lubricating layer at the wall, generating apparent slip.

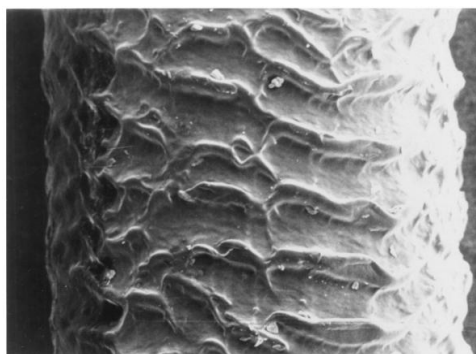


Figure 4.9 : Sharkskin surface of extruded low-density polyethylene observed in the stainless steel die.

The most common approach to sharkskinlike surface is that extruded polymer chains are stretched during this tensile deformation, which causes the highly entangled polymer to respond like a rubber. The large stresses on the surface cause cracks to open, probably by an undefined slip-stick mechanism analogous to the formation of Schallamach detachment waves in a rubber [44].

In our case, as PEHA is behaving as processing aid by decreasing the viscosity of baroplastics, to overcome this problem another high molecular weight baroplastic PS-*b*-PEHA-*b*-PS tri-block copolymer with higher PEHA% content (150K, 50% PEHA, BP08) was extruded to prove that increasing soft segment ratio provide processing of higher molecular weight block copolymers (Figure 4.8-c). Similarly, in the composition effect section, it will be proven that increasing PEHA% make easier processing.

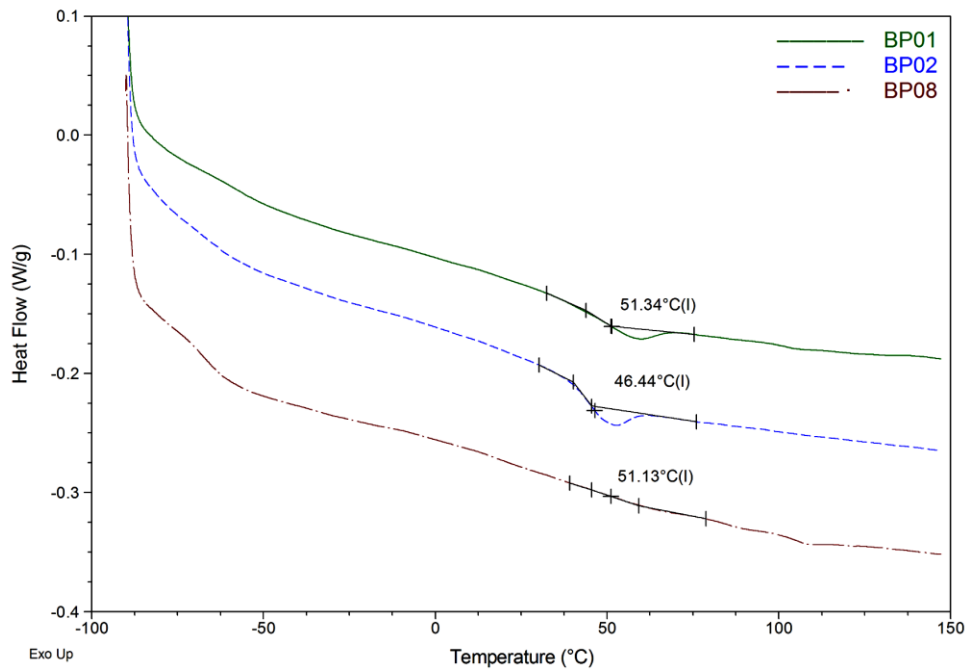


Figure 4.10 : DSC Thermograms of extruded PS-*b*-PEHA-*b*-PS tri-block samples for BP01 (30K, 40%PEHA), BP02 (124K, 40%PEHA) and BP09 (150K, 50% PEHA).

4.2.3.2 Composition effect

In previous studies, upper and lower limits for PEHA content for processable baroplastics at room temperature were determined by our group as 35% and 65% respectively that is already cited in Inceoğlu's PhD thesis [29]. PS amount lower than 35% cause an evident weakness on material. As expected, this soft material was processed under lower pressures. On the other hand, if PS content is higher than

65%, the product was brittle and opaque, actually like a compressed powder. At these compositions, the absence of mobility and coherence provided by low T_g phase was clearly perceived.

Another observation in this study, is done to discover the effect of content percentage of block segments on processing, especially in extrusion. To this end, baroplastic block copolymers with same topology, close molecular weight but different segmental compositions were processed using extrusion mold (Figure 4.11). The first difference realized was the variation of pressure. During study, minimum extrusion pressure is recorded for different PEHA contents and results were presented in Table 4.2.

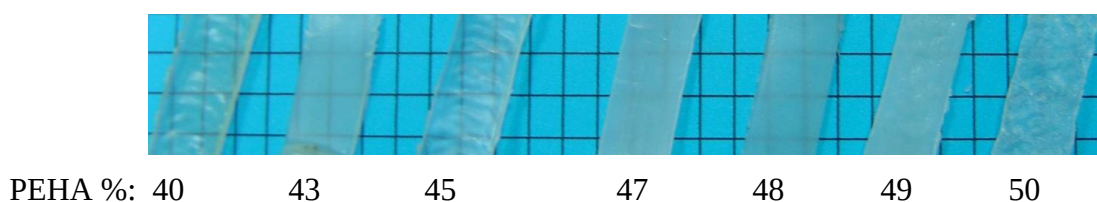


Figure 4.11 : The strip film images of PS-*b*-PEHA-*b*-PS baroplastic tri-block copolymers in different compositions obtained by extrusion process.

Table 4.2 : $M_{w,LS}$ and processing pressures of PS-*b*-PEHA-*b*-PS baroplastic tri-block copolymers.

Polymer	PEHA%	$M_{w,LS}$	Process pressure Ton (kg/cm^2)
BP01	40	33.6K	3.0 (150)
BP03	43	48.1K	6.0 (300)
BP04	45	40.8K	4.0 (200)
BP05	47	51.9K	2.0 (100)
BP06	48	38.7K	2.0 (100)
BP07	49	59.6K	1.5 (75)
BP08	50	37.3K	1.5 (75)

As mentioned above, the composition of block copolymer affects directly the process pressure. As predictable, and parallel to findings, increase of low T_g block results in softer material which can be shaped applying lower pressure. $T_{g,mix}$ values obtained from DSC measurements of extruded tapes is given in Figure 4.12.

Missing of a specific trend in $T_{g,mix}$ must not be confused with the expected trend of T_g derived from Fox equation for these indicated compositions. Because the mixed phase appeared by the process pressure is independent from block copolymer's

composition. $T_{g,mix}$ value depends only on the ratio of the PEHA and PS that are transformed from ordered state to disordered state and this hazardous ratio can be calculated by Fox equation. The main problem here, is that Fox equation gives only the composition of mixed phase nevertheless not render the quantity of any segment transformed to disordered state that can be helpful for understanding baroplasticity ratio (mixed phase/ordered phase).

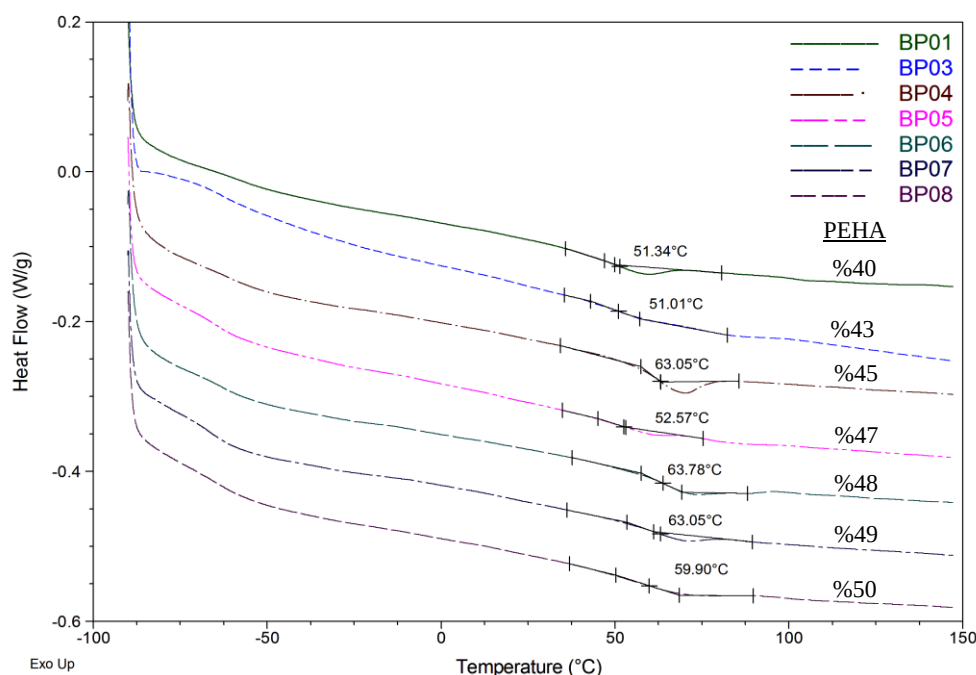


Figure 4.12 : DSC thermograms of extruded PS-*b*-PEHA-*b*-PS baroplastic tri-block copolymers.

4.2.3.3 Topology effect

Several polymer pairs with tri-block and star block topologies are compared for investigation of topology effect on processing. As mentioned in the literature [45], the main feature of star-shaped polymers differing them from the linear copolymers of identical molar masses (M_n), is their compact structure thanks to the smaller hydrodynamic volume and radius of gyration. This property results in lower viscosity that is helpful in processing applications.

Figure 4.13 shows DSC measurements of extruded PS-*b*-PEHA-*b*-PS tri-block copolymer containing 50% PEHA ($M_n = 30K$, BP08) and PEHA-*b*-PS-*b*-PEHA tri-block copolymers containing 51% PEHA ($M_n = 36K$, BP10) samples used for observing the effect of inversing inner and outer segments and it was concluded that this inversion has not an clear effect on processability in linear block copolymers.

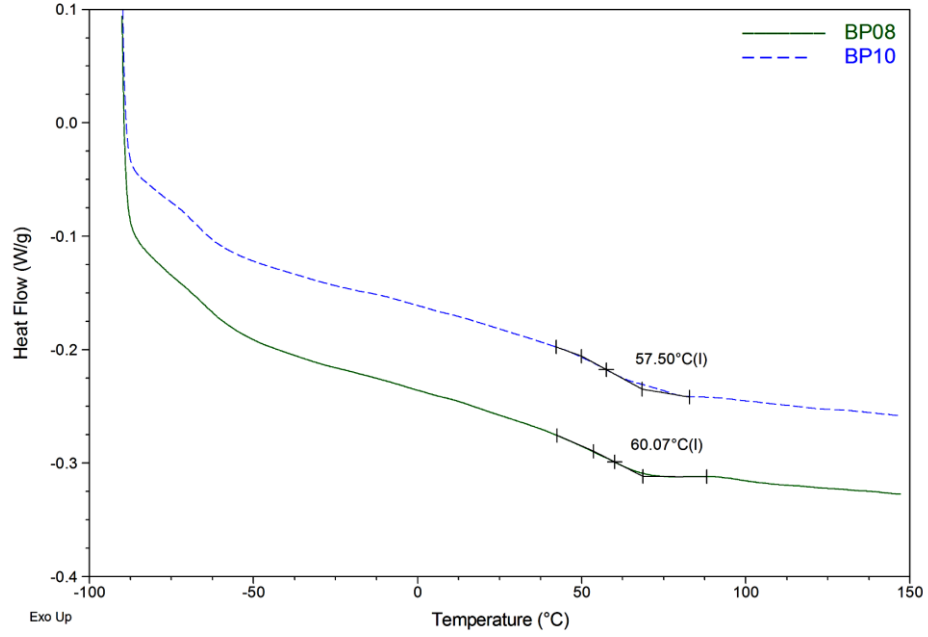


Figure 4.13 : DSC thermograms of extruded PS-*b*-PEHA-*b*-PS tri-block copolymer (50% PEHA, 30K, BP08) and PEHA-*b*-PS- *b*-PEHA star-block copolymer (51% PEHA, 36K, BP10).

Another comparison is done between PEHA-*b*-PS-*b*-PEHA tri-block copolymer ($M_{W,LS} = 38.5K$, BP06) and (PS-PEHA) $_4^*$ star-block copolymer ($M_{W,LS} = 155K$, BP12)both containing 48% PEHA in order to reveal the difference of star type and linear type block copolymers. Two samples are processed under close pressures ($\sim 100 \text{ kg/cm}^2$, 2 tons) despite high molecular weight of star-block copolymer.

As conclusion, in the light of this and Inceoglu's PhD [29] thesis studies it is evident that star-block copolymers require lower processing pressures than linear polymers due to their compact molecular structure which leads lower viscosity. Moreover, upper limit of molecular weight concerning well processing for star-block copolymers is higher than tri-block copolymers.

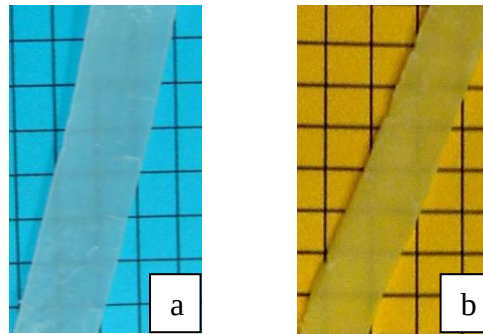


Figure 4.14 : Extruded samples of a) PEHA-*b*-PS-*b*-PEHA tri-block copolymer (48% PEHA, $M_{W,LS} = 38.5K$, BP06) and b) (PS-PEHA) $_4^*$ star-block copolymer (48% PEHA, $M_{W,LS} = 155K$, BP12).

4.2.4 Recycling performance of baroplastics

As expressed in theoretical part, melt processing of polymeric materials require high temperatures, over their T_m values. Melt plastics, are conducted through or inside the mold by applying pressure. These two necessary values are provided often by electrical energy. Five "R" are effective to prevent this energy consumption and polymeric waste growing due to limited recyclability. One of five is "redesign" as mentioned in part 2.4. Consequently, recycling abilities of our redesigned polymers, baroplastics, are investigated.

This work is done using PS-*b*-PEHA-*b*-PS tri-block copolymer (47% PEHA, 41K, BP05) and tape extrusion mold. Initially extruded baroplastic tapes under 3 tons (150 kg/cm²), are chopped into little pieces mechanically and are placed again into the extrusion mold. This job is repeated for 20 times.

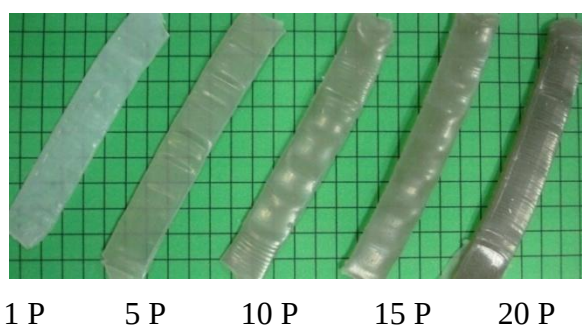


Figure 4.15 : 1, 5, 10, 15 and 20 times recycled strip shaped baroplastic tri-block copolymers (PS-*b*-PEHA-*b*-PS, 47% PEHA, 41K, B05).

1, 5, 10, 15, and 20 times recycled baroplastic tri-block copolymer tapes can be seen in Figure 4.15, respectively. "1p" corresponds to the initially extruded tape sample likewise "20p" corresponds to the 20 times extruded sample. This sequence is aborted after 20p because of discoloration, which is simply because of the metal and other contamination problem were occurred during the processing. As mentioned in mold design section, extrusion molds were worn because of friction arising between piston and mold surface. Further on this problem was solved by redesigning and manufacturing the mold by a more durable steel.

GPC traces of unprocessed and 20 times recycled samples prove by presenting very close molecular weights and polydispersity that degradation is out of subject even after the sample is 20 times recycled (Figure 4.16).

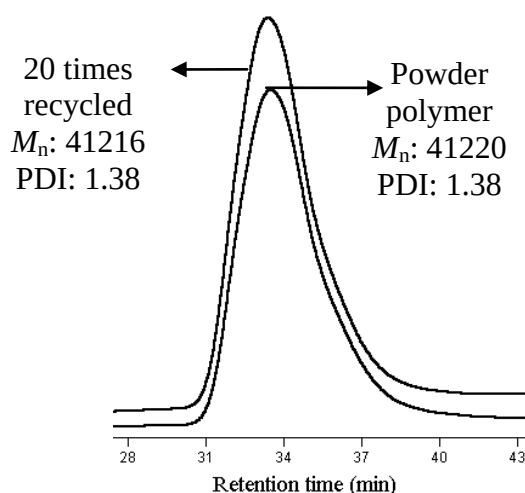


Figure 4.16 : GPC traces of raw and 20 times recycled PS-*b*-PEHA-*b*-PS tri-block copolymers (47% PEHA,BP05).

DSC thermograms of recycled samples presented in Figure 4.17 are quite impressive. By the iterated recycling, the $T_{g,mix}$ values of samples shows a shift leftwards, through the soft phase's T_g ($T_{g,PEHA}$). This situation can be explained by the additional participation of ordered PEHA to the mixed phase during each process cycle by the applied pressure. In other words total mixing was not achieved by a single process, but was gradually growing by processing cycles.

As explained previously, % composition of the mixed phases can be calculated by placing $T_{g,mix}$ values derived from DSC measurements (Figure 4.17), in Fox equation.

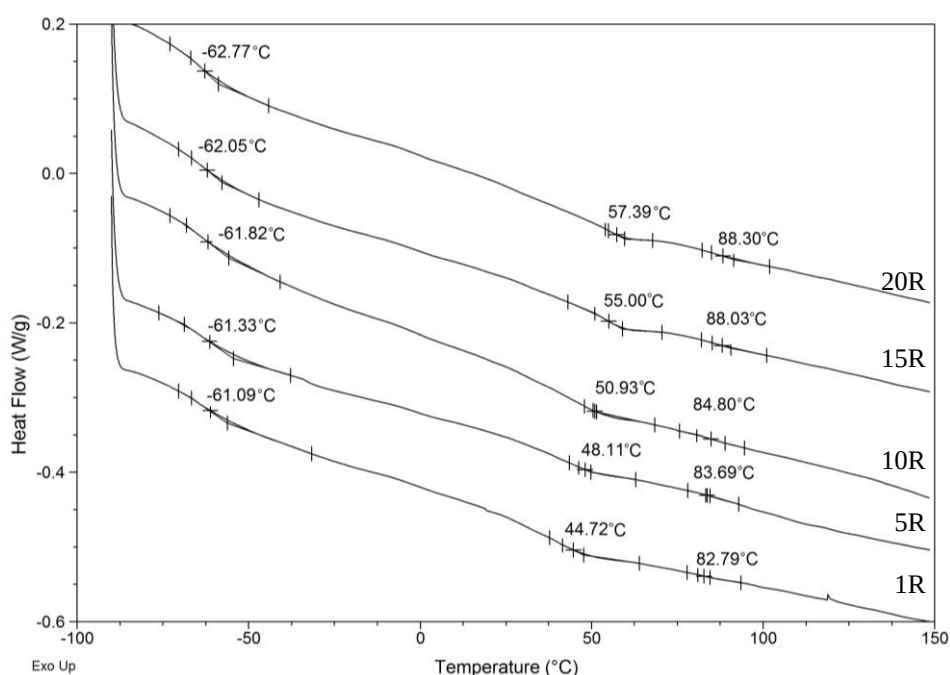


Figure 4.17 : DSC thermograms of 1,5,10,15,20 times recycled PS-*b*-PEHA-*b*-PS tri-block copolymers (47% PEHA, 41K, BP05).

Further on, under the agreement of persistent transformation of blocks from ordered to disordered phase for a single sample processed repeatedly, it can be predicted that after “n” times processing of a baroplastic, the system will become totally disordered like a miscible block copolymer. Hence, the $T_{g,mix}$ values of this case can be calculated easily as -25.55 °C by substituting T_g and weight fraction values into Fox equation.

Table 4.3 : $T_{g,mix}$ values and calculated PS% contents of the mixed phases for recycled PS-*b*-PEHA-*b*-PS baroplastic tri-block copolymer (47% PEHA).

Recycling number	$T_{g,mix}$ (°C)	PS (wt%)
1	57.39	83.54
5	55.00	82.57
10	50.93	80.89
15	48.11	79.69
20	44.72	78.23
n	-25.55	61.08

With the purpose of getting theoretically 173 as the “n” number of recycling, a graphical approach could be helpful as seen in Figure 4.18.

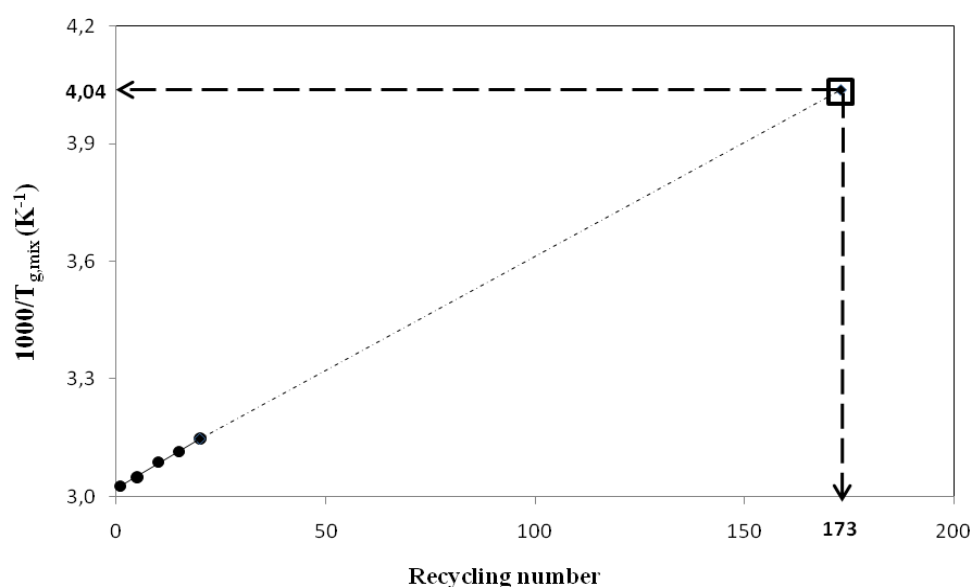


Figure 4.18 : Graphical estimation of the recycle number for total miscibility of baroplastic tri-block copolymer (PS-*b*-PEHA-*b*-PS, 47% PEHA, 41K, BP05).

It must be highlighted that each recycle produce a new polymer with different morphological structure. Moreover, after “n” times recycling, two normally immiscible blocks of a block copolymer, become miscible without passing through the ODT.

4.3 Mechanical Measurements (DMA, Tensile Tester)

4.3.1 T_g measurements by DMA tension test

DSC and DMA are valuable thermal analysis techniques that can be used to accurately characterize both thermal and mechanical properties of materials over a wide temperature range. Both can be used to determine the T_g of the polymers.

DSC record temperatures and heat flows as a function of time under controlled atmosphere. The signals on DSC thermograms are associated with endothermic or exothermic transitions occurred in materials. On the other hand DMA measures the modulus (stiffness) and damping (energy dissipation) properties of materials while deformed under a periodic stress. DMA is especially helpful for evaluating mechanical properties of polymeric materials under the effect of time, frequency, or temperature effects because of their viscoelastic nature. Because of DMA's inherent sensitivity to the glass transition, it is an ideal technique for identifying the T_g of complex systems however samples in form of film or tape are gigantic relative to few milligrams of DSC samples. Besides, this difference of sample weight of DMA provide high signal intensity which is came by using heating rates over 10 °C/min at DSC measurements. In spite, the limitation of DMA measurements is the heating rate, which must be lower than 5 °C/min to ensure homogeneity of thermal gradient.

DMA measurements are performed to a set of extruded baroplastic sample with similar topology but different composition using tension clamps (Figure 4.19). Same samples were used for determination of composition effect and DSC measurements were presented in relevant section. T_g values obtained using these two methods are listed in Table 4.4. In detail, "Inflection (start-end)" and "Onset of Storage Modulus" methods were used for DSC and DMA analysis respectively. A representative example for overlaid DSC and DMA measurements can be seen in Figure 4.20. The result is likewise mentioned in literature, measured T_g values are very close but DSC results are lower than DMA results [46].



Figure 4.19 : Tape sample view during DMA measurement.

Table 4.4 : DSC and DMA measurements of T_g values for different compositions PS-*b*-PEHA-*b*-PS tri-block copolymers.

Polymer	% PEHA	$T_{g,mix}$	
		DSC	DMA
BP01	40	51.32	60.45
BP03	43	51.48	51.69
BP04	45	62.09	64.78
BP05	47	52.67	N/A
BP06	48	63.75	51.46
BP07	49	63.03	73.13
BP08	50	60.08	64.72

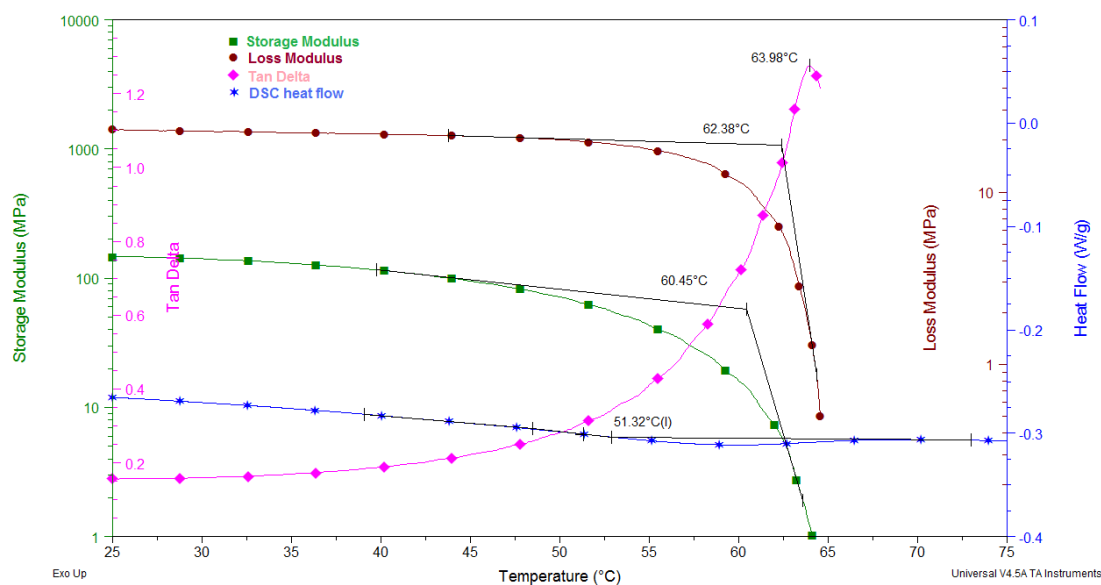


Figure 4.20 : Overlay of DSC and DMA $T_{g,mix}$ measurements of PS-*b*-PEHA-*b*-PS tri-block copolymer (% 40 PEHA, 30.3K, BP01).

The main purpose of this crosscheck, using another technique, was to prove that the endothermic signal appearing on DSC thermograms ($T_{g,mix}$) between T_g values of constituent polymers is really a glass transition temperature. Hence, it is achieved by investigation of sudden decrease in modulus.

4.3.2 Elastic modulus measurements

It is important to characterize the mechanical strength of a material before object for an application. DMA stress/relaxation tests are performed to get mechanical properties of baroplastic samples, but the tension clamps were not suitable for elastomeric materials and they caused the interrupt of the test because of sample slip or failure. So, the results of these measurements were done under unreliable conditions are shown in Figure 4.21 and 4.22.

The young modulus values measured from Figure 4.21 are 13.68 Mpa for PS-*b*-PEHA-*b*-PS, containing 40% PEHA, 3.87 MPa for PS-*b*-PEHA-*b*-PS, containing 47% PEHA and 2.071 Mpa for PEHA-*b*-PS-*b*-PEHA, containing 53% PEHA. As can be foreseen, strength of block copolymer increases with the decrease of soft segment percent. This statement is valid also for the PS-*b*-PEHA-*b*-PS baroplastic tri-block copolymers consist of 43% and 45% PEHA segment having 28.46 and 38.10 MPa modulus respectively.

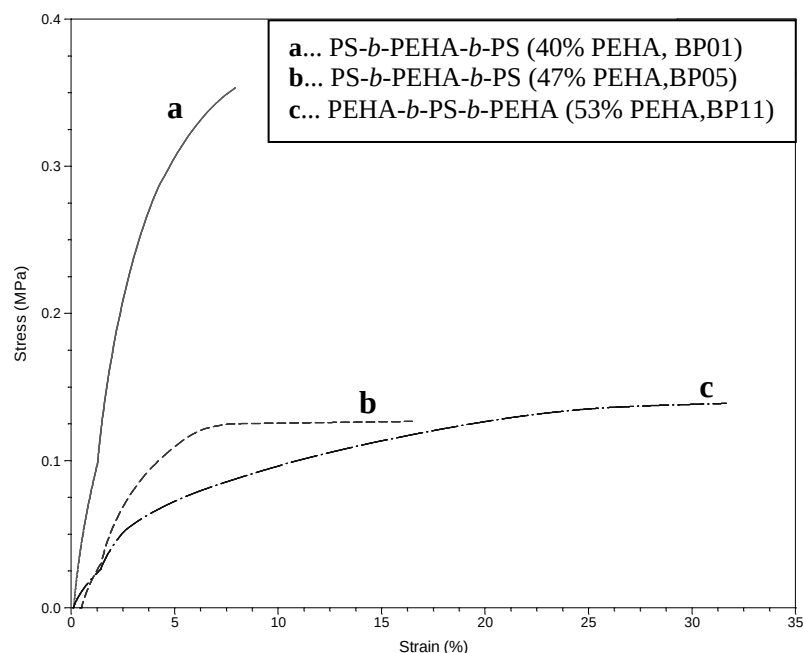


Figure 4.21: Stress-strain curves of PS-*b*-PEHA-*b*-PS (40% PEHA, BP01 and 47% PEHA, BP05) and PEHA-*b*-PS-*b*-PEHA (53% PEHA, BP11) block copolymers.

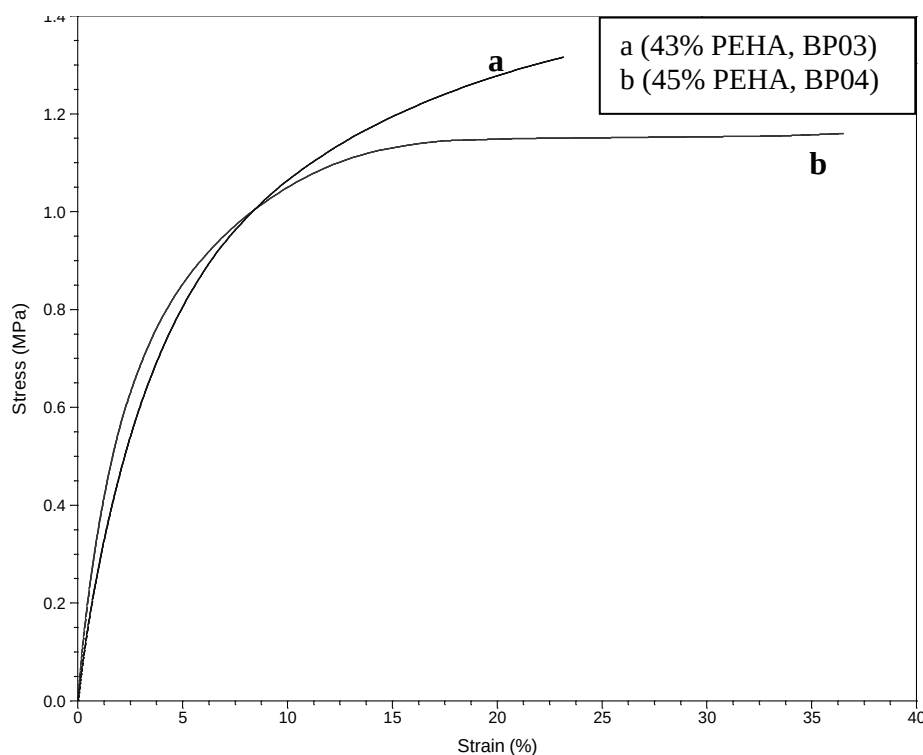


Figure 4.22 : Stress-strain curves of PS-*b*-PEHA-*b*-PS triblock copolymers a) 43% PEHA BP03 and b) 45% PEHA BP04.

For better measurements of elastic modulus, another instrument, Zwick universal testing machine equipped with clamps for elastomeric materials is used. The results for same samples are given in Table 4.5.

Table 4.5 : Comparison of mechanical properties of PS-*b*-PEHA-*b*-PS tri-block copolymers with different compositions.

Polymer	PEHA%	Young's Modulus (MPa)
BP01	40	-
BP03	43	~90
BP04	45	~60
BP05	47	-
BP06	48	~50
BP07	49	-
BP08	50	~20

4.4 Surface Measurements (Goniometer)

In recent works on surface analysis of polymer solids, it was reported that in multicomponent polymers, surface segregation occurs as the low surface tension component is preferentially enriched on the film surface [47]. However on this study, surface tension, γ_c , of PEHA and PS segments composing the baroplastic block copolymer have close surface tension values as noted in the literature ($\gamma_{c,PEHA} = 31$ mN/m, $\gamma_{c,PS} = 33$ mN/m) [48].

4.4.1 Measuring surface tension of test liquids

For determination of the total surface free energy, SFE, of the samples surfaces, Zisman plot was used. As mentioned in theoretical part, this method stands on contact angle measurements of multiple test liquids having different surface tensions.

In this research, to compose the Zisman plots of surfaces, contact angles and surface tensions of five test liquids that were available in our laboratory are measured: water, monopropylene glycol, methanol, glycerol and ethylene glycol. Contact angle measurement procedures will be explained in the next section. As for surface tension, pendant drop method is used (Figure 4.23). Surface tension values measured by KSV CAM software and given in literature [49] were listed in the table 4.6.

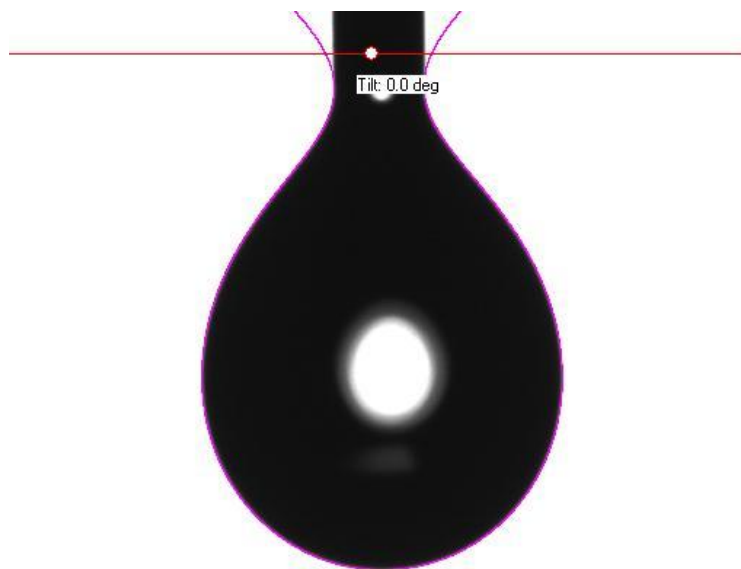


Figure 4.23 : Surface tension measurement of water by pendant drop method.

Table 4.6 : Surface tension values of test liquids.

Test Liquid	Surface Tension Measured (mN/m)	Surface Tension Literature (mN/m)
Water	73,04	72,80
Glycerol	63,94	64,00
Ethylene Glycol	48,09	47,70
Monopropylene Glycol	37,45	36,00
Methanol	23,08	22,70

4.4.2 Contact angle and surface free energy measurements

In this work, contact angle measurements were done by the equilibrium drop method. Camera was captured sixty frames for each drop then CAM software has fitted curves to these drops by Young Laplace model (Figure 4.24).

For each image left and right contact angles was calculated and mean value was recorded. Hence, mean value of all images is accepted as contact angle of that drop. For each sample, contact angle of 5 drops of each liquid on fresh surfaces is measured in order to eliminate testing errors. Consequently, the arithmetic mean of best three value is recorded as contact angle value of that liquid on measured sample. However, due to the non-controlled ambient conditions (e.g. humidity, fluctuating temperature) and surface roughness caused by processing,

Contact angle measurements results and Zisman plot of solvent cast and processed film of PS-*b*-PEHA-*b*-PS tri-block copolymer, (47% PEHA, BP05) were presented at Table 4.7 and Figure 4.25.

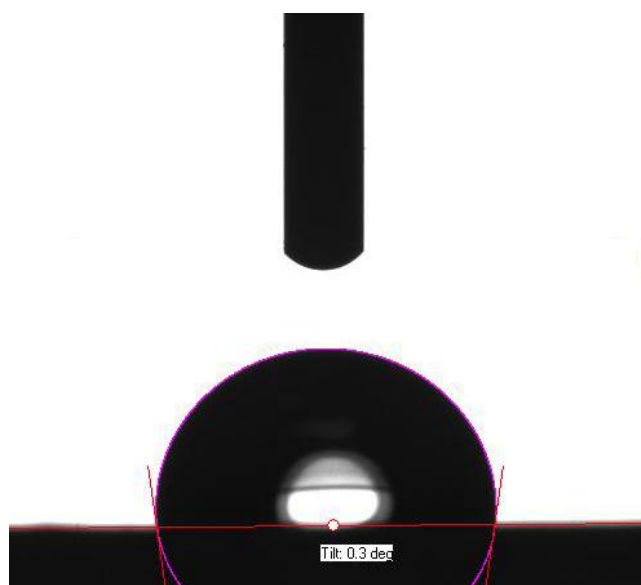
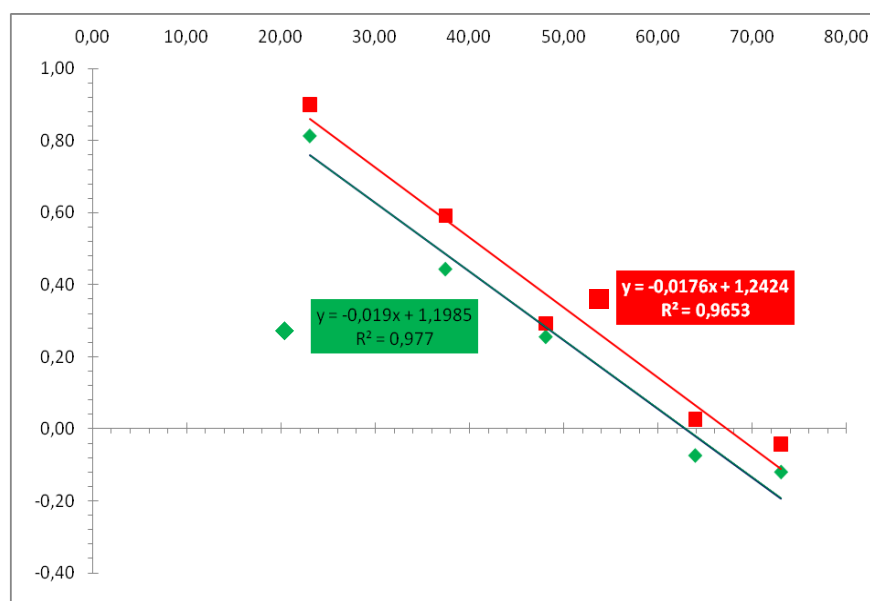


Figure 4.24 : Contact angle measurement of water on PS-*b*-PEHA-*b*-PS 43%, BP03

Table 4.7 : Contact angle values of PS-*b*-PEHA-*b*-PS (47%, BP05).

Test Liquid	Surface Tension of Test Liquid	Contact Angle of Sol. Cast Film	Contact Angle Processed Film
Water	73.04	97	92
Glycerol	63.94	94	88
Ethylene Glycol	48.09	75	73
Monopropylene Glycol	37.45	64	54
Methanol	23.08	36	26

Surface energies derived from the trendline equations of contact angle measurements of solvent casted and processed samples are 7.77 mN/m and 13.77 mN/m respectively.

**Figure 4.25 :** Overlaid Zisman Plots of solvent cast and processed PS-*b*-PEHA-*b*-PS tri-block copolymer (47%, BP05).

4.4.3 Recycle effect on surface free energy

For investigation of recycle effect on surface free energy, PS-*b*-PEHA-*b*-PS (43% PEHA, BP03) tri-block copolymer films are processed 5 times between two special steel plate at 6 Tons. The results were shown in Table 4.8.

Table 4.8: Contact angle values of PS-*b*-PEHA-*b*-PS (43% PEHA, BP03)

Test Liquid	Surface Tension of Test Liquid	Contact Angle of Sol. Cast Film	Contact Angle of Processed Film	Contact Angle of Recycled Film
Water	73.04	99	94	96
Glycerol	63.94	86	94	92
Ethylene Glycol	48.09	73	70	75
MPG	37.45	60	58	62
Methanol	23.08	24	24	27

Surface energies derived from the trendline equations of contact angle measurements of solvent casted, processed and recycled samples are 15.75 mN/m, 16.29 mN/m and 13.82 mN/m, respectively.

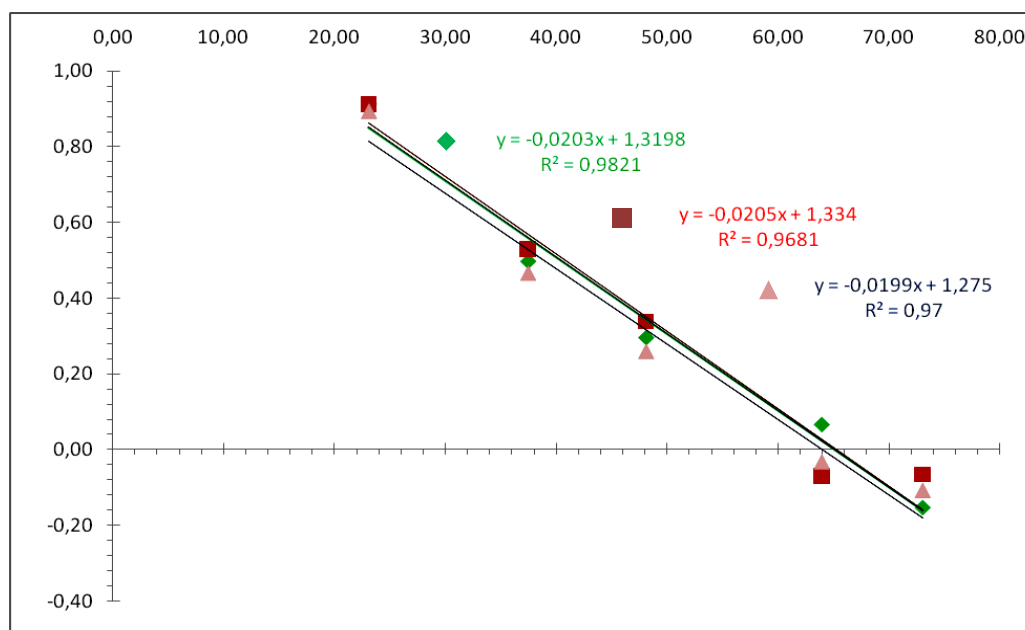


Figure 4.26 : Overlaid Zisman Plots of solvent cast, processed and 5 times recycled tri-block copolymer, PS-*b*-PEHA-*b*-PS (43% PEHA, BP03)

4.5 Morphological Measurements (AFM)

TappingMode[®] atomic force microscopy imaging was used to visually stand over phase behaviors under the effects of processing and recycling. For AFM measurements of baroplastics, four types of samples were prepared. For unprocessed materials, solution cast films was prepared on mica substrate. Dichloromethane was used as solvent to adjust 5% (w/v) solution. Annealing around 120 °C, over T_g value of segments was performed to erase thermal history and to ensure total microphase separation before processing. Once and multiple (5, 10, 20 times) extruded baroplastic tapes were used as extruded samples, respectively. Recycled baroplastic tapes annealed to return in ordered state were measured by AFM to prove total recycling.

Baroplastic sample used in this study is PS-*b*-PEHA-*b*- PS, with 47% PEHA content. In the first image, at top of the left, it is clearly seen that before process, the annealed sample shows a sharp phase orientation. After the first process, under pressure at room temperature, this impressive order is disappeared and a dispersed morphology

is composed of ordered (phase-separated) and disordered (mixed phase) structures (Figure 4.27). Till this section the partially miscibility phenomenon was presented with DSC results, thus, it has been visually demonstrated too. In the following phase images of 5, 10 and 20 times recycled materials, it can be recorded that the mixed phase appeared at the first process, is grown step by step in parallel with the reduction of the microphase separation.

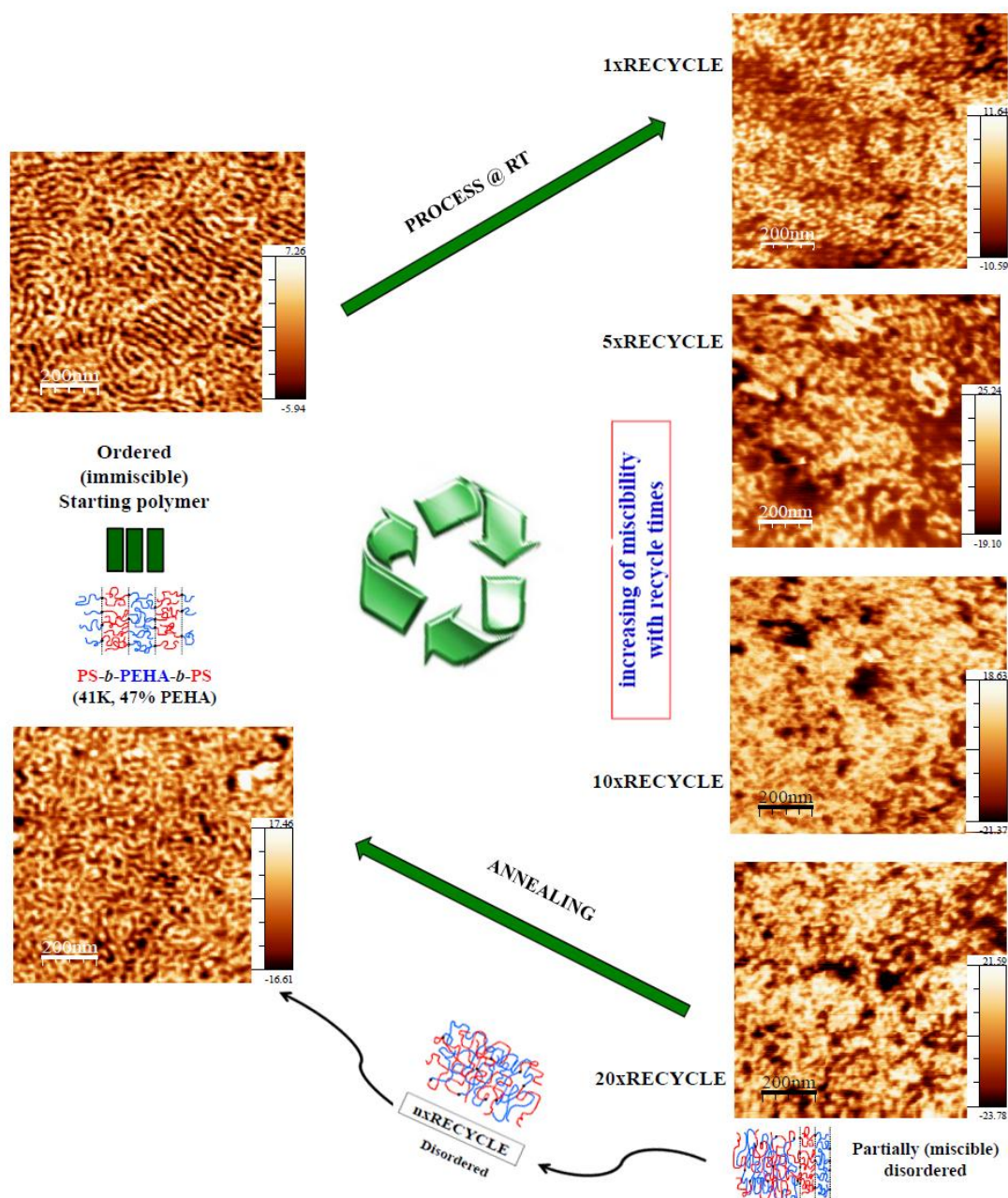


Figure 4.27 : AFM images of before processing, after processing, recycled and annealed after processing films of PS-*b*- PEHA-*b*-PS containing 47% PEHA

Further on, 20 times extruded sample was annealed and due to the annealing effect on molecular conformation, microphase separated structure was reconstructed. After seeing the ordered structure in AFM image of this annealed sample, it is clearly demonstrated that the material was “resetted”. Thus, at any recycle stage, the material can be return to its initial state by using this reset steps whereby we open a window to the infinite recycling.

5. CONCLUSION

This thesis is pointed on block copolymers consist of immiscible soft and hard segments but showing pressure-induced miscibility at room temperature which is named baroplasticity. It was recently published that di, tri, star-block copolymers and core-shell nanoparticles consist of PS and PEHA segments within 35 and 65% PEHA composition range have baroplastic properties. In this study, synthesized copolymers are characterized by thermal, mechanical, microscopical and optical methods.

After synthesis of block copolymers, to check its baroplasticity, polymer powders were processed by compression mold under pressure provided by hydraulic presses. Further on, to be more sure they are extruded using the wire or strip mold at room temperature.

Formation of mixed domains having a single T_g value, $T_{g,mix}$, in the microphase separated matrix having two distinct T_g values, is the effect of partially miscibility in immiscible block copolymers due to the pressure applied for processing.

DSC measurements were essential reference at each step of this study, being aware in $T_{g,mix}$ as distinct expression of the transition from ordered to disordered structure by applying pressure at room temperature. Favorable DMA results supporting DSC findings on $T_{g,mix}$ were derived. Moreover, this behavior was presented visually by AFM analysis.

A series of conditions were experimented to execute accurate and repeatable DSC measurements. Thus, heating rate and sample mass parameters were taken 10 °C/min and 7 mg, respectively.

Optimum processing time and pressure were investigated by performing processes under different pressures and different time intervals. It was demonstrated that 5 min is enough for processing the baroplastic under appropriate pressure, in addition it was understood that exceeding pressure is wasted.

Two baroplastic PS-*b*-PEHA-*b*-PS block copolymers with similar composition (40% PEHA) but having different molecular weights (30 and 124K) were used to observe

molecular weight effects. It was recorded high molecular weight requires higher processing pressure and cause “Sharkskinlike” surface distortions because the limited mobility of high molecular weight chains. Additionally, it was proven that increasing PEHA percent provide processing of high molecular weight copolymers.

Baroplastic linear block copolymers with inversed topologies (PS-*b*-PEHA-*b*-PS and PEHA-*b*-PS-*b*-PEHA) were compared and it was concluded that this inversion has not a clear effect on processability. However when a linear and a star-block copolymer (PEHA-*b*-PS-*b*-PEHA and (PS-PEHA)*4) was in case, it was seen that star block copolymers have further advantages especially in processability of high molecular weight block copolymers.

It was studied also block copolymer composition effect on processability using a series of PS-*b*-PEHA-*b*-PS tri-block copolymers with different PEHA contents in a range of 40-50% and close molecular weights around 40 Kg/mol. They were processed by tape extrusion mold and during processing it is noticed that higher PEHA containing block copolymer requires lower pressure likewise decreasing PEHA content requires higher processing pressure.

Despite difficulties due to the clamps, mechanical tests of these samples were exhibited by DMA and tensile tester. Consequently, as expected, increasing soft segment content was resulted in an evident decrease in strength of baroplastic material.

Surface tension and contact angle measurements were done to probe surface energy of baroplastics and the effect of processing on surface properties. However, the results were not repeatable and accurate due to the rough surface and non-controlled ambient conditions.

One of the significant topics of this study was recycling. Till this thesis 20 processing cycles (chop+extrude) has been performed to the sample without any molecular degradation that was supported by GPC measurements. It was seen that miscibility was gradually growing by processing cycles as driven from $T_{g,mix}$ decreasing observed from DSC measurements. And theoretically shown that after “n” processing cycle, baroplastics would show totally mixed phase structure. Then it was discovered that multiple recycled polymer has the ability to regain its initial phase-separated morphology after annealing.

All of these steps were supported by AFM measurements that display phase separation before processing; increasing disorder by recycles number and return to initial order after annealing. Therefore, it was proved that baroplastic materials can be recycled infinitely.

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