ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

DEVELOPMENT OF PBT/RECYCLED PET BINARY BLENDS

M.Sc. THESIS

Hazal OĞUZ

Department of Materials&Metallurgical Engineering

Materials Engineering Programme

Thesis Advisor: Assist. Prof. Dr. Mohammadreza NOFAR

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

PBT/GERİ DÖNÜŞTÜRÜLMÜŞ PET HARMANLARININ GELİŞTİRİLMESİ

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Hazal Oğuz, a M.Sc. student of İTU Graduate School of Science Engineering and Technology student ID 506141414, successfully defended the thesis entitled “DEVELOPMENT OF PBT/RECYCLED PET BINARY BLENDS”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my dearest family,

FOREWORD

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June 2017

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ABBREVIATIONS

PET : Poly (ethylene terephthalate)
PBT : Poly (butylene terephthalate)
TSE : Twin screw extruder
LCST : Lower critical solution temperature
UCST : Upper critical solution temperature
TEM : Transmission electron microscopy
SEM : Scanning electron microscopy
AFM : Atomic force microscopy
SSE : Single screw extruder
IM : Injection molding
BDO : 1,4-butanediol
DMT : Dimethyl terephthalate
TPA : Terephthalic acid
DSC : Differential scanning calorimetry
BHET : Bis-(2-hydroxyethyl)-terephthalate
EG : Ethylene glycol
PMDA : Pyromellitic di-anhydride
MFR : Melt flow rate
DMA : Dynamic mechanical analysis
FT-IR : Fourier transform infrared spectroscopy
HPLC : High performance liquid chromatography
GC : Gas chromatography
DAD : Diod-array detector
MS : Mass spectroscopy
FID : Flame ionization detector
PVC : Poly (vinyl chloride)
PE : Poly ethylene
TCE : Tetrachloroethylene
PVA : Poly (vinyl acetate)
TGDMM : Tetra-glycidyl diamino diphenyl methane
HDT : Heat deflection temperature
C-NMR : Carbon nuclear magnetic resonance
SANS : Small angle neutron scattering
H-NMR : Hydrogen nuclear mahnetic resonance
XRD : X-ray diffraction
MVR : Melt volume rate
TGA : Thermal gravimetric analysis
WAXD : Wide angle X-ray diffraction
MFI : Melt flow index
MFR : Melt flow rate
TGA : Thermal gravimetric analysis

SYMBOLS

ΔG_m : Gibbs free energy of mixing
ΔH_m : Enthalpy of mixing
ΔS_m : Entropy factor of mixing
η : Intrinsic viscosity
γ : Shear rate
T_g : Glass transition temperature
T_m : Melting temperature
ΔH_{mPBT} : PBT crystal melting temperature
$\Delta H_{mr\text{-}PET}$: Recycled PET crystal melting temperature
T_{cr} : Crystallization temperature
ΔH_{cr} : Crystallization enthalpy

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DEVELOPMENT OF PBT/RECYCLED PET BINARY BLENDS

SUMMARY

For many years, polymer science and technology presents an attractive field in researches on materials. For engineering applications, polymers can be classified as thermoplastics, thermosets and elastomers. Thermoplastic polymers possess a wide range of physical, chemical, thermal and mechanical properties. They possess areas of usage in commodity, engineering and advanced applications.

A polymer blend is basically defined as a physical mixture of two or more polymers that have been blended together to obtain a new material with varying physical and mechanical properties. Polymer blending is a cost effective way to develop new materials with desired final properties, improved processability of the materials and widen usage of recycled plastics. They can be designed at specific compositions to satisfy the properties that are desired in various applications, while individual polymers have their inherent property profiles with limited number of applications. Polymer blends can be classified according to their phase behavior into either miscible or immiscible. While miscible polymer blends are single-phase down to molecular level, immiscible polymer blends are phase separated in the microstructure. Further compatibilization is required for immiscible polymer blends for formation of stable blends at the amorphuous phase.

Poly (butylene terephthalate) (PBT) and poly (ethylene terephthalate) (PET) are aromatic polyester thermoplastics which are mostly used in engineering applications. Chemical stuctures of PBT and PET are quite similar with each other and they may undergo transesterification reactions under high temperatures. Therefore, PBT and PET form stable blends without requiring compatibilizers due to their miscibility at the amorphous phase. However, cystallization rate of PBT is higher than PET due to existence of butylene flexible groups in its molecular structure. Furthermore, in comparison with PET, PBT has better processability due to its higher melt strength. PBT/PET blends have been developed principally to improve processability, surface appearance and dimensional stability of molded parts. These blends also take advantage of low cost of PET and the rapid crystallization rate of PBT. PBT/PET blends are utilized in home appliances and automotive applications where high stiffness, heat and chemical resistance and glossy surface appearance is required.

For more than 50 years, global production of plastics raised and became one of the fastest-growing global materials in industry. However, recovery and recycling, remain a serious challenge. Millions tons of plastics end up in oceans and landfills each year. In this thesis study, by considering the increase in environmental pollution and being supportive to the environmental sustainability, recycled PET flakes from bottle wastes were used in the blends. Recycled polymers in comparison with virgin polymers could be degraded by many factors. The deterioration of recycled polymers in quality and stability, mechanical and physical properties, thermal properties and surface appearance could limit their further applications. Therefore, determination of the degree of mixing with other polymeric fractions, degradation caused by contaminations, previous processing conditions and low molecular weight compounds is essential to quarantee the use of recycled polymers to manufacture new products. In particular, in presence of water and poly (vinyl chloride) in the recycled PET promotes chain scission and decrease in molecular weight during re-processing at high temperatures. One of the solutions to improve the degraded properties of the recycled polymers is blending with virgin polymers. Another solution in order to overcome the problems caused by depression in molecular weight and improve the melt strength is using chemical agents that possess reactive functional groups. These chemical agents behave as a bridge between corrupted chains of polymers through their functional end groups. This is called as chain extension. The use of certain additives with reactive functional groups during melt processing is called as reactive extrusion, since polymer chemistry is modified during melting by using the extruder as a reactor.

In this thesis study, twin-screw extruder (TSE) was used for producing PBT/recycled PET blends. Injection molding was used to prepare testing specimens. Raw materials and extruded pellets were dried in an oven overnight to avoid further degradation in the presence of moisture during extrusion and injection molding processes. A commercial chain extender with Joncryl ADR 4468 ® trade name was used in the blends. Joncryl is a multi-functional styrene acrylic oligomer with epoxy functional groups. First of all, 0.05, 0.25, 0.40 and 0.80 wt% of Joncryl was physically mixed with recycled PET flakes and extruded to obtain extended recycled PET. During blending, 25, 50 and 75 wt% of recycled PET flakes was physically mixed with PBT and extruded. Addition of Joncryl into the blends was carried out via two different extrusion method. In the first method, which was named as all together method, PBT, recycled PET flakes and Joncryl were physically mixed and extruded all together to the pellets from a hopper. In the second method, which was named as premixing method, recycled PET flakes were extended with Joncryl in extrusion previously. Extended PET pellets were dried in an oven overnight, and then physically mixed with PBT at certain ratios and extruded from a hopper to obtain final blends.

In this thesis study, the effect of vaiorus concentrations of recycled PET on PBT/recycled PET binary blends were investigated. Furthermore, the effect of different blending methods on the final blend performances were examined. Various concentrations of chain extender additive was used in both production methods. As an example, PBT/recycled PET were blended and extruded at 75:25 ratios. Addition of chain extender is carried out by using two different processing methods, as mentioned above. In the all together method, 0.2 wt% of chaine extender was physically blended with around 75 wt% of PBT and 25 wt% of recycled PET flakes and extruded all together from a hopper. In the premixing method, recycled PET flakes were blended with 0.8 wt% Joncryl and extruded from a hopper. After drying, 25 wt% of this masterbatch was blended with 75 wt% of PBT and extruded from a hopper. The final Joncryl content was adjusted to be 0.2 wt% as in the first method. Only in 50:50 and 25:75 PBT/recycled PET blends, effect of different chain extender concentrations on the blend properties were examined. To achieve the final 0.2 wt% content of chain extender also in 50:50 and 25:75 PBT/r-PET blends, extended recycled PET with 0.4 and 0.25 wt% of chaine extender was used, respectively. Only in 50:50 and 25:75 PBT/recycled PET blends, effect of different final Joncryl concentrations on the blend properties were examined. The extended r-PET with 0.8 wt% of chain extender mixed with PBT at the ratios of 25, 50 and 75 wt%. Effect of this premix concentration on the blend properties were also investigated.

Thermal degradation, crystallization behavior, viscoelastic properties, tensile and impact properties of the blends were investigated. Thermal properties and crystallization behavior of the blends were investigated by using thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). Dynamic mechanical analysis (DMA) and melt flow index (MFI) was used for investigation of viscoelastic properties of the blends. Tensile strength and modulus was obtained from tensile testing. Impact strengths of the blends were obtained from Izod notched impact testing.

In thermal analysis, nucleation point effect of chain extender were observed in branched r-PET molecules. All blends either with chain extender or not showed single glass transition temperature during first and second heating cycled in DSC, which could be attributed to miscibility at amorphous state. Separate crystal melting temperatures in first heating cycle turned into a single peak with some shoulders in second heating, consequently miscibility could be observed depending on cooling rate. At constant chain extender concentration, blends prepared with all-together mixing method showed higher crystallinity. In DMA analysis, blends prepared with pre-mixing method showed higher storage modulus. Complex viscosity also supported the same behavior. Damping values from tan delta graphs was relevant with impact resistance of the materials. Increasing amount of chain extender decreased melt flow rate in MFI analysis, consequently increased melt strength by increasing molecular weight. All blends prepared by all together mixing method showed lower melt flow rate. E modulus and tensile strength of all blends was in the same range and was not affected from the compositions, chain extender concentration or processing strategies.

PBT/GERİ DÖNÜŞTÜRÜLMÜŞ PET HARMANLARININ GELİŞTİRİLMESİ

ÖZET

Polimer bilimi ve teknolojileri, uzun yıllardır, malzeme konusunda yapılan araştırmaların ilgi alanlarından birini oluşturmaktadır. Mühendislik uygulamalarında kullanılan polimerler, termoplastikler, termosetler ve elastomerler olarak üç grupta sınıflandırılabilir. Termoplastikler; geniş fiziksel, kimyasal, termal ve mekanik özellikleri ile günlük, mühendislik ve gelişmiş uygulamarda sıklıkla kullanılan malzemelerdir.

Polimer harmanları, farklı fiziksel ve mekanik özelliklere sahip yeni malzemelerin elde edilmesi için, iki ya da daha fazla polimerin fiziksel karışımı ile meydana gelmektedir. Polimer harmanlama, istenilen özelliklerde malzemenin üretilmesi, plastiklerin performansının arttırılması gibi amaçlar doğrultusunda geliştirilen, geri dönüştürülmüş plastiklerin kullanımını yaygınlaştıran maliyet etkin bir yöntemdir.

Poli (butilen tereftalat) (PBT) ve poli (etilen tereftalat) (PET), aromatik polyesterler sınıfına ait mühendislik termoplastikleridir. PBT ve PET kimyasal yapıları birbirine benzeyen ve yüksek sıcaklıklarda transesterifikasyon reaksiyonuna girebilen termoplastiklerdir. Bu sebeple, uyumlaştırıcı kullanılması gerekmeksizin amorf durumda birbiri içinde karışan harman oluştururlar. Ancak, PBT, PET ile kıyaslandığında yapısındaki esnek butilen grupları sayesinde daha yüksek kristalizasyon hızına sahiptir. Ayrıca, PBT daha iyi eriyik mukavemete sahip olduğundan, proses edilmesi daha kolaydır. PBT/PET harman malzemeleri ilk olarak prosesi, yüzey görüntüsünü ve kalıplanmış parçaların boyutsal stabilitesini geliştirebilmek amacı ile üretilmiştir. Bu malzemeler PBT' nin yüksek kristalizasyon hızı ve PET' in düşük maliyetinden yararlanmaktadır. PBT/PET harman malzemeleri, uygun mekanik dayanıma, yüksek ısı ve kimyasal dayanıma sahip olması gereken ev ve mutfak aletlerinde, otomotiv parçalarında kullanılmaktadır. PBT/PET harman malzemeleri ve kompozitleri ayrıca yüksek parlaklığa sahip olması gereken görsel plastik parçalarda da sıklıkla kullanılmaktadır.

Bu tez çalışmasında, artan çevresel kirlilik göz önünde bulundurularak PBT içerisine şişe atıklarından geri dönüştürülmüş PET çapakları eklenmiştir. Geri dönüştürülmüş PET çapaklarının molekül yapısı, pek çok sebep ile bozunmuş olabilir. Fiziksel, mekanik, termal ve yüzey özelliklerindeki bozunmalar geri dönüştürülmüş polimerlerin bir sonraki uygulamarını zorlaştırmaktadır. Özellikle nem ve polivinilklorid (PVC) varlığında geri dönüştürülmüş PET yüksek sıcaklıklarda prosese girdiğinde molekül zincirlerinin kopması hızlanabilmekte ve son ürün özellikleri düşebilmektedir. Bozunan özellikler, başka bir polimer ile harmanlama yolu ile geliştirilebilir. Ayrıca, geri dönüştürülmüş plastiklerin molekül zincirlerinin yeniden bağlanması için zincir bağlayıcı kimyasal ajan adı verilen katkılar da kullanılabilmektedir. Bu katkılar, moleküllerine bağlı fonksiyonel gruplar sayesinde eriyik proses sırasında kırılan polimer molekül zincirleri arasında köprü oluşturarak, geri dönüştürülmüş polimerin molekül ağırlığını, eriyik mukavemetini ve son ürün

performansını arttırabilmektedir. Reaktif gruplara sahip katkılar kullanılarak yapılan eriyik prosesler reaktif eriyik proses olarak adlandırılmaktadır.

Bu tez çalışmasında, PBT/geri dönüştürülmüş PET harmanları çift vidalı ekstrüder kullanılarak üretilmiştir. Ekstrüder ile üretilen pelletler enjeksiyon kalıplama kullanılarak test numuneleri haline getirilmiştir. Zincir bağlayıcı ajan olarak ticari adı Joncryl ADR 4468 ® olan epoksi reaktif gruplara sahip multi-fonksiyonel stiren akrilik katkı malzemesi kullanılmıştır. Öncelikle, geri dönüştürülmüş PET çapakları, sırasıyla ağırlıkça % 0.05, % 0.25, % 0.40 ve % 0.80 Joncryl ile fiziksel olarak karıştırılarak ekstrüder prosesinde pellet haline getirilmiştir. Harman hazırlanırken geri dönüştürülmüş PET, PBT içerisine ağırlıkça % 25, 50 ve 75 oranlarında eklenmiştir. Joncryl, PBT/geri dönüştürülmüş PET harmanlarına eklenirken iki yöntem kullanılmıştır. Birinci yöntemde, PBT, geri dönüştürülmüş PET çapakları ve Joncryl katkı malzemesi fiziksel olarak karıştırılarak ekstrüderde pelletler üretilmiştir. İkinci yöntemde, geri dönüştürülmüş PET çapakları belli oranlarda Joncryl ile karıştırılarak ekstrüderde pelletler üretilmiştir. Üretilen bu pelletler, kurutma işleminin ardından PBT ile fiziksel olarak karıştırılarak tekrar ekstrüderde harmanlanmış ve son ürün haline getirilmiştir.

Bu tez çalışmasında, farklı oranlarda geri dönüştürülmüş PET kullanmanın PBT/geri dönüştürülmüş PET harmanları üzerine etkisi incelenmiştir. Ayrıca, geliştirilen iki ayrı yöntem ile üretimin son ürünün özellikleri üzerine etkisi araştırılmıştır. Örnek olarak, öncelikle ağırlıkça % 75 PBT ve % 25 geri dönüştürülmüş PET malzeme fiziksel olarak karıştırılarak, extrüderde pelletler üretilmiştir. Zincir bağlayıcı ajan katkısı, daha önce bahsedildiği gibi iki farklı yöntem kullanılarak harmanlara eklenmiştir. İlk yöntemde, ağırlıkça % 0.2 zincir bağlayıcı ajan, yaklaşık olarak ağırlıkça % 75 PBT ve % 25 geri dönüştürülmüş PET ile fiziksel olarak karıştırılıp, ekstrüderde pelletler üretilmiştir. İkinci yöntemde ise, ağırlıkça % 0.8 zincir bağlayıcı ajan, öncelikle geri dönüştürülmüş PET ile ekstrüderden geçirilerek ön karışım hazırlanmıştır. Hazırlanan ön karışım, kurutma işleminin ardından, ağırlıkça % 75 PBT, % 25 ön karışım olacak şekilde karıştırılıp ekstrüderden geçirilmiştir. İkinci yöntem ile hazırlanan malzeme, ilk yöntem gibi sonuçta % 0.2 ajan içermektedir. Yalnızca, 50:50 ve 25:75 PBT/geri dönüştürülmüş PET harmanlarında, farklı zincir bağlayıcı ajan konsantrasyonlarının etkisi araştırılmıştır. % 0.8 zincir bağlayıcı ajan ve geri dönüştürülmüş PET içeren ön karışım, PBT içerisine ağırlıkça % 25, 50 ve 75 oranlarında eklenmiştir. Böylece ön karışım konsantrasyonunun harman malzemesi özellikleri üzerindeki etkisi incelenebilmiştir.

Geliştirilen harman malzemelerin termal bozunma özellikleri termal gravimetrik analiz (TGA) ile, termal özellikleri ve kristalizasyon davranışları, diferansiyel taramalı kalorimetri (DSC) yöntemi kullanılarak incelenmiştir. Viskoelastik özellikler, dinamik mekanik analiz (DMA) ve eriyik akış indeksi (MFI) teknikleri kullanılarak incelenmiştir. Akma dayanımı ve elastik modül değerleri çekme deneyi, darbe dayanımı Izod darbe deneyi sonucunda elde edilmiştir.

1. INTRODUCTION

Polymer chains are macromolecules consisted of the repetition of small chemical units termed as monomers. Majority of them are petroleum based however polymers originated from renewable resources are recently developed and tended to be widely used. Polymers can be classified in various ways. For engineering applications, the most practical classification of polymers is based on their molecular structure and thermal behavior. Under this order, polymers are classified as thermosets, thermoplastics, and elastomers. Thermoplastic polymers are long molecules that are physically entangled and hence soften and flow by heat and pressure. Upon cooling, they solidify and could easily be shaped. On the other hand, thermoset polymers are short molecules resins which could be chemically cross linked with the addition of cross linking agent and thereby are incapable of undergoing repeated cycles of softening and solidifying [1].

For more than 50 years, global production of plastics raised and became one of the fastest-growing global materials in industry. From 1950 to 2012, the plastics usage growth was around 9 % per year, starting from 1.7 million tons to the nearly 300 million tons in 2015. Comparatively with conventional metallic or ceramic based materials, they possess low cost and light weight drive the market to prefer plastic materials. However, recovery and recycling, remain a serious challenge because millions of tons of plastics end up in oceans and landfills each year. Almost 35 % of plastics are disposed in the landfills, where they could create s serious threat to the environment and global warming [2]. Almost 13 million tons of plastic wastes ended up in oceans in 2010 and the cumulative quantity of them to enter the ocean from the land is predicted to rise by an order of magnitude by 2025. Turkey was proclaimed as one of the twenty countries that pollute the oceans with plastics in 2010 [3]. Recovering plastics from the waste stream for recycling or energy recovery has a great potential to minimize the environmental pollution problems. In Europe, 26 % of total post-consumed plastics were recycled in 2012, while 36 % was incinerated for energy recovery however, 38% of these plastics buried in the landfill [2].

One of the major polymers that is widely being used in commodity applications where they could extensively turn to be a waste in nature and hence a threat to environment is poly (ethylene terephthalate) (PET). PET is the most favorable packaging material worldwide for water and soft drinks bottles due to its low weight, high stiffness, excellent clarity and good barrier properties towards oxygen and moisture. Together with the increasing amount of PET bottles all over the world, recollection of post-consumed bottles and recycling them is an inevitable matter [4]. It is reported by Arena *et al.* [5] that the production of 1 kg of recycled PET flake instead of virgin PET saves approximately 30 mega joule of energy, which is equivalent to the energy content of about one-liter gasoline. However, post-consumed PET mostly comes from unknown origins and have uncertain processing and service histories, varying degrees of degradation and impurities, fillers such as colorant or reinforcing agents leading to unstable properties and difficulties in their re-processing [6].

In recent years, one of the methods to overcome the reduced properties of recycled polymers and thereby to improve the features of the final product is blending with other polymers that have superior properties with respect to those weak features of the recycled polymer. Blending recycled polymers with cheaper polymers but with appropriate features could also reduce the final cost of the products. Blends of poly (butylene terephthalate) (PBT) and PET are commercialized thermoplastic polyester products which are mostly processed in injection molding to produce products with sufficient required properties, heat resistance and glossy surface appearance. In this master thesis, PBT blends with post-consumed recycled PET were developed with different compositions while reactive twin screw extrusion (TSE) was also used in presence of chain extender to further improve the deteriorated properties of the noted blends consisted of recycled PET. Injection molding was also employed subsequent to TSE to prepare the testing samples. The miscibility, crystallization behavior, viscoelastic features, mechanical and thermal properties of the blends were extensively investigated.

2. LITERATURE REVIEW

2.1 Multiphase Thermoplastic Polymer Blends

A polymer blend is mainly defined as a mixture of two or more polymers that have been blended together to compose a new material with varying physical and mechanical properties [7]. Besides the ease of development of new polymeric blend systems and cost-effectiveness, the following material- related benefits can be cited:

- Providing new cost effective materials with desired properties
- Extending engineering resins' performance
- Improving processability of the materials
- Offering the yield for using recycled plastic wastes [7, 8].

2.1.1 Miscibility and thermodynamic equilibrium

Polymer blends can be classified with their phase behavior into either miscible or immiscible [7, 9, 10]. While miscible polymer blends (single-phase) are homogenous down to molecular level, immiscible polymer blends are heterogeneous where separated polymer phases exist in the microstructure [7].

In contrast to solutions, polymer blends are mostly immiscible; only 1320 cases of miscible polymer blends have been found by Krause and Goh. However, these are rare and poorly defined that it is possible to consider them as exceptions to the general rules of polymer/polymer immiscibility [9, 11]. The most widely used technique for determination of miscibility is measurement of the glass transition temperature [9]. Immiscible blends show separate glass transition temperatures corresponding to each blending polymer. Upon their compatibility, the glass transition temperatures could get close to each other depending on the composition and degree of compatibility between polymers due to partially miscibility. On the other hand, completely miscible blends have only one averaged glass transition temperature [10].

State of miscibility and phase behavior of polymer blends have well studied so far for different systems [7, 10]. Conceptually, state of miscibility is determined by thermodynamics of interactions between the blend components. These interactions are mainly functions of physical and chemical structures of blend components [10]. As mentioned earlier, polymer blends can be completely miscible, partially miscible or immiscible, depending on the value of the Gibbs free energy of mixing (ΔG_m) [7]. The free energy of mixing is given by the following equation:

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{2.1}$$

For miscible polymer blends, ΔG_m value should be negative value. ΔS_m is the entropy factor and is defined as a measure of disorder, is always positive and, therefore, is favorable for miscibility especially for low-molecular-weight solutions. In contrast, polymers have monomers with a high molecular weight and consequently the enthalpy of mixing (ΔH_m) is also deciding factor for miscibility. ΔH_m is defined as the heat that either consumed (endothermic) or generated (exothermic) during mixing. When strong specific interactions such as hydrogen bonding occur between the blend components, the mixing is exothermic then the system is leaded to miscibility [8, 10]. The state of miscibility of polymer blends is dependent on temperature. A classical phase diagram of polymer blends could be shown as in Figure 2.1 [12]. Miscible polymer blends may undergo phase separation upon heating, showing lower critical solution temperature (LCST) behavior. On the other hand, some immiscible polymer blends at room temperature become miscible upon heating, showing upper critical solution temperature (UCST) behavior. It is possible to find examples of polymer blends showing both LCST and UCST behaviors [13]. The phase separation in the mixture divides into two types, i.e., nucleation and growth type and spinodal decomposition type as shown in Figure 2.2 [12].

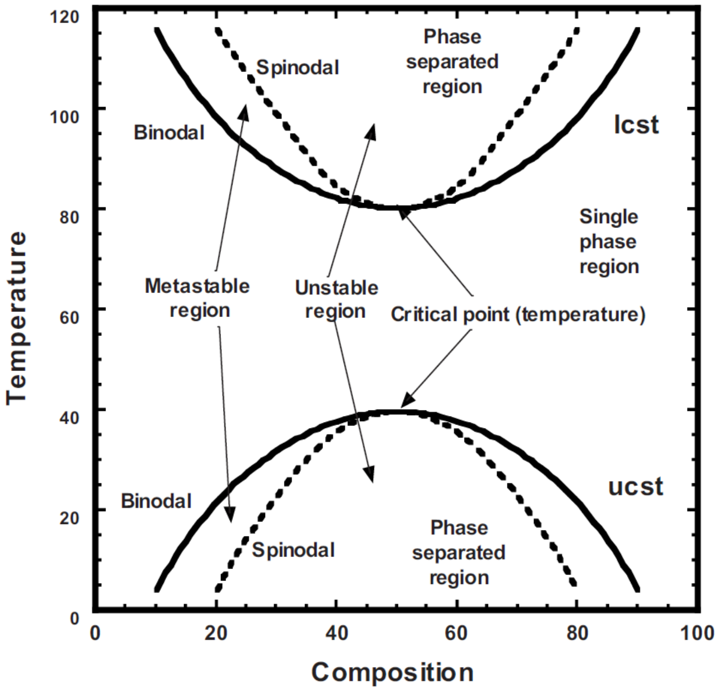


Figure 2.1 : Schematic phase diagram for binary polymer blends [12].

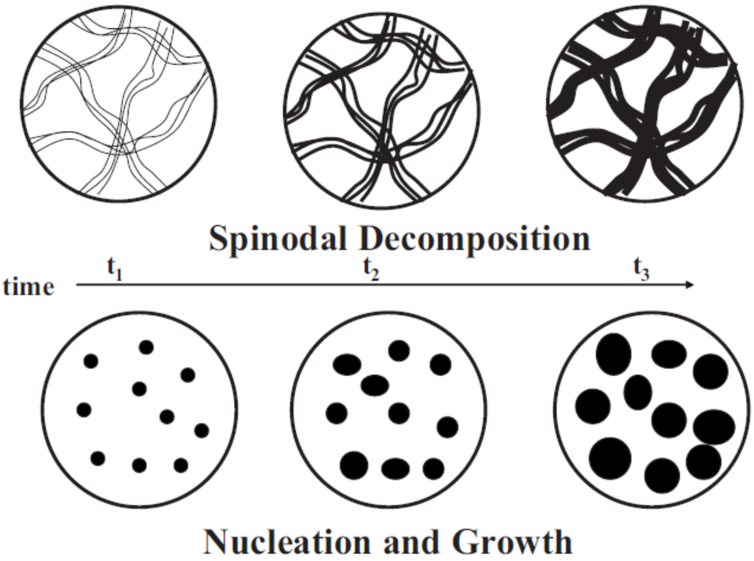


Figure 2.2 : Schematic phase diagram for binary polymer blends [12].

Nucleation and growth during phase separation occurs only in the metastable region shown in Figure 2.1 [14, 15]. In spinodal decomposition phase segregation is stopped and two phase morphology is stabilized [16]. Depending on the blending ratio within the immiscible spinodal region, the thermal, mechanical, rheological and other properties of the immiscible polymer blend could be varied. This property variation could further be affected depending on the generated final blend’s morphology [14-16].

2.1.2 Morphology and properties

As mentioned above, miscible polymer blends are single phase - homogenous down to molecular level while immiscible polymer blends are phase separated – heterogeneous structures. Most of the polymer blends are immiscible and hence phase separated [7]. Depending on the blending ratio, various structures could be obtained. For instance, by having one polymer as the major phase and the other blending polymer as the minor phase a drop and sea morphology could be obtained and co-continuous structure could be achieved when two similar copolymer contents are blended. The achievement of different morphologies in immiscible blends is essential to determine the structure-property relationships [11]. Various morphologies and range of properties of immiscible polymer blends are illustrated in Figure 2.3 [17]. A seen, depending on what morphology is obtained different final properties such as high toughness and strength, excellent barrier properties and high melt strength could be achieved. The major morphological types of polymer blends are droplets in matrix and co-continuous phase structure. Other types of morphologies include core shell, fibrillar, onion ring-like morphologies [18]. The characterization techniques such as optical microscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM) could be employed to examine the morphology of a polymer blend [17].

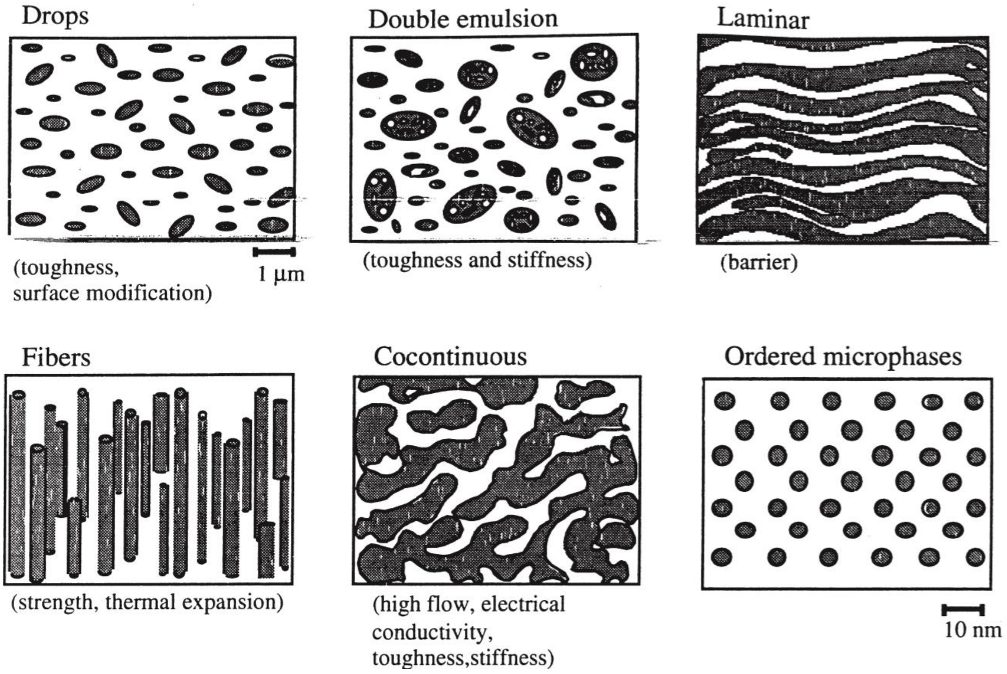

Drops
(toughness, surface modification)
Double emulsion
(toughness and stiffness)
Laminar
(barrier)
Fibers
(strength, thermal expansion)
Cocontinuous
(high flow, electrical conductivity, toughness,stiffness)
Ordered microphases

Figure 2.3 : Schematic of various morphologies of immiscible polymer blends [17].

2.1.3 Applications and manufacturing

Manufacturing of polymer blends has attracted attentions in polymer engineering within the last three decades. The ability to combine existing polymers into new compounds with commercial properties offers many advantages such as reducing the expense compared to the development of new monomers and polymers to yield a similar property profile. Polymer blends can be designed at specific compositions to satisfy the properties that are desired in various applications, while individual polymers have their inherent property profiles with limited number of applications. Due to the flexibility in generating wide range of properties by controlling the blend composition as well as the blend morphology various novel applications could be defined for engineering polymers in such applications as daily appliances, electronics and automotive applications [12]. For instance, blends of polypropylene and polyamide are widely being used in automotive industries due to the tailored properties that could be achieved through different compositions [8].

Polymer processing could further affect the structure-property relation of polymer blends and plays an important role in the plastic industry. Such various blend morphologies could be obtained via changing the processing technology and processing parameters [19]. In technologies to manufacture thermoplastic polymeric products melting, forming and solidification steps must be pursued. Melting occurs by heating the thermoplastic polymer or through the use of pressure simultaneously and allows the molecular chains of the polymers to slide over each other to enable the process and form the new shape. The flowing polymer is formed by using dies (using extruder), molds (via injection molding), and other methods (such as compression molding). These processing steps are profoundly dependent on a polymer's glassification temperature and/or melting/crystallization temperature [20]. Processing methods that are currently being used widely could be named as: extrusion, injection molding, blow molding, thermoforming, rotational molding, and electrospinning [20]. In this section, extrusion and injection molding processes are being discussed.

2.1.3.1 Extrusion

Extrusion is one of the most common processing technique in the plastic industry and is being used since 1800s [21]. Extrusion is mainly a compression process in which material is forced to flow through a die nozzle to provide long continuous product with simple geometries such as filaments, pipes, sheets, and etc. In polymer extrusion, feedstock in pellet, flake or powder shape is fed by gravity through hoppers into the rotating screw/screws whose turning moves the material along the barrel where the polymer is heated to melt and forced to flow through a die opening (Figure 2.4). There are two main components of the extruder; the barrel and the screw. The die is not a component but rather it is a special tool that must be fabricated for the particular profiles such as filaments or sheets [22].

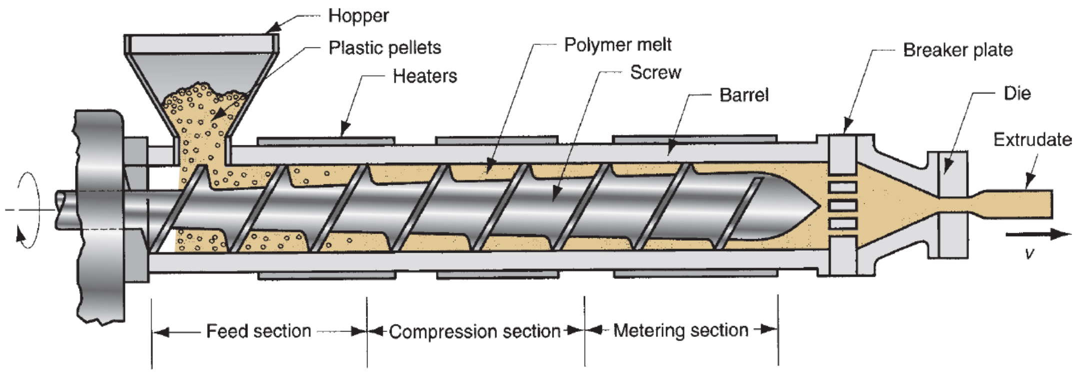


Figure 2.4 : Schematic of a single-screw extruder [22].

The internal diameter of the extruder barrel typically ranges from 25 to 150 mm. The length of the barrel is longer than its diameter, with L/D ratio usually varies between 10 to 40. Generally high ratios are used for thermoplastic materials in order to achieve a more homogenous melt structure. The screw has several functions and is divided into sections that correspond to these functions. Feed section is the first region through which the raw material is moved from the hopper port toward the heating zones. Second region is compression section where the polymer is transformed into liquid continuously, air entrapped amongst the raw material is extracted from the melt via vacuum port, and the material is compressed. The last step is the metering zone, along which the melt structure becomes homogeneous and sufficient pressure is developed to pump it through the die opening. Extruders could be classified into single and twin screw, SSE and TSE, respectively [20, 22].

Twin-screw extruder (TSE) is employed in order to generate a better mixture compared to a single-screw extruder (SSE). The screws of a TSE are sectioned along with the barrels; thus the screw can be designed in a way to facilitate the proper mixing for each system by generating severe shear and elongational forces in between two screws [20]. Common types of TSEs available for thermoplastic polymer compounding are co-rotating and counter-rotating. While a single stream travel between two screws in opposite directions in counter-rotating TSE, two streams travel in parallel directions along the two screws at the same direction in co-rotating TSE. The better mixing quality, however, could be obtained in a co-rotating TSE which could be preferably used in polymer nanocomposite manufacturing and any compounding. Hence, co-rotating TSE is the most common type in compound manufacturing. The screw configuration could further be modified in TSEs in order to manufacture various types of compounds by controlling the applied elongational and shear fields [23]. Both counter- and co-rotating screw are shown at Figure 2.5 [24].

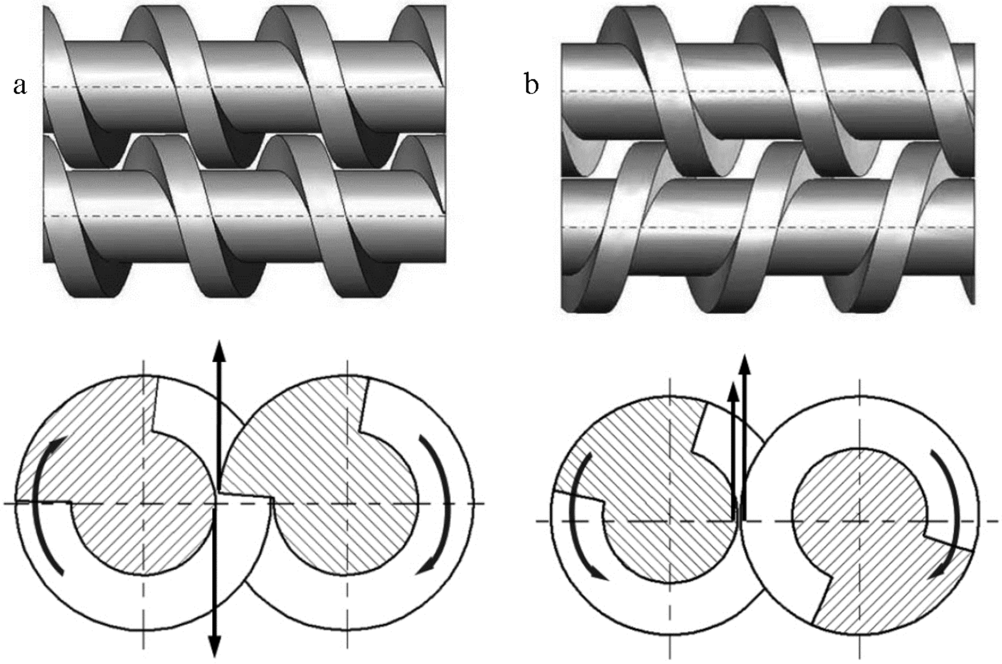


Figure 2.5 : Schematics of a co-rotating (a) and a counter-rotating (b) twin screws [24].

2.1.3.2 Injection molding

Injection molding (IM) is another commonly used polymer processing technology in which the thermoplastic polymer melts along a barrel consisting of a single screw and then forces to flow under high pressure into a mold cavity, where it solidifies into a desired shape. The molded part is then removed from the cavity. Through IM technology, it is possible to produce three dimensional complex shapes [22].

An IM machine consists of two components called as the plastic injection and the mold clamping unit. The plastic injection unit is more or less like an extruder and consists of a barrel that the polymer pellets are fed from one end through a hopper. There is a single screw inside the barrel which operates in addition to turning for melting and mixing the polymer that rapidly moves the melt forward to inject it into the mold. The functions of the mold clamping unit are holding the two halves of the mold in suitable alignment with each other, keeping the mold closed during injection by applying a clamping force enough to resist the injection force; and opening and closing the mold at the appropriate times in the molding cycle. The schematic of an IM is depicted in Figure 2.6. The processing steps are further disclosed in Figure 2.7. These steps could be summarized as below. The process starts with the mold open and the machine is ready to start a new molding: (a) The mold is closed and clamped. (b) A shot of polymer melt, which is at the right temperature and has the right viscosity by heating and the mechanical working of the screw, is injected under high pressure into the mold cavity. When the polymer melt encounters to the cold surface of the mold, it cools and begins to solidify. Pressure of ram is maintained to pack additional melt into the cavity to compensate for shrinkage during cooling. (c) The screw is rotated and drawn back by the action of non-return valve open to permit fresh polymer to flow into the forward section of the barrel. In the meantime, the polymer in the mold has completely solidified. (d) The mold is opened, and the part is ejected and removed [22].

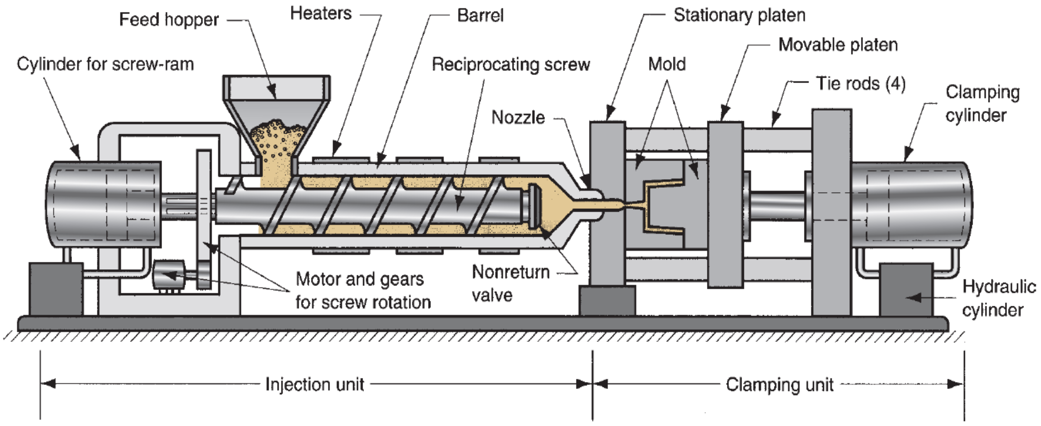


Figure 2.6 : Schematic of an injection molding machine [22].

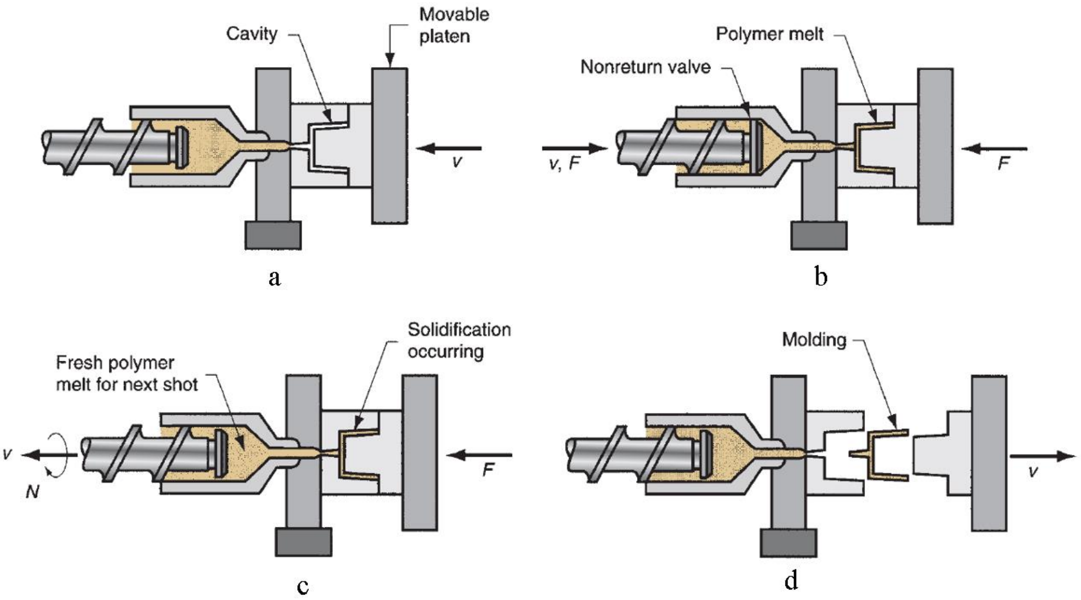


Figure 2.7 : Typical molding cycle for a thermoplastic polymer [22].

2.2 Poly (butylene terephthalate) (PBT)

2.2.1 Synthesis and molecular configuration

Poly (butylene terephthalate) (PBT) is an aromatic polyester based thermoplastic synthesized by reaction of 1,4-butanediol (BDO) either with dimethyl terephthalate (DMT) or terephthalic acid (TPA) in the presence of a polyesterification catalyst. Titanium alkoxides are main industrial catalysts which are used in PBT production in an attempt to catalyze both transesterification and direct esterification reactions [25, 26].

Traditionally, the synthesis of PBT starts with reaction of BDO and DMT monomers. The reaction occurs in two steps, transesterification and polycondensation. The first step is the transesterifcation reaction between DMT and BDO, which produces the diester, bis (4-hydroxybutyl-terephthalate), or ester oligomers with hydroxybutyl ester end groups. Figure 2.8 shows the diester structure produced from transesterification reaction in BDO and DMT [27]. Transesterifications, also named as ester exchange or ester interchange reactions, consist of carboxy-ester, hydroxy-ester, and ester-ester reactions. Hydroxy-ester interchange, also called as alcoholysis, plays an important role in most industrial productions of aliphatic-aromatic polyesters such as PBT. During the transtesterification reaction of DMT and BDO, methanol is removed from the system as a byproduct [26].

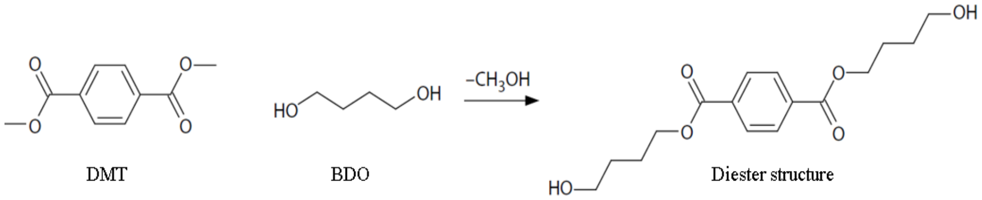


Figure 2.8 : Transesterification reaction of DMT and BDO [27].

The second step is the polycondensation reaction of the diester or ester oligomers. During polycondensation reaction at certain conditions, the molecular weight of PBT is increased. In this step, BDO is invariably removed from the system as a byproduct to continue the reaction. When the desired molecular weight of PBT is achieved, the polycondensation reaction is completed. Figure 2.9 shows the polycondensation reaction to synthesize PBT [27].

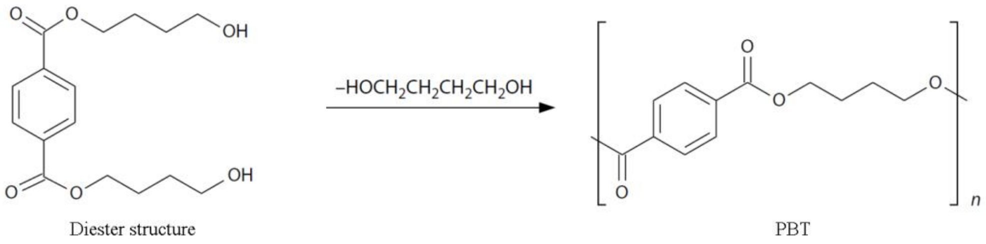


Figure 2.9 : Polycondensation reaction to synthesize PBT [27].

Another synthesizing method of PBT starts with the reaction of DMT and TPA monomers. The first step of this method is direct esterification. During the direct esterification, water is removed from the reaction vessel. The second step is to produce PBT from the ester oligomer named bis (4-hydroxybutyl-terephthalate). The ester oligomer formation is very similar to both synthesis methods, with either DMT or TPA as the starting monomer. Figure 2.10 shows the PBT synthesis steps from monomers of BDO and TPA [27].

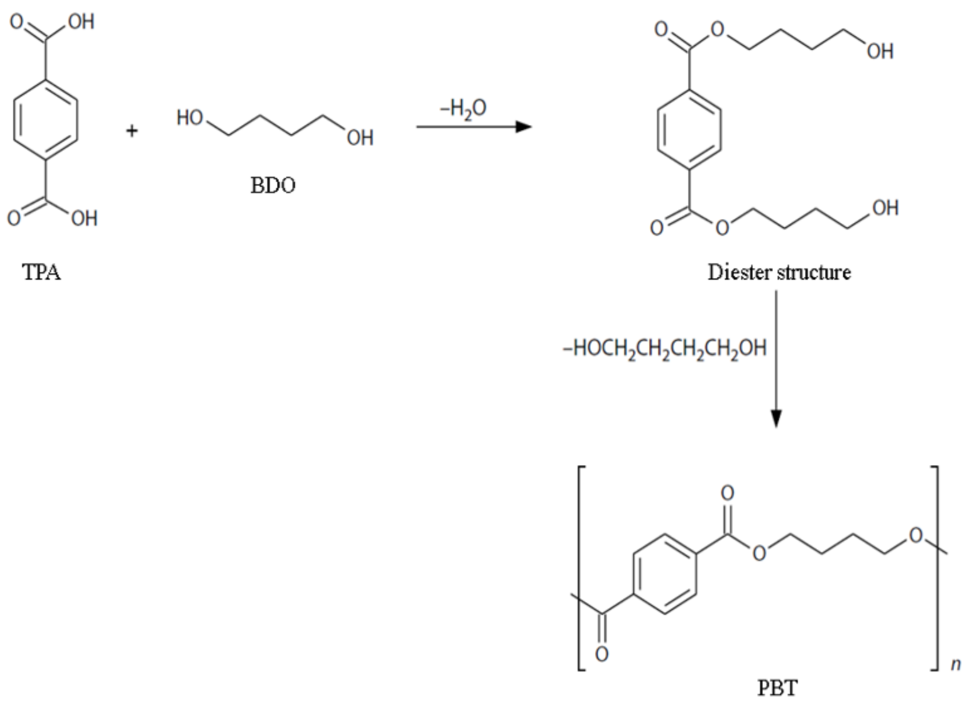


Figure 2.10 : PBT synthesis steps from TPA and BDO [27].

One of the main advantages in the synthesis of PBT from DMT monomer (i.e., the first method), compared with the synthesis from TPA (i.e., the second method), is that environmental aggressive chemicals such as bromides and acetic acid are not used and DMT has relatively easier purification process [26]. However, due to the progression of TPA purification technology and the lower price of TPA as a raw material, a new process to produce PBT by using BDO and TPA has become less costly compared to the traditional process using DMT [27].

PBT consists of both a flexible link (i.e., butylene groups) which facilitates the crystallization kinetics of PBT and a rigid segment (i.e., terephthalate groups) [28]. The crystallization behavior of PBT and its dependency on the molecular structure is discussed in detail in thermal properties section below.

2.2.2 Thermal properties

PBT is a semi-crystalline polymer with a degree of crystallinity ranges from 35% to 40%. It has glass transition temperature between 35-50 ^{o} C, while the melting temperature is usually between 222 and 232 ^{o} C. The degree of crystallinity, glass transition temperature, and the melting temperature of a polymer depend on the thermal history of the material. To give an example, crystallinity of PBT can reach 60% by annealing. Due to the perfection of the crystals, the melting temperature and glass transition temperature can also shift toward higher values after annealing for long time [26]. The butylene groups in the molecular structure of PBT provides a high chain mobility and flexibility in PBT. Therefore, PBT shows higher crystallization rate compared to that in PET, which possess ethylene group in its molecular structure [27].

The differential scanning calorimetry (DSC) curve of PBT often shows peaks with some shoulders [27]. It is reported that melting peak structure is due to the formation of different distributions and perfections of crystals. This wide range of crystal melting temperature would provide a high heat resistance feature to PBT [25].

2.2.3 Mechanical properties

PBT is used in a wide range of applications due to its high chemical resistance, low moisture absorption, good mechanical properties and consistency, which shows little change in part dimensions or mechanical properties as a function of environmental factors [25].

Fast crystallization of PBT offers a favorable process in extrusion and injection molding applications. The degree of crystallinity strongly affects the mechanical properties of PBT by providing the mechanical strength in the presence of crystallites [26].

The typical mechanical properties of PBT is listed at Table 2.1 [27, 29, 30]. As shown PBT possess high ductility and toughness with desired strength and stiffness, which further expands its application in various engineering products.

Table 2.1 : Typical mechanical properties of PBT [27, 29, 30].

Properties	Units	Average Values
Tensile Strength	MPa	52
Tensile Elongation	%	150
Tensile Modulus	MPa	2300
Flexural Strength	MPa	80
Flexural Modulus	MPa	2000
Izod Notched Impact Strength (at room temperature)	kgf cm/cm	5

2.2.4 Rheological properties

Polymer rheology is basically the science of viscoelastic behavior of polymers in melt condition. Understanding the properties of a polymer melt is essential to understand the characteristics of melt processing, forming and foaming of polymers. Viscosity is termed as the resistance of the material to flow and is dependent on many parameters such as shear rate, temperature, and time that a melt flow is subjected to the shear. Polymer melts are mostly non-Newtonian fluids with shear thinning behavior where the viscosity decreases with increasing shear rates [31].

PBT has advantages of fast cycle times, higher productivity and easier processability due to its higher crystallization rate and melt strength in comparison with PET [30]. Liu *et al.* [32] investigated the rheological properties of PBT with high melt flow index. As shown at Figure 2.11, PBT exhibited a non-Newtonian behavior with a typical shear thinning behavior. Intrinsic viscosity decreased with increased shear rates. They indicated that temperature has an important influence on the viscosity, increased temperature lowered the apparent viscosity. With addition of temperature, the mobility of molecular chains increased, while the molecules interaction, the flow resistance and the apparent viscosity decreased.

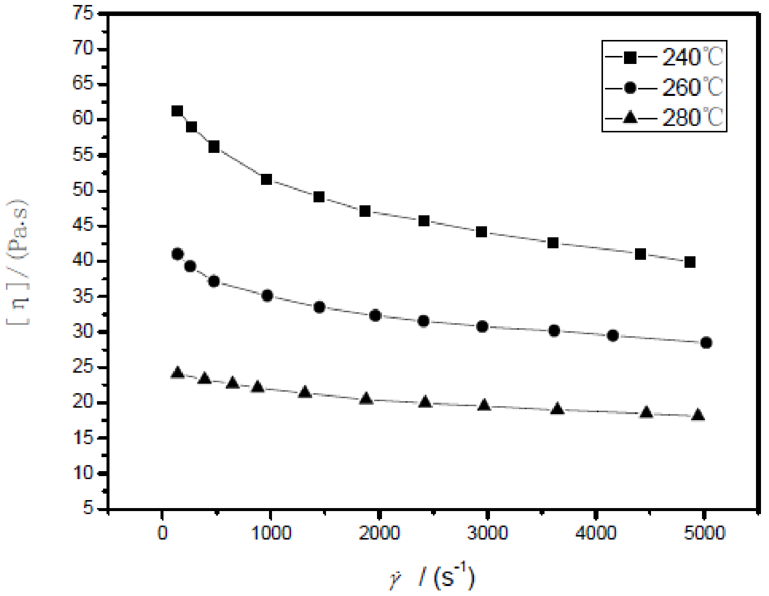


Figure 2.11 : Intrinsic viscosity (η) of PBT as a function of shear rate (γ) at various temperatures [32].

2.2.5 Applications of PBT

PBT is an engineering thermoplastic which is used in such applications including electronics and communication equipment, kitchen and household appliances, lighting systems, pumps, medical devices, handles, power and hand tools, bobbins and spindles, and automotive parts [25, 26].

In most injection molding applications, PBT is reinforced and enhanced with inorganic fillers such as mineral fillers and glass fibers to gain high modulus and strength with a relatively low cost. Considering high heat resistance of PBT, it is also commercially formulated to various levels of flame resistance with flame retardant additives [27]. Fast crystallization, cycle times in injection molding and good dimensional stability of PBT offers rapid and efficient commercial benefit [25].

2.3 Poly (ethylene terephthalate) (PET)

2.3.1 Synthesis and molecular configuration

Poly (ethylene terephthalate) (PET) is an important commercial engineering thermoplastic with good thermal and mechanical properties, low permeability and chemical resistance. PET has similar molecular structure to PBT except ethylene groups are involved instead of butylene links. Therefore, the main difference between PBT and PET is that PET has a slower crystallization kinetics due to lack of molecular flexibility in presence of ethylene group connected to an aromatic group [27]. PET synthesized in two steps: the first step is pre-polymerization where bis-(2-hydroxyethyl)-terephthalate (BHET) monomer is formed, the second step is melt polycondensation. In pre-polymerization step, ethylene glycol (EG) as the diol and either TPA as an acid or DMT as an alcohol undergo a reaction. Pre-polymerization step of PET synthesis process consists of two different reactions: either direct esterification reaction where TPA reacts with EG or transesterification reaction where DMT reacts with EG [27, 33, 34]. The route of PET synthesis is shown in Figure 2.12 [27].

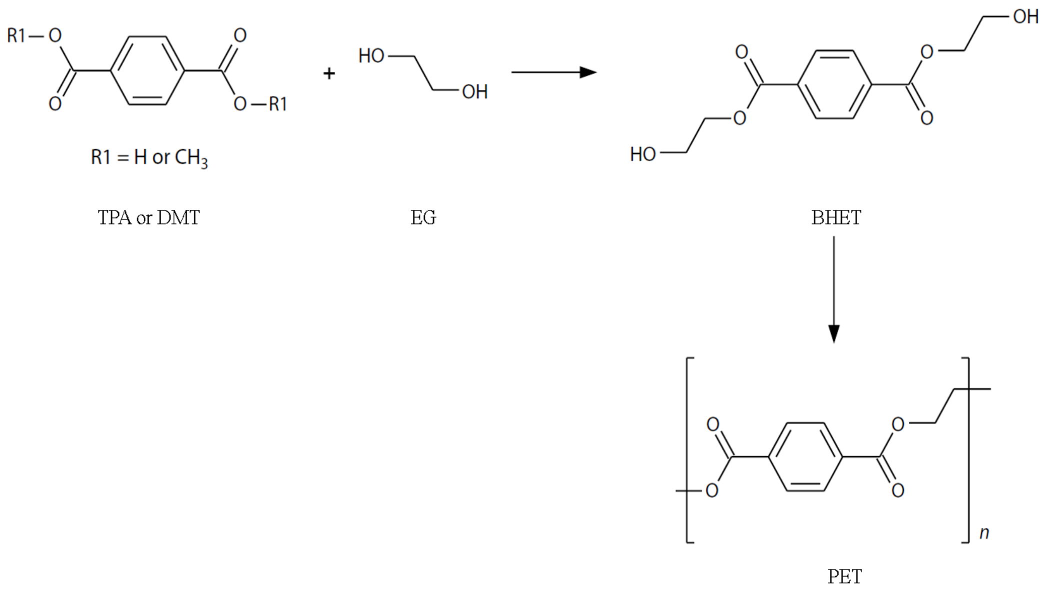


Figure 2.12 : PET synthesis route [27].

During the pre-polymerization step either using DMT or TPA, BHET monomer is produced [27]. While water is the by-product of the direct esterification reaction of TPA with EG, methanol is the by-product of transesterification reaction of DMT and EG [35]. In the melt polycondensation step BHET monomer further polymerized under reduced pressure with heat to produce PET resins at certain degree of polymerization [27, 33, 34].

2.3.2 Thermal properties

Commercial PET has melting temperature in the range of 250-265 ^{0}C, while fully annealed PET has a melting point of 280 ^{0}C. The glass transition temperature of PET nearly equals to around 67 ^{0}C in an amorphous state, 81 ^{0}C in a semi-crystalline state, and 125 ^{0}C in a crystalline and fully oriented state [33, 36]. PET also shows melting endotherm peaks with some shoulders in DSC heating thermograms representing wide range crystal size and perfection. To be more specific, the presence of different crystal types, different crystal perfection and molecular weight distribution could cause this phenomenon [37].

As noted, one of the primary limitations of PET is related to its slow crystallization kinetic from the melt [38]. Slow crystallization of PET is due to the short ethylene spacer between the aromatic rings, and thereby lower chain mobility. However, the crystallinity of PET can be strongly influenced by the molecular weight. Low molecular weight allows the chain to align easily in comparison to higher molecular weight with high degree of entanglement and reduced flexibility. This could result in higher crystallinity for the low-molecular weight grades of PET [27].

Unlike PBT, with a regular molecular structure, PET can crystallize if cooled slowly from the melt. If it is quenched, however, only amorphous phase would be formed because of its too slow crystallization rate. If the amorphous PET in the solid state is heated slowly above its glass transition temperature, when the molecules have sufficient kinetic energy to nucleate crystals and facilitate their growth, non-isothermal induced crystalline structures could be formed which is called non-isothermal cold crystallization [39]. If this phenomenon occurs at a given temperature for a certain period of time as an annealing, this would be named as isothermally induced cold crystallization. Furthermore, at elevated temperatures crystal structures with higher degree of perfection with higher melting temperature could be formed due to the re-organization of the less perfect crystals [33]. This phenomenon occurs in a range of temperature between glass transition and melting temperatures, and as noted is commonly known as cold crystallization. Figure 2.13 shows the heating and cooling thermograms of a PET illustrating melt and cold crystallization as well as the melting peak of the noted crystals [40]. In industrial injection molding parts by adjusting the mold temperature, the cold crystallization of PET was introduced to increase the stiffness and strength [39].

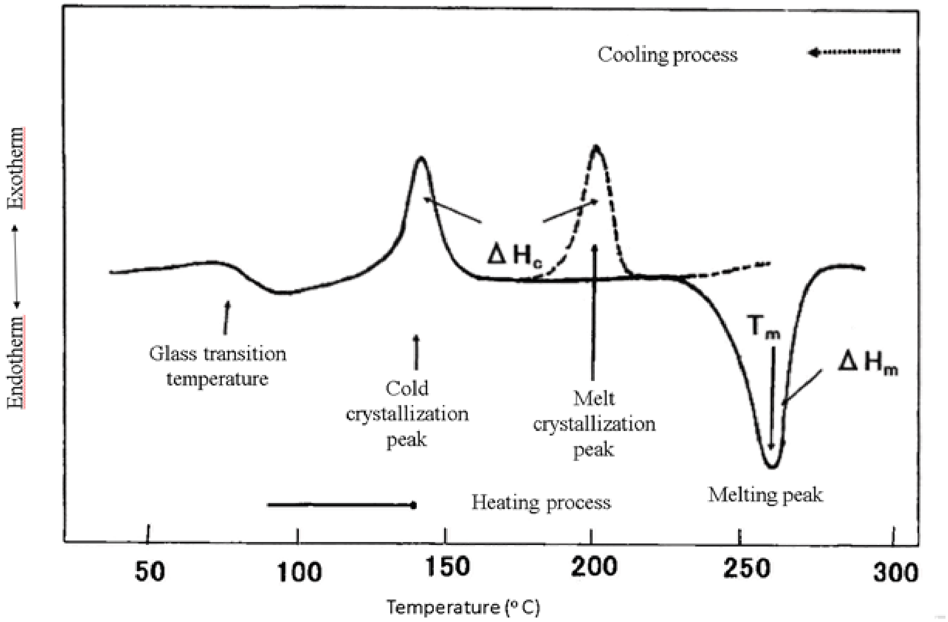


Figure 2.13 : DSC diagram in both first heating and cooling processes for PET [40].

The crystallinity of PET results in good resistance to most alcohols, acids, alkalis and oils. The barrier properties to gases are usually related to the free volume of the polymer. Polymers having high crystallinity provide excellent barrier properties owing to the close packing of molecular chains [27].

2.3.3 Mechanical properties

PET is used in many applications ranging from extruded parts to fibers due to its low cost, high chemical and heat resistance and stiffness. However, PET has not been considered for applications involving injection molding due to its high melting temperature followed by its slow crystallization kinetics [41]. The mechanical typical properties of PET are listed in Table 2.2 [27].

Table 2.2 : Typical mechanical properties of PET [27].

Properties	Units	Average Values
Tensile Strength	MPa	55-75
Tensile Elongation	%	50-165
Tensile Modulus	MPa	2000-4000
Izod Notched Impact Strength (at room temperature)	J/m	13-35

2.3.4 Rheological properties

PET is manufactured at different specifications since different applications require different properties. Intrinsic viscosities of PET with respect to the required processing and application are shown in Table 2.3 [27].

Table 2.3 : Intrinsic viscosities for different PET processing and applications [27].

Intrinsic viscosity [η] (dL/g)	Processing	Applications
0.68	Injection molding	Cups, connectors
0.76	Blow molding, film extrusion, electrospinning	Bottles for mineral water, containers, cas film, fiber
0.80	Blow molding	General bottle applications
0.84	Blow molding, thermoforming	Bottles for carbonated drinks, oils, cosmetics and food
0.90	Blow molding	Detergent bottles, jars, dreep-draw cups

Different PET resins show different characteristics in their rheological properties due to the degree of branching that could be introduced by addition of chain branching agent. In the study of Rosu *et al.* [42], it is stated that linear PET shows light shear thinning behavior, while branched PET showed a significant shear thinning behavior with a high zero shear viscosity.

Owing to the increasing melt strength properties, PET has attracted many attentions [43-45]. Forsythe *et al.* [45] investigated the rheological properties of high melt strength PET produced by reactive extrusion. They used pyromellitic di-anhydride (PMDA) as a chain extender additive at various concentrations to enhance the melt strength of PET. As stated in Figure 2.14, low viscosity Newtonian flow behavior of unmodified PET became increasingly viscous at higher contents of PMDA with higher viscosities at lower shear rates. At higher shear rates, the increase shear thinning rate in branched form is observed more clearly. Melt flow rate (MFR) also decreased from 22 g/10 min to 15 g/10 min and 11 g/10 min after addition of 0.10 wt% and 0.20 wt% of PMDA, respectively.

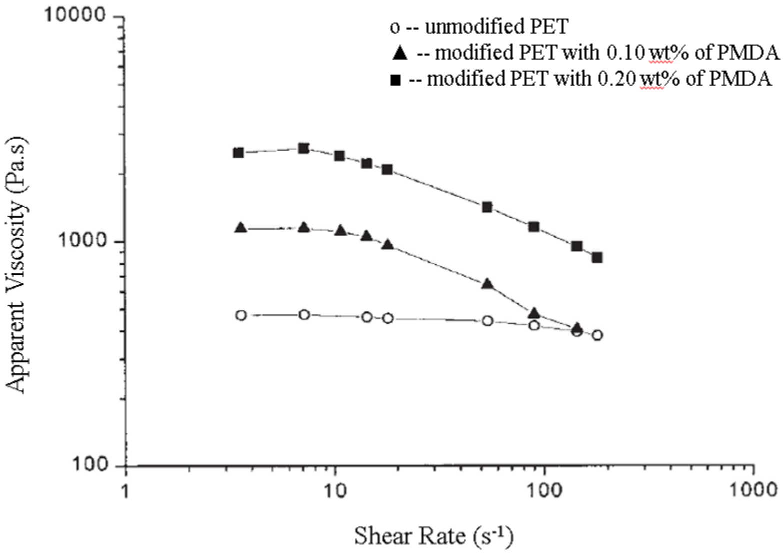


Figure 2.14 : Effect of PMDA addition on the steady shear viscosity of PET [45].

While Daver et al. [46] investigated the rheological properties of virgin bottle grade PET, recycled PET and modified recycled PET with PMDA. As stated in Figure 2.15, over the entire frequency range, the recycled PET showed the lowest value while virgin PET showed the highest complex viscosity. The complex viscosity increased with the increased content of PMDA as a consequence of increase molecular weight. They indicated branching with 0.30 wt% PMDA showed a significant shear thinning behavior within a wider frequency range.

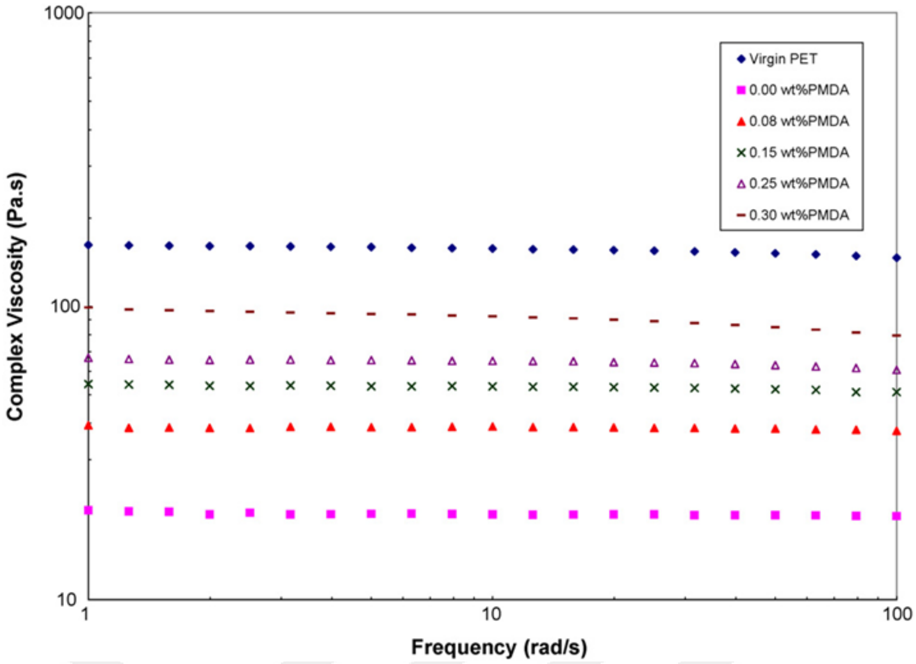


Figure 2.15 : Complex viscosity vs. frequency of virgin PET, unmodified recycled PET and modified PET with various concentrations of PMDA [46].

2.3.5 Applications of PET

Among the other commercial polyesters PET is the most commonly used material due to its excellent thermal, mechanical properties and lowest cost compared to other engineering thermoplastic polyesters [21]. PET is a widely used engineering thermoplastic in manufacturing of textile fibers, soft-drink bottles, packaging films and automotive structural components such as mirror back, luggage racks, electrical parts, and head lamp reflectors [47, 48].

Fibers which are made from PET by melt spinning are mostly used in every form of clothing, home furnishing such as carpets, pillows, sheets and other uses such as ropes, hoses and cords [36].

Having a high clarity and transmittance, depending on the processing parameters, provides PET a promising candidate in manufacturing bottles, films and sheets. Besides, PET is highly chemical resistant material and has good barrier properties against oxygen and water vapor and thereby has been approved for food contact applications. Major portion of the soft drink bottles in the world are made from PET [27, 36].

2.4 Polymer Recycling

2.4.1 Properties of recycled polymers

Recycled polymers in comparison with the equivalent virgin polymers may be deteriorated by many factors. They mostly come from unknown origin, and may be subjected to degradation processes and have been contaminated during previous usage [49]. The deterioration of recycled polymers in quality and stability, mechanical and physical properties, thermal properties and surface appearance limit their applications [50]. Determination of these key properties, as indicated in Figure 2.16, is essential to guarantee the use of recycled polymers to manufacture new products [49, 51].

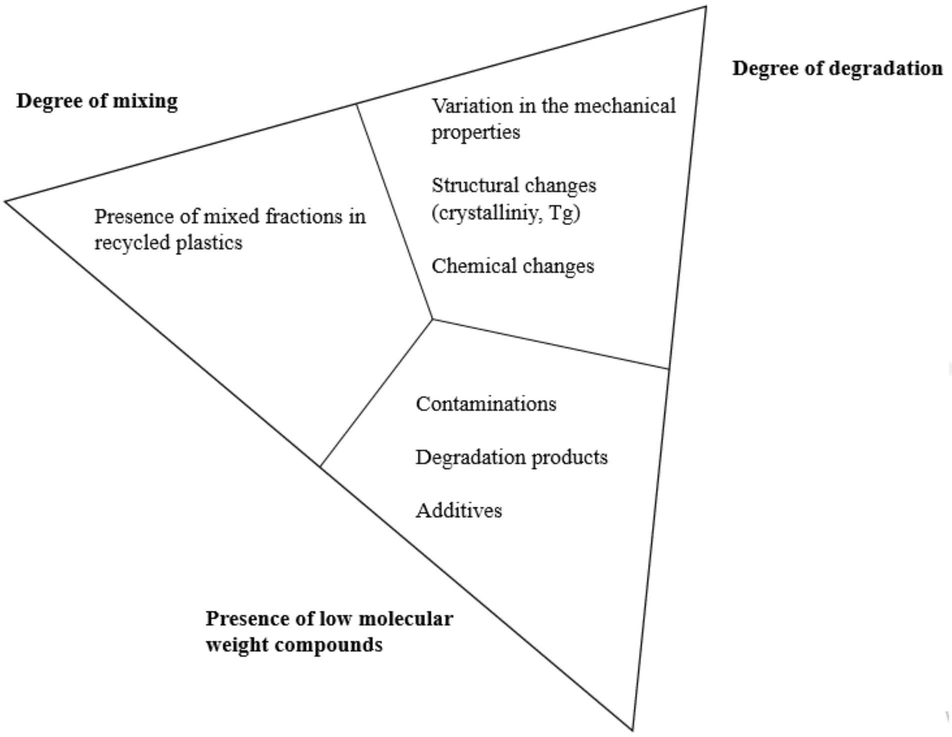


Figure 2.16 : Parameters to consider the feasibility of using recycled polymers [49, 51].

2.4.1.1 Degree of mixing

Degree of mixing represents the presence of other polymeric materials as impurities in recycled plastics. It is a critical parameter that influences the structure and mechanical properties of recycled plastics. In case of incompatibility between recycled polymers and polymeric impurities, even at low concentrations, leads to poor adhesion properties in the recycled interface and, therefore deterioration in overall macroscopic properties [49, 51].

2.4.1.2 Degree of degradation

Polymers may undergo oxidation reactions at different stages of their service life, and the new functional groups are produced during oxidation process. These functional groups cause sensitivity of the recycled polymers to encounter further thermal and photo-degradation. Determination of the degree of degradation that influences the structural, thermal and mechanical properties of the recycled plastics is essential for the future performance of the recycled products [49].

2.4.1.3 Presence of low molecular weight compounds

Although the presence of low molecular weight additives (e.g., catalysts, stabilizers, antioxidants, plasticizers etc.) within a thermoplastic polymer could promote the processability and final features of a product, during the recycling these additives turn to be contaminations and hence are playing suppressive role for recycling process. The molecular degradation of the polymer itself could also generated low molecular weight segments that could appear as contaminations during the recycling. Therefore, in recycled plastics, low molecular weight compounds either from the additives of molecular degradation of the polymer would cause suppression of properties and their usage as new products [49].

In order to investigate the degree of mixing and degradation of recycled polymers and presence of low molecular weight compounds, microscopic and macroscopic properties could be examined [52]. Changes in thermal properties such as crystallinity, melting behavior, thermal history; in physical properties such as morphology and viscoelastic behavior and in mechanical properties such as tensile and impact strength can be determinative parameters to examine the degree of degradation involved in recycled polymers. While DSC and dynamic mechanical analysis (DMA) are employed to detect the changes in the thermal and thermomechanical properties, Fourier transform infrared spectroscopy (FT-IR) is utilized to detect the functional group changes. Microscopic techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) can be used to investigate the effects of previous degradation and possessed impurities on the morphology. Chromatographic techniques such as high performance liquid chromatography (HPLC) and gas chromatography (GC) are used for determination of low molecular weight compounds. Different detectors such as diode-array detector (DAD), mass spectrometry (MS), and flame ionization detector (FID) can be employed to identify and quantify of these compounds in the recycled polymers [49, 52]. Thermo-mechanical degradation during processing and mechanical recycling is usually yields chain scission, which ends up with a reduction in molecular weight of the recycled polymers and hence an increase in the melt flow rate. Rheological measurements and melt flow rate of recycled polymers are commonly employed to assure quality properties of recycled polymers that can also be an indicator of polymer degradation. The latest is one of the most reliable methods to measure the degradation degree of a recycled polymer due to the accurate measurement of viscoelastic features of a polymer melt that the molecular weight effect could more clearly be disclosed [49].

2.4.2 Primary (re-extrusion) recycling

Primary recycling, which is known as re-extrusion, is the re-introduction of waste, single-polymer plastic parts to extrusion process due to production of the similar material. In order to apply this process, the waste plastics should have the similar features to the original products; the recycled waste is either mixed with neat material or used as a second grade material. Primary recycling is a low cost process, however it requires only semi-clean, uncontaminated and single type waste materials [54, 55].

Re-extrusion of post-consumer plastics may also be involved into primary recycling. The main source of such waste stream is generally the households. In this context, a selective and segregated collection of household wastes is required which makes recycling of them a challenging work [54].

2.4.3 Secondary (mechanical) recycling

Secondary recycling is basically the process of recovering of post-consumer plastic materials for re-use in manufacturing of plastic products through mechanical approach. Secondary recycling, which is known as mechanical recycling, was commercialized all over the world back in 1970s. Complex and contaminated wastes cause a difficult mechanical recycling. In order to obtain a high quality, clear, clean and homogeneous end-products, steps of separation, washing and preparation of wastes is essential [54]. The main disadvantage of mechanical recycling is the deterioration of the material’s properties in every cycle that is caused by molecular weight reduction of the plastic product in the presence of water and acidic impurities [56]. Mechanical recycling of plastic wastes involves a number of treatments and preparation steps as shown in Figure 2.17 [54].

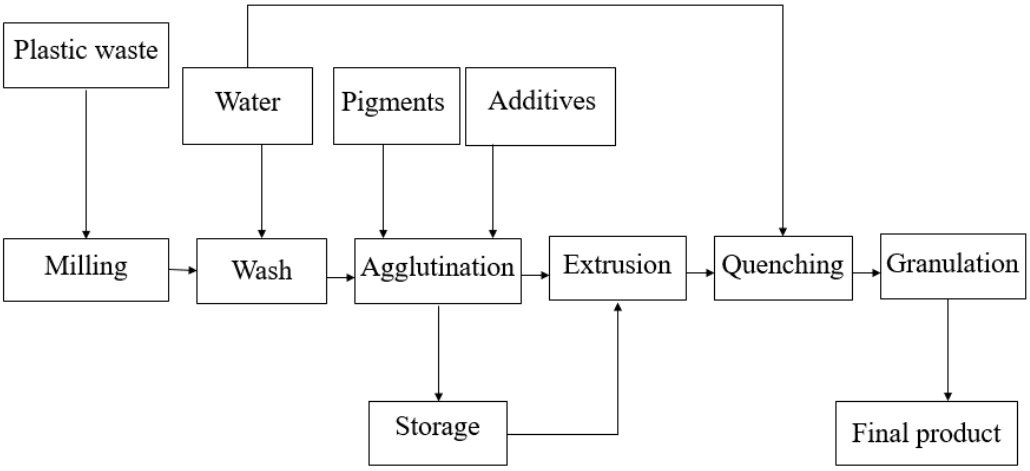


Figure 2.17 : Mechanical recycling steps of polymers [54].

The steps of mechanical recycling are basically as follow:

Cutting/shredding: The first step in mechanical recycling involves size reduction of the plastic wastes to form pellets, flakes or powders for further processing.

Contamination separation: Dust, paper and other impurities should be separated from the waste. Separation usually takes place in a cyclone.

Floating: Different types of plastic flakes are separated in a floating tank benefiting from their density differences.

Milling: The separated single-polymer wastes in previous steps are milled together. Milling step is usually performed as a first step by many recycling companies.

Washing and drying: This step involves washing with water. Chemical washing with caustic soda and surfactants is also applied in some cases if glue removal from plastic is required.

Agglutination: In this step, the product is gathered together either to be stored and sold after the addition of certain additives, or sent for the further processing.

Extrusion: The prepared plastic wastes in the form of flakes or chopped strands can be extruded and then pelletized and dried to produce single-polymer plastic granules [54].

2.4.4 Tertiary (chemical) recycling

Tertiary recycling, which is known as chemical recycling, involves advanced technologies that convert the plastic materials into smaller molecules usually in the form of liquid or gas. These small molecules are suitable to be used as a feedstock for manufacturing of new petrochemicals and final plastic products [54].

In contrast with the physical recycling, chemical recycling is based on transformation of polymer chains. The polymer backbone is degraded into monomer units or randomly divided into larger chain fragments with formation of gaseous products. The chemical recycling is performed either by solvolysis through degradation by solvents including water or by pyrolysis through degradation by heat in absence of oxygen or air, or under vacuum. The monomers which are produced by the chemical recycling are then purified by distillation and drying, and used for manufacturing of new polymeric chains [56].

In the case of having expensive wastes but in presence of contaminations, chemical recycling could be the best choice to purify and recycle these waste materials [54].

2.4.5 Quarternary (energy recovery) recycling

Quaternary recycling refers to energy recovery. It is possible to generate energy through plastic wastes in the form of thermal energy by incineration. It is the best waste management option especially when the gathering, classification and separation of plastics are difficult or economically not feasible, or the waste is toxic and has hazardous effects on human health and environment. The wastes are then burned in presence of air to convert the hydrocarbons into carbon dioxide and water in reactor called as incinerator. The heat produced by burning plastic wastes is in the form of superheated steam. The superheated steam can be used for generating electricity via turbine generators, and the residual heat from the waste stream for heating the buildings. The melt residue from the incinerator is released from hazardous toxics and can be buried as waste landfill [55].

2.5 Polymer Recycling

2.5.1 Sources of recycled PET

Nowadays, two PET grades dominate the global market: fiber-grade PET and bottle-grade PET, which differ basically in molecular weight, intrinsic viscosity, and optical appearance and their production methods depend on the amount and type of co-monomers, stabilizers, metal catalysts and colorants [57].

The waste of PET can be obtained from different streams such as bottles, foils, plates, cord from tires etc. For each stream there can be a problematic case for recycling such as contaminations coming from various sources, different types of additives, and molecular weight differences of PET grades. These problematic cases can affect the quality and repeatability of the final recycling products [58].

PET can be recycled by using general recycling processes such as primary, secondary, tertiary and quaternary methods however, the mechanical and chemical recycling are the most common routes due to the nature of recycled PET materials.

2.5.2 Mechanical recycling of PET

Comparing to chemical recycling, mechanical recycling of PET by melt re-processing is easy and requires only low starting investments with minimum environmental damages. However, the major problem in mechanical recycling of PET is the reduction in molecular weight and melt viscosity, which is caused by thermal and hydrolytic degradation in the presence of contaminations and moisture impurities at elevated temperatures [33, 57].

Contaminations of recycled PET has an important effect on chemical and physical property reduction through thermal decomposition during re-processing at high temperatures [59]. The recycled PET can be contaminated by many substances such as; water, coloring impurities, acetaldehyde, the acid producing contaminants and other substances like detergents, fuel and etc. [57]. Minimizing the contaminants from recycled PET is an essential first step in mechanical recycling process to obtain recycled PET with desired features [33, 57].

Removal of contaminations consists several processes such as sorting, grounding and washing of recycled PET such as PET waste bottles or fibers. The sorting process is employed to separate PET wastes from poly (vinyl chloride) (PVC), polyethylene (PE) and other plastics [33, 57]. Only 90% of the total PVC content in recycled PET can be removed manually before grinding process. It is possible to employ multistage grinding, an automatic separation method to detect chlorine atoms of PVC to separate more PVC from recycled PET wastes [33]. Following the sorting process, recycled PET is ground into flakes, and then washed. There are two ways of washing process: a solvent washing with using tetrachloroethylene (TCE), and an aqueous washing that consists of two steps; a hot wash with 2% sodium hydroxide solution and detergent at 80 °C followed by a cold wash with water only [57].

During re-processing, recycled PET is subjected to thermal, mechanical degradation and hydrolytic chain scission. In the presence of even as low as 100 ppm PVC chain scission of recycled PET could be expedited via production of hydrochloric acid [33, 57, 60]. Other destructive acids are acetic acid, which is produced by poly (vinyl acetate) (PVA) closures degradation, and rosin acid and abietic acid, which are produced from adhesives. The acidic contaminations act as catalysts for chain scission reactions during melt processing of recycled PET [57]. Moisture contamination in recycled PET should be below 0.02% in order to avoid molecular weight reduction through hydrolysis reactions. It can be prevented by proper drying after flake washing process which is the main source of water in recycled PET preparation. Flakes of colored bottles and printed ink labels also cause undesired colors during re-processing. Improvement of sorting and washing processes in mechanical recycling may decrease coloring contaminants. Acetaldehyde is another contaminant that exists in PET and recycled PET as a result of degradation reactions. Stabilizers are also used in order to reduce the amount of acetaldehyde in PET [33, 57].

2.5.3 Chemical recycling of PET

Recycling of PET through a chemical approach is nearly parallel to manufacture of the polymer on a commercial scale [57]. In chemical recycling, PET is processed by partial depolymerization into oligomers or total depolymerization into monomers. The oligomers and monomers are then re-polymerized, and as a result regenerated polymers could be formed. Aforementioned regenerated polymers, monomers or both may be blended with neat materials. Purification steps of monomer/polymer regeneration process in addition to washing may involve distillation, crystallization and additional chemical reactions [61]. Various processes for chemical recycling of recycled PET are available such as glycolysis, methanolysis, hydrolysis, and other processes such as aminolysis and ammonolysis [57, 61]. Most of the chemical recycling processes consist of esterifying the polymer with excess of reagents such as diamines, alcohols, diols, or water [55, 61].

Despite mechanical recycling, in chemical recycling hydrolysis is considered as a recycling method of recycled PET by the reaction of PET with water in an alkaline, acid or neutral environment. Hydrolysis leads to total depolymerization of PET to its monomers TPA and EG. The reaction requires processing conditions at high temperature and pressure where no additives, such as neutralizer and catalyst are required [61].

Methanolysis is the recycling method of recycled PET via methanol at high temperatures and high pressures with the main products being DMT and EG. It is possible to purify the produced DMT and use it to product new PET. Methanolysis is less sensitive to the existence of contaminations in the recycled PET compared to other chemical recycling methods [61].

Glycolysis is the recycling method of recycled PET via glycolsis, in the presence of transesterification catalysts, such as metal acetates. Recycled PET can be depolymerized via glycolysis to obtain polyols or oligomeric diols, or glycolyzed into its monomeric units, BHET or DMT. BHET can also be used as a substrate to product PET and other polymers [61].

2.5.4 Properties of recycled PET

PET is extensively used in large-scale industrial productions all over the world, especially in manufacturing of textile fibers, soft drink beverage bottles and packaging films. Recycling of PET is essential due to global environmental concerns. However, PET undergoes thermal, chemical, mechanical and oxidative degradation during recycling processes. These degradations limit its usage in many applications by lowering the molecular weight of the polymer and, consequently, its viscosity, melt strength, thermal and mechanical properties. Recycled PET is intended as the raw material for applications requiring high engineering rheological and mechanical properties [43]. As discussed above, the major factor that limits the use of recycled PET in new products is the level of contaminations. Minimum requirements of recycled PET flakes to be re-processed is reported in Table 2.4 [33, 61].

Table 2.4 : Minimum requirements of recycled PET to be re-processed [33, 61].

Properties	Units	Values
Intrinsic Viscosity	dL/g	>0.7
Melting Temperature	°C	>240
Water Content	wt%	<0.02
Flake Size (D)	mm	0.4<D<8
Dye Content	%	<10
Yellowing Index	-	<20
Metal Content	ppm	<3
PVC Content	ppm	<50
Polyolefin Content	ppm	<10

In particular, the presence of water and PVC in the recycled PET promotes chain scission during processing at elevated temperatures. At high processing temperatures, hydrolysis reactions break the PET chains with carboxyl acid and hydroxyl ester end groups. The thermal degradation also results in chain cleavage with carboxyl acid and vinyl ester end groups. Hydrolysis and thermal degradation reactions of recycled PET are shown in Figure 2.18 [33].

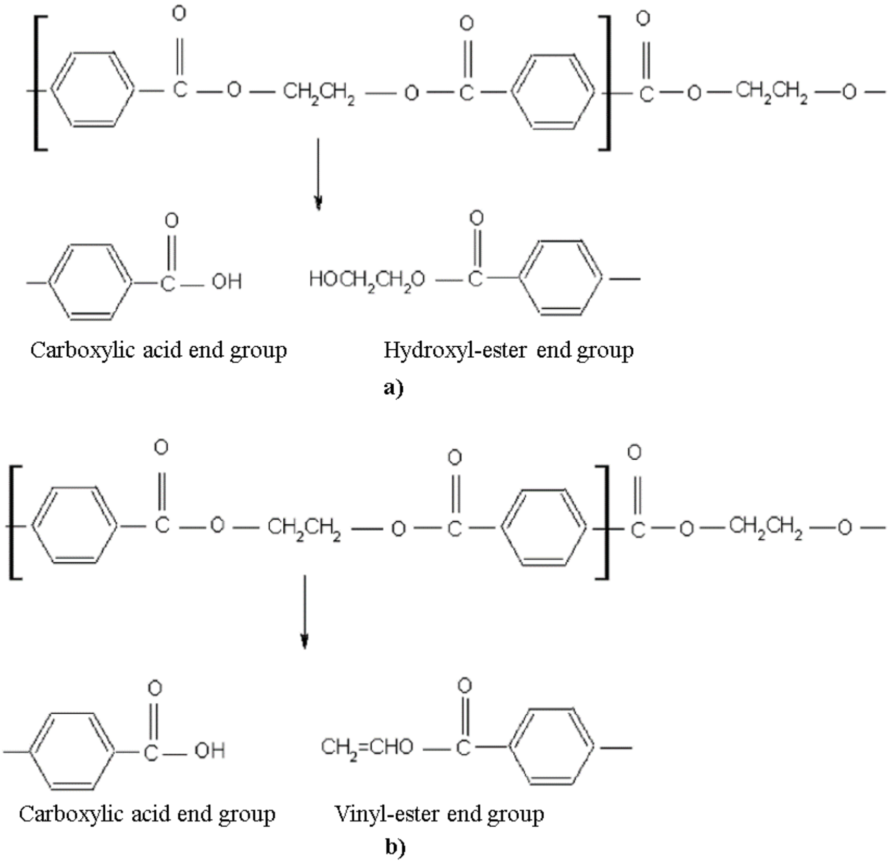


Figure 2.18 : Degradation reactions of PET: (a) hydrolysis reaction and (b) thermal degradation reaction [33].

Thermal degradation of PET promotes the carboxyl content and decrease in hydroxyl content. Sudden changes in the concentration of PET end groups can cause reaction with the presented modifiers PET in itself and thus formation of cross linked structures. It has been reported by many researchers that the degradation phenomena of PET during recycling processes lead to a decrease in melt viscosity and molecular weight [47, 62-64]. Torres et al. [63] noticed that the decrease in intrinsic viscosity and molecular weight of recycled PET is more severe after injection molding when compared to those of virgin PET after injection molding. They indicated that recycled PET is more sensitive to thermal and hydrolytic degradation due to the presence of moisture residue and contaminants such as PVC and adhesives compared to virgin PET. Oromiehie and Mamizadeh [64] examined effect of different extrusion techniques on the properties of recycled PET, virgin PET and their blends. They also indicated that the sensitivity to thermal and hydrolytic degradation of recycled PET is severer than virgin PET. Recycled PET showed a further decrease in the melt viscosity, average molecular weight because of the hydrolytic chain scission and thermomechanical degradation during processing.

2.5.5 Improving properties of recycled PET

In order to overcome the problems caused by depression in molecular weight, there are some chemical reactive methods that could compensate molecular weight reduction. The most regularly utilized technique is the usage of chemical agents which incorporate di- or multifunctional groups to crosslink the molecules. These chemical agents behave as a bridge between corrupted chains of polymers through their functional end groups. This is called as “chain extension” [65]. Improving rheological properties and melt strength of PET by modification provides opportunity to use it in applications such as foaming, extrusion, and extrusion blow molding. Improvement of low intrinsic viscosity materials can be achieved through extension/branching reactions with chain extenders [38].

Chain extenders are used in order to rebuild the molecular weights and improve the rheological properties of the degraded polymers to increase their melt strength during extrusion, which may react with hydroxyl (-OH) and carboxyl (-COOH) end groups by poly-addition and thus increase the chains’ length [43, 59-61]. The use of certain additives, such as radical generators with reactive functional groups during melt processing is called “reactive extrusion”, since polymer chemistry is modified during melting by using the extruder as a reactor [49].

It is also possible to raise the molecular weight and thereby the intrinsic viscosity of polymers by performing solid-state polymerization although the use of chain extender is preferred. The main advantages of chain extension compared with solid-state polymerization are lower system costs without the need of additional investment, faster reaction and more flexibility [38, 66]. There is a wide range of commercially available chain extenders as applicable for PET. Depending on the nature, reactivity and number of functional groups present on the chain extender molecules different properties could be obtained in the final product [35]. Bi-functional chain extenders such as di-epoxides, di-isocyanates, di-anhydrides or bis (oxaline)s promote linear chain extension. Pyromellitic di-anhydride (PMDA) is a commonly used bi-functional linear chain extender in PET. On the other hand, tri- or tetra-functional chain extenders such as tetra-epoxides, tetra-functional tetra-glycidyl diamino diphenyl methane (TGDMM) could generate branched structures in PET [38].

Many researchers investigated the effect of addition of chain extenders with different chemistries into recycled PET to overcome the molecular weight and melt strength depression and hence to enhance the thermal, mechanical, rheological properties of recycled PET [44, 46, 67-74]. Awaja and Daver [68] studied the effect of different concentrations of PMDA as a chain extender and the effect of residence time in the extruder on the intrinsic viscosity and hydroxyl-carboxyl content of recycled PET. Both hydroxyl and carboxyl content of recycled PET decreased with the addition of chain extender. Increasing chain extender concentration resulted in significant decrease in hydroxyl content and an increase in intrinsic viscosity of recycled PET. They noticed that the chain extension process mainly depends on chain extender concentration than the residence time. Incarnato *et al.* [69] investigated the effect of different concentrations of PMDA on rheological properties of recycled PET. They reported that the complex viscosity increases with chain extender at low frequencies in comparison to untreated recycled PET, and addition of chain extenders resulted in shear thinning behavior at high frequencies. The shear thinning behavior of the recycled PET treated with chain extender had been attributed to the introduction of long chain branches and an increase in molecular weight. Daver *et al.* [46] also investigated the effect of different concentrations of PMDA in rheological properties of recycled PET in comparison to virgin PET. They also showed that increasing chain extender content leads to increase in molecular weight in recycled PET. Japon *et al.* [44] also studied the use of multi-functional epoxy-based chain extenders having different degrees of functionality to increase the melt strength of PET. They noted that chain extenders with multi-functional epoxides offer a combination of the following parameters: increasing the reactivity and inducing long chain branching, thus an extension-thickening behavior and accompanying increase of extensional viscosity. In order to investigate the efficiency of chain extender, torque measurements in a Brabender internal mixture is employed. While untreated PET showed a torque decrease as time goes on due to degradation, PET samples included tri- and tetra-functional chain extenders showed an increase in torque. They indicated that as the reaction proceeds, more functional groups of the chain extenders were consumed by the reaction with the carboxyl groups produced by degradation reactions of PET, epoxy homo-polymerization and by reaction with the PET hydroxyl groups and these reactions leaded to cross-linking.

Crystallinity of PET is an important parameter for end-use applications, and it mainly depends on the molecular structure of the polymer [47, 65]. Torres *et al.* [63] stated that the presence of impurities in the recycled PET acts as crystal nucleating sites that facilitate the heterogeneous crystallization. Awaja *et al.* [68] showed that the crystallinity of chain extended recycled PET is decreased with increasing extrusion residence time with high chain branching. It is reported at some studies that the crystallinity depression is expectable during chain extension due to increase in molcuelar entanglement leaded by high degree of branching and cross linking [47, 65, 67, 70]. Raffa *et al.* [43] investigated the effect of both di-functional and multi-functional chain extenders on recycled PET. Both chain extenders caused a significant depression of the crystallization temperature and of the corresponding enthalpies. On the other hand, it is reported by Rosu *et al.* [42] that addition of branched PET to linear PET promotes crystallinity. Li *et al.* [75] noticed that especially at low crystallization temperature and at low branching extent the crystallization rate increases. While small content of branching agent enhanced crystallinity, high amount reduced the crystallinity due to depression of molecular mobility.

2.6 PBT/PET Binary Blends

PBT and PET are commercial polyester resins that are widely being used in various applications. The PBT/PET blends have been developed principally to improve processability, surface appearance, heat deflection temperature (HDT), impact strength and dimensional stability [21]. Those blends are utilized for producing visible parts of appliances that require the appeal of smooth and glossy surface with the properties of high stiffness, strength and heat resistance. They are also used in electrical and automotive applications. The primary reason for developing PBT/PET blends appears to be the improvement of surface appearance and gloss in the injection-molded parts in comparison to those made from the individual resins. These blends also take advantage of low cost of PET and the rapid crystallization rate of PBT [23].

2.6.1 Miscibility and blend morphology

PBT and PET form stable blends without requiring compatibilizers due to their miscibility at the amorphous phase as firstly indicated by Escala and Stein. Based on the analysis of DSC, infrared studies, and X-ray scattering, they indicated the compatibility of PBT/ PET blend at the amorphous state as judged from the existence of a single glass-transition temperature intermediate between those of individual components. However, in crystalline stare, separate crystalline phases were formed with no evidence of co-crystallization and, in other words, immiscibility in crystalline state. In this case, slight mutual melting point depression were observed [76]. Avramova [77] also reported a single glass transition temperature for all compositions of PBT/PET blends, indicating the miscibility of the polymers at the amorphous phase. The blends showed single crystallization peak and multiple melting peaks with some depression in melting temperatures.

Escala and Stein [76] suggested that the compatibility in PBT/PET blends might arise from the transesterification (ester interchange) reactions between both polymers, consequently formation of copolymers in the blend during melt processing. Transesterification reaction between PBT and PET has been studied by researchers [77-81]. This reaction depends on the initial miscibility of the homopolymers in the molten state and on the processing conditions leading to the formation of block copolymers in the first stage and random copolymers ultimately. Therefore, the transesterification reaction can affect the morphology and the properties of the blends.

Even though transesterification can improve the miscibility of the polymer blends, it can also decrease the performance of the blend due to an excess of ester interchange reactions [81]. Backson *et al.* [79], Matsuda *et al.* [82] Kim *et al.* [83] examined the transesterification in PBT/PET blends using C nuclear magnetic resonance (C-NMR) analysis. C-NMR is a sensitive and efficient technique to analyze the sequence structure of polymer chain qualitatively and quantitatively. FT-IR and small angle neutron scattering (SANS) are other techniques to employ for measurement of the ester-interchange reaction and transesterification products [80]. Matsuda *et al.* [82] applied 600 MHz H-NMR to investigate relationship between sequence distribution and the melting temperature of poly (ethylene/butylene terephthalate) copolymers after transesterification reaction between PBT and PET. Wang *et al* [80] and Tianshui *et al.* [81] investigated the effect of nano silica particles on transesterification of PBT/PET blends. Both researchers indicated that nano silica particles acted as an inhibitor of transesterification between PBT and PET by utilizing the reaction of the hydroxyl end groups of both PBT and PET with hydroxyl surface groups of nano silica. As a consequence, the reduction of hydroxyl groups of the polymers leaded to the inhibition of transesterification reactions.

Morphology of polymer blends is highly dependent on the properties of each components and processing conditions. Despite the prove of miscibility in DSC thermograms in previous studies, Aravinthan and Kale reported that scanning electron micrographs of PBT/PET blends at close blending ratios formed morphologies such as those of co-continuous and fibrillar which shows their immiscibility [84].

2.6.2 Thermal properties

As noted earlier, the miscibility of PBT/PET blends has been firstly determined by researchers by employing DSC analysis. It is a common knowledge that PBT/PET blends show an average glass transition temperature, one crystallization peak without presence of co-crystals and two melting peak with a slight mutual depression. Glass transition temperatures versus PET concentration in PBT/PET blends are reported in study of Escala and Stein, as shown in Figure 2.19 [76]. Only one glass transition temperature was observed for all blends. The variation of glass transition temperature seems to be linearly proportional to the change of the composition. Melting temperatures of both components were existed in the blends with a slight depression depending on the composition. Melting temperatures of PBT and PET versus PET concentration in the blend are reported in the study of Escala and Stein, as shown in Figure 2.20 [76].

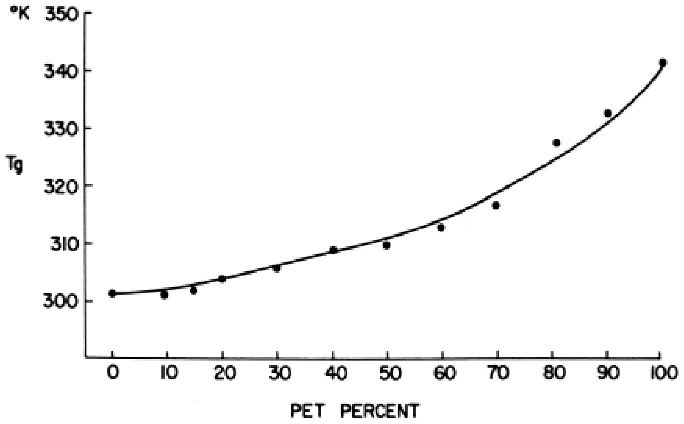


Figure 2.19 : PBT/PET blends glass transition temperature versus PET concentration as determined by DSC [76].

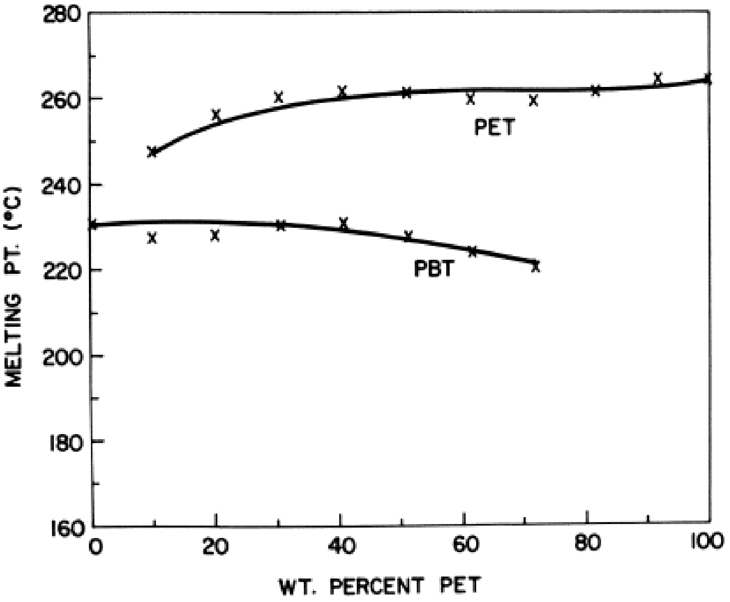


Figure 2.20 : Melting temperatures of PBT and PET versus PET concentration in the blend as determined by DSC [76].

Major drawback of PET is its slow crystallization and difficulty in processing such as in injection molding. One of the reasons to blend PET with PBT is faster crystallization rate of PBT and hence improving the PET’s processability [67, 78, 85-87]. Effects of concentrations of each component, degree of transesterification between PBT and PET, degree of branching and addition of fillers, reinforcements effects on crystallization rate of PBT/PET blends is investigated in many studies.

Ito *et al.* [78] investigated how different processing methods affect the transesterification degree of PET/PBT blends as well as their crystallization behavior. While extrusion at higher temperatures leaded to higher degree of transesterification, extrusion at lower temperature and solution casting processes resulted in a lower degree of transesterification. They reported that the crystallization was enhanced with partial transesterification copolymerization. Under isothermal condition at the temperatures over 200 °C, they confirmed that PBT crystallization accelerated by the existence of PET crystals in the blend which presented intermediate degree of transesterification. According to study of Ito *et. al.*, transesterification copolymers enhanced crystallization of one of the components with the existence of the crystals of another component.

Szostak [86] investigated the effect of different compositions of PBT and reported that introducing PBT into PET increases the crystallization rate of the blend while decreasing the crystallization temperature and increasing the degree of crystallinity. Tao *et al.* [88] stated that the presence of PBT provided PET to nucleate more easily by broadening its processing temperature.

Zhang Z. *et al.* [85] and Rajakumar *et al.* [87] studied the effect of addition of montmorillonite and glass fiber on thermal properties of PBT/PET blends, respectively. According to the study of Rajakumar *et al.* [87], addition of 3 wt. % montmorillonite accelerated the crystallinity of the blend compared to that of virgin PBT and PBT/PET blend. They also DMA to estimate deformation level of the material under an applied load. While lower storage modulus states that the material is easily deformed under load, the reduction in the storage modulus through glass transition temperature can provide an information about degree of crystallinity. Storage modulus of the PBT increased with the addition of 20 wt. % PET, likewise storage modulus of the blend is further increased by addition of 3-5 wt. % montmorillonite. DMA results confirmed the acceleration of crystallinity in DSC results. Glass fiber is commonly used reinforcement in engineering polymers to obtain higher performance. Glass fiber reinforced PBT/PET composites are commercially available in the market with the trading names such as Celanex, Valox, Schulman etc. It is previously stated by different researchers that glass fiber acted as a nucleating agent and improves the crystallization of both PBT and PET [89, 90]. Zhang *et al.* [85] examined the non-isothermal crystallization kinetics of glass fiber reinforced

PBT/PET composites having different contents of glass fiber at the cooling rates ranging from 5 °C/min to 25 °C/min. They reported that low glass fiber content increased the crystallization rate due to their heterogeneous crystal nucleation power, however, higher contents decreased this rate as excessive fibers could hinder the molecular mobility.

Liu *et al.* [91] investigated the effect of various mixing temperatures and concentrations of chain extender on thermal properties and chain structures of PET/PBT blend by DSC analysis. It is reported that addition of chain extender accelerated the degree of transesterification which is determined by C-NMR analysis when the mixing temperature was above 270 °C. Subsequently, the sequence length of the reactive blends produced initially by chain extension became shorter and more rapidly than that of blends without addition of chain extender. They indicated that this behavior leaded to the formation of more coiled chains, slower crystallization rate and lower melting temperature. Jacques *et al.* [92] also reported that increase in molecular weight with chain extender hindered the chain mobility and therefore lowered the crystallization rate.

Heat deflection temperature is also an indicator of thermal properties of polymers and an important parameter for estimation of heat resistance of a material under service conditions. According to study of Aravinthan and Kale [84], increasing concentration of PET into PBT increased HDT because of higher HDT value of PET compared to PBT.

2.6.3 Mechanical properties

While PBT has advantages over PET with its faster crystallization rate and better processability, there are slight differences between their mechanical properties. Different approaches on impact and tensile properties of blends of PBT and PET exist in literature. It is reported by Mikiatev and Borukaev [30] that increasing PET content in the blend over the value of 20 wt% caused a significant reduction in impact strength of the blend as shown in Figure 2.21. Szostak [86] also stated the same behavior in PET/PBT blends and reported that increasing PBT content in the blends improved the impact strength.

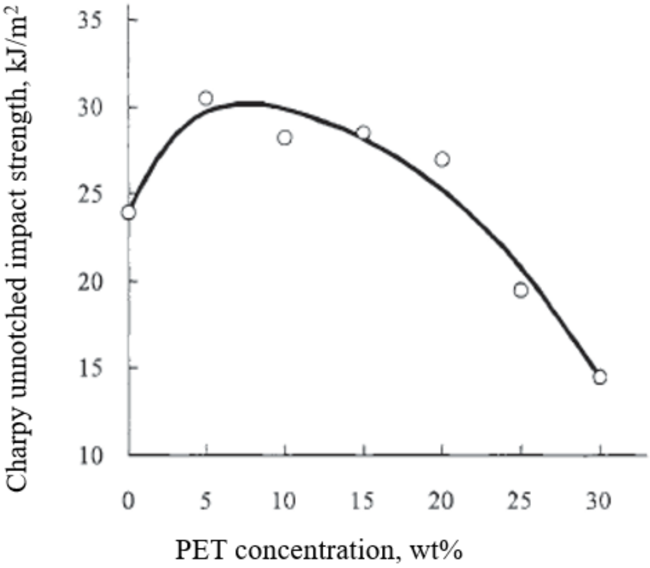


Figure 2.21 : A plot of impact strength against the PET content in PBT/PET blends [30].

Mikiatev and Borukaev [30] showed that beyond 20 wt% of PET, due to the phase separation phenomenon, the impact strength of the blend was suppressed. Baxi et al. [93] investigated the effect of different concentrations of different impact modifiers on performance enhancement of PET/PBT blends at the ratio of 60:40. The reinforcement and network formation of the impact modifiers (Elvaloy AC and polypropylene copolymer B220 MN) in the matrix was observed in SEM analysis. These features resulted in the highest impact strength with around 163% increase in comparison with non-modified PET/PBT blend.

It is stated by Aravinthan and Kale [84] and Szostak [86] that PET has relatively higher tensile strength than PBT. Increasing the amount of PET in PBT/PET blends slightly increased the tensile and flexural strength [86, 94]. At the study of PBT/PET blend at different concentrations, Aravinthan and Kale [84] reported that highest tensile and impact strength were obtained in 50:50 PBT/PET blend. They stated that this synergistic improvement in the mechanical property was due to the co-continuous morphology which was observed in 50:50 PBT/PET blend.

2.6.4 Rheological properties

Firstly, Mishra and Deopura [95] investigated the rheological behavior of blends of PET with up to 10 wt% PBT by employing a capillary rheometer. They reported that the addition of small amount of PBT (3 wt%) into PET resulted in an increase in the viscosity due to the increased molecular entanglement. More than 4 wt% PBT in PET, they observed a decrease in the viscosity and interpreted the results due to the appearance of phase segregation. Melt flow rate (MFR) values at different PET concentrations in the PBT/PET blends is reported by Mikitaev and Borukaev. While addition of PET up to 20 wt% in PBT didn’t change the MFR significantly, further increase in PET content resulted in an increase in MFR values and a decrease in melt strength. They reported that PET has a specific character, which acts as a relaxation agent for the polymer matrix that enlarges the interface boundary. Thereby, addition of PET over 20 wt% may cause a conversion of compatibility between PBT and PET to a partial compatibility [30].

2.7 PBT/Recycled PET Binary Blends and Their Properties

Patents and scientific papers exists in the subject of PBT/recycled PET blends. CN 102911486 (B) reported a formulation prescription consisted of glass fiber reinforced PBT/recycled PET material with processing additives such as compatibilizers, impact modifiers, and antioxidants. The patent claims that the performance of PBT/recycled PET material prepared by their formulation equals to that of PBT/virgin PET [96]. US Patent 20140163156 (A1) reported a formulation prescription consisted of virgin PBT, different types of recycled PET and glass fiber at various blending ratios, as well as stabilizing and nucleating agents, and impact modifier. By modifying the content and type of recycled PET and the content of nucleating agent they optimized the crystallization behavior and hence processing via injection molding [97]. KR 20130021502 (A) reported an environmentally friendly flame retardant PBT/recycled PET composition which is applicable to electrical/electronic and automotive parts [98].

Baxi *et al.* [99] investigated the thermal, mechanical and microstructural properties of PBT/PET blends mixed with recycled PET. They prepared their samples by addition of 60 or 90 wt% of recycled PET into virgin PET/PBT blend either with composition of 40:60 or 20:80. They interpreted the mechanical property enhancement in the blend system of 60 wt% recycled PET into 40:60 virgin PET/PBT blend due to the branching or crosslinking of the polymeric chains between recycled PET and blends structure. The crystallinity measurements were carried out with the X-ray diffraction (XRD) technique and they showed that the crystallinity of the blend system of 40:60 virgin

PET/PBT blends with addition of recycled PET was higher to that of 20:80 virgin PET/PBT blends with addition of recycled PET.

Rahmat *et al.* [100] studied the effect of chain extender content on mechanical properties and viscosity of PBT/glass fiber reinforced recycled PET composites. They have used styrene-acrylic multifunctional oligomer, a polyepoxide with a commercial name of Joncryl ADR-4368 as a chain extender. They observed a significant viscosity rise as well as melt volume rate (MVR) drop after addition of 0.5 wt% and 0.65 wt% of chain extender into 50:50 PBT/glass fiber reinforced recycled PET. The limited dosage of chain extender is determined as 0.65 wt% according to their study due to the gel formation caused by high level of branching and crosslinking. They employed flexural and un-notched Charpy impact tests to estimate mechanical properties of the samples. Addition of chain extender resulted in improvement in flexural strength of the blends. When the chain extender content increased up to 0.65 wt%, the sample could not break as branching and crosslinking increased the toughness strength as a result of limited chain mobility. While addition of glass-fiber reinforced recycled PET decreased the impact strength of PBT, the addition of chain extender improved the impact strength of even the blend composites.

2.8 Novelty of the Current Research

There are a few studies in literature on PBT/recycled PET binary blends. Generally, virgin PET is preferred to blend with PBT. Investigations on thermal, mechanical, viscoelastic, and rheological properties of either PBT/PET binary blends or PBT/PET composites reinforced with nano-additives or glass fibers exist in the literature. As mentioned earlier, recycled PET possess limited number of applications due to its deteriorated properties. Deterioration could be caused by chain scission in the presence of water, contaminations and other polymeric impurities. These properties could be improve by blending with virgin polymers or addition of certain additives which include reactive functional groups to modify the molecular structure. Addition of chain extenders to repair the broken chains of recycled PET molecules was examined by many researchers. It is possible to find in literature such studies that investigate the effects of concentrations and functional groups on various properties of recycled PET.

Differing from the literature, in this thesis study, by considering the excess of environmental pollution and being supportive to the environmental sustainability, recycled PET flakes obtained from bottle wastes were blended with PBT. A commercial chain extender with Joncryl ADR 4468 ® trade name was used in the blends. The effect of various concentrations of recycled PET on PBT/recycled PET binary blends was investigated. Furthermore, Joncryl was added to the blends through two different processing methods: all toghether and premixing method. In the first method, PBT, recycled PET flakes and Joncryl were physically mixed and extruded all together from a hopper to the pellets. In the second method, recycled PET flakes were extended with Joncryl at different ratios in extrusion previously. These extended recycled PET were dried in an oven overnight, and then physically mixed with PBT at certain ratios and extruded from a hopper to obtain final blends. Extensive studies on crystallization behavior, viscoelastic properties and mechanical properties of the blends were examined.

3. EXPERIMENTAL

3.1 Materials

A commercial PBT with 17 ± 4 cm^3/10 min melt volume rate was supplied from Sasa Polyester Inc. Co. in Adana, Turkey. Recycled PET flakes obtained from bottle wastes were supplied from Çevre PET Inc. Co. in Adana/Turkey. The properties and contamination contents of supplied recycled PET flakes are listed in Table 3.1.

Table 3.1 : Properties and contamination contents of supplied recycled PET flakes.

Properties	Unit	Values
Intrinsic Viscosity	dL/g	0.65-0.75
Water Content	wt%	0.3-0.7
Flake Size (D)	mm	8-10
White Color Ratio	%	75-85
Blue Color Ratio	%	15-25
Metal Content	ppm	10
PVC Content	ppm	20
Paper and Fiber Content	ppm	10
Adhesives Content	ppm	10

A commercial chain extender with Joncryl ADR 4468 ® trade name was supplied from BASF. Joncryl is a multi-functional styrene acrylic oligomer which includes epoxy reactive groups with a chemical structure as in Figure 3.1. The typical properties of Joncryl is listed in Table 3.2.

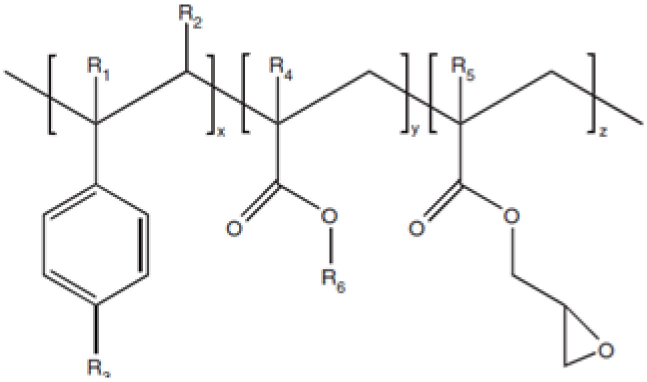


Figure 3.1 : Chemical structure of Joncryl ADR 4468 ®.

Table 3.2 : The typical properties of Joncry ADR 4468 ®.

Properties	Unit	Values
Glass Transition Temperature	°C	59
Molecular Weight	-	7250
Epoxy Equivalent Weight	g/mol	310

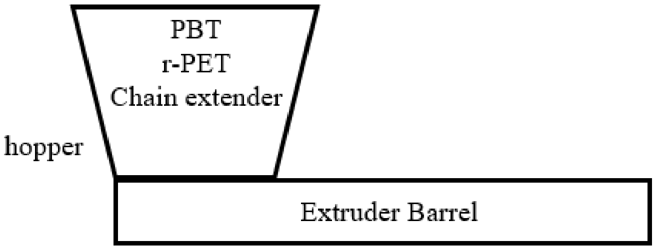
3.2 Experimental Design

First of all, chain extender at different ratios was mixed with recycled PET flakes and extruded to obtain extended recycled PET. Codifications and compounding ratios of chain extender in recycled PET flakes are summarized in Table 3.3.

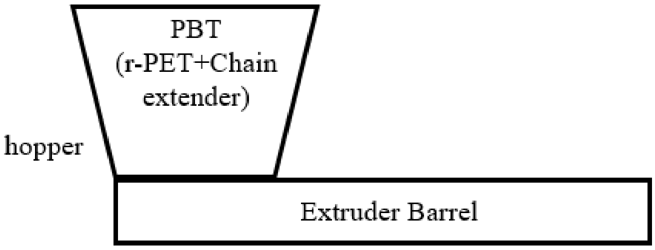
Table 3.3 : Compounding ratios of recycled PET flakes with Joncryl.

Recycled PET/Chain Extender	Recycled PET (wt%)	Chain Extender (wt%)
r-PET	100	0
r-PET+CE0.05	99.95	0.05
r-PET+CE0.25	99.75	0.25
r-PET+CE0.40	99.60	0.40
r-PET+CE0.80	99.20	0.80

During blending, previously, 25, 50 and 75 wt% of recycled PET was mixed with PBT and extruded. Chain extender was added to PBT/recycled PET blends through two different methods. In the first method, which was named as all together method, PBT, recycled PET flakes and chain extender were physically mixed and extruded all together from a hopper to pellets. In the second method, which was named as pre-mixing method, recycled PET flakes were extended with chain extender in extrusion process, primarily. Extended PET pellets were dried in an oven overnight at 70 ^{o} C, and then mixed with PBT at certain ratios and extruded from a hopper to obtain final blends. Illustrations of these processing methods was given in Figure 3.2.



a) Alltogether mixing method



b) Pre-mixing method

Figure 3.2 : Schematics of different processing methods through blending: all together method (a), pre-mixing method (b).

In this thesis study, various parameters were invesitgated such as: the effect of chain extender concentration on r-PET and various concentrations of r-PET, using different processing methods while addition of chain extender, and various concentrations of Joncryl on the blend properties. The compounding ratios and the codifications of the blends were given in Table 3.4. As an example, PBT/r-PET were blended and extruded at 75:25 ratios. Addition of chain extender is carried out by using two different processing methods, as mentioned above. In the alltogether method, 0.2 wt% of extender was physically mixed with around 75 wt% of PBT and 25 wt% of r-PET flakes and extruded all together from a hopper. In the pre-mixing method, recycled PET flakes were extended with 0.8 wt% chain extender in extrusion process, previously. After drying, 25 wt% of this extended r-PET was mixed with 75 wt% of PBT and extruded from a hopper. The final chaine extender content was adjusted to be 0.2 wt% as in the first method. To achieve the final 0.2 wt% content of extender also in 50:50 and 25:75 PBT/r-PET blends, extended r-PET with 0.4 and 0.25 wt% of chain extender was used, respectively. Only in 50:50 and 25:75 PBT/r-PET blends, effect of different final extender concentrations on the blend properties were examined. The extended r-PET with 0.8 wt% of chain extender mixed with PBT at the ratios of 25, 50 and 75 wt%. Effect of this premix concentration on the blend properties were investigated.

Table 3.4 : Compounding ratios and codifications of PBT/recycled PET blends.

Codification of the samples	PBT (wt%)	Recycled PET (wt%)	Chain Extender (wt%)
A7525	75	25	0
A752502	75	25	0.20
P752502	75	25	0.20
A5050	50	50	0
A505002	50	50	0.20
P505002	50	50	0.20
A505004	50	50	0.40
P505004	50	50	0.40
A2575	25	75	0
A257502	25	75	0.20
P257502	25	75	0.20
A257506	25	75	0.60
P257506	25	75	0.60

3.3 Processing and Sample Preparation

3.3.1 Reactive extrusion using twin-screw extruder

PBT, r-PET flakes and extended r-PET pellets were dried in an oven at 70 ^{o} C overnight to reduce moisture content and avoid further degradation before blending and compounding. A laboratory scale twin screw extruder (Prism TSE 24) with 24 mm screw diameter and 28 L/D ratio was used for preparing the compounds. The temperature profile was set to 235-245-255-260-260-255-245 ^{o} C from the feeder to the die with a constant screw rotation speed of 200 rpm. The filament shaped extrudates were cooled in a water bath and then cutted into pellets in a granulating unit.

3.3.2 Injection molding

All samples were dried in an oven at 70 ^{o} C overnight before injection molding process to reduce the moisture content as mentioned above. Injection molding machine Arburg Allrounder 320 ^{o} C with 25 mm screw diameter and 24 L/D ratio was used to prepare the standard tensile and impact test samples. The barrel temperature was set to 260-265-265-270-275 ^{o} C from the hopper to the nozzle. The mold was controlled at room temperature and injection pressure was set to1500 bar.

3.4 Characterization

3.4.1 Thermal properties

3.4.1.1 Thermal gravimetric analysis (TGA)

Thermal degradation temperatures and residual concentrations of bottle-grade virgin PET, processed r-PET were determined by using TA Instrument TGA Q 500 thermal gravimetric analyzer. Analysis were carried out at a heating rate of 20 ^{o}C/min from room temperature to 950 ^{o} C. The percentage of the residues at 600 ^{o}C were recorded.

3.4.2 Crystallization behavior

3.4.2.1 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to determine the quantitate and qualitative information about physical or chemical changes which involve exothermic and endothermic processes or varieties of crystallization behavior in the enthalpy changes of the samples [93]. The melting and cooling related thermal studies of the samples were performed by using TA-Instrument DSC Q 200 under 50 ml/min flow rate of inert nitrogen gas. Thermal analysis of samples performed at a constant rate of 5 ^{o}C /min by heating the samples from 30 to 300 ^{o}C followed by cooling to 30 ^{o}C and reheating to 300 ^{o}C during the second scan. Further studies on crystallization behavior of r-PET_processed, PBT_processed, A7525, A5050, A505002, P505002, A2575 samples were examined through DSC at different cooling rates of 2, 5, 10 and 20 ^{o}C /min followed by reheating to 300 ^{o}C with heating rate of 5 ^{o}C /min.

3.4.3 Viscoelastic properties

3.4.3.1 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) can be basically described as application an oscillating force to a sample and analyzing the response of the material to that force. The ability to lose energy as heat (damping) and to recover from deformation (elasticity) can be obtained from the analysis. Material’s stiffness (the modulus), which is dependent on the temperature and the applied stress, indicates how well a material will work in a specific application in service conditions. An advantage of DMA is that it is possible to obtain modulus values each time a sine wave is applied, that allows to sweep across a temperature or frequency range. In DMA, a complex modulus, an elastic modulus, and loss modulus are calculated from the material response to the sine wave. These moduli allow better characterization of the material due to the ability of the material to return energy (storage modulus), to lose energy (loss modulus) and the ratio of these effects (tan delta), which is also called as damping [101].

Temperature sweep tests were applied to specimens through dynamic mechanical analysis by using TA Instrument DMA Q 800 under dry air in dual cantilever mode. The rectangular standard test specimens' dimensions were thickness of 3.18 ± 0.2 mm, width of 12.80 ± 0.2 mm and length of 59.75 ± 0.2 mm. Heating rate was set to 2 °C /min from 30 °C to 130 °C at a constant frequency of 1 Hz, 0.03% strain and 15 μm amplitude.

3.4.3.2 Melt flow index (MFI)

Melt flow index (MFI) is mainly identified as the weight or volume of the polymer extruded in 10 minutes through a capillary which possesses a specific diameter and length, by pressure applied through a stable weight under selected temperature conditions. MFI value depends on molecular weight, molecular weight distribution and different levels of branching in the structure. It is kind of a control parameter which enables to estimate the melt strength of the polymer [102]. Melt flow rate (MFR) values of the samples were obtained from MFI test according to ISO 1133 standard. The temperature was set to 260 °C and the stable weight is set to 2.16 kg. Three samples were obtained in every 15 seconds, and weight of the samples were measured and recorded. The average value of the three results is reported with g/10min unit in this thesis.

3.4.4 Mechanical properties

3.4.4.1 Tensile test

Tensile modulus and tensile strength at yield of dog bone shaped (Figure 3.3) specimens at 23 °C were measured by using a tensile testing machine, Zwick Z 020, according to ASTM D638M-91a test standard. The dimensions of tensile test specimens are listed in Table 3.5. The cross-head speed was set to 50 mm/min and gauge length (Lo) was set to 70 mm. The average value of the five results is reported in this thesis.

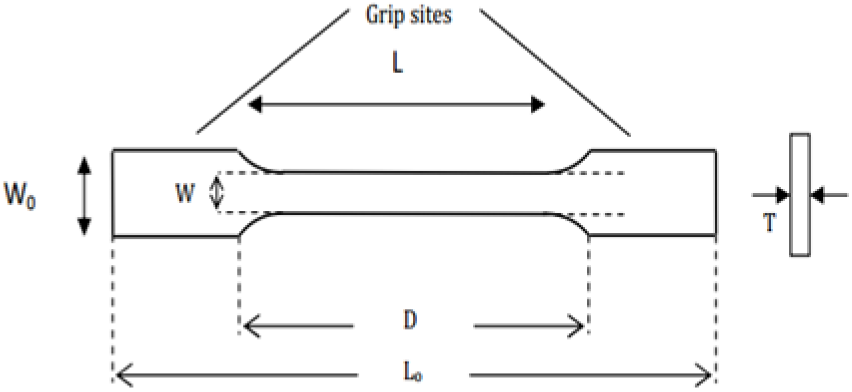


Figure 3.3 : Schematic of tensile test specimen.

Table 3.5 : Compounding ratios and codifications of PBT/recycled PET blends.

Dimensions	Values (mm)
Lo – overall length	75
W – width of narrow section	5
L – length of narrow section	30
Wo – width of overall	10
D – distance between grips	50
T - thickness	2.1

3.4.4.2 Impact test

The Izod impact strength of the standard samples was measured using a standard pendulum type hammer mounted on a machine (Zwick Roell HIT 5.5P), according to ISO 180 standard. Rectangular test specimens' dimensions were thickness of 4 ± 0.2 mm, width of 10 ± 0.2 mm, and length of 80 ± 0.2 mm Standard 2 mm V notch is generated in the impact samples by using a manual notch cutter machine. The notched surfaced of the specimen faced to the pendulum in the test machine. The average value of the ten results is reported in this thesis.

4. RESULTS AND DISCUSSION

4.1 Thermal Properties

4.1.1 Thermal gravimetric analysis

The amounts of residues at 600 °C in both water bottle grade prime PET and processed r-PET were examined in TGA analysis to estimate the effects of inorganic contaminations on properties of the materials. 11.2 and 11.7 wt % of residue was observed in prime PET and processed r-PET, respectively as stated in Figure 4.1 and Table 4.1. There was not a significant difference between the amounts of inorganic residues that could affect the final materials' properties when r-PET is used instead of prime PET.

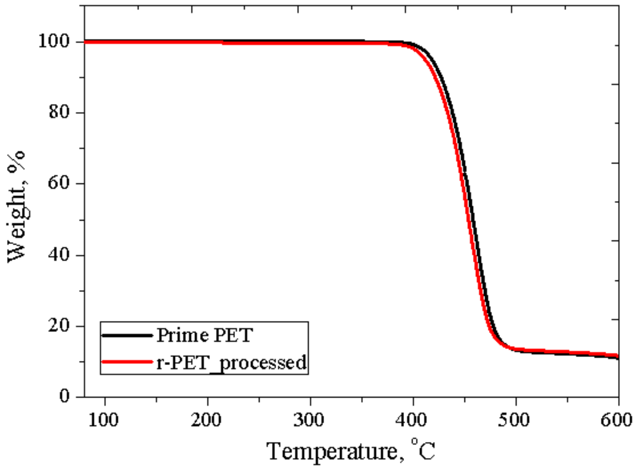


Figure 4.1 : TGA curves of prime PET and processed r-PET.

Table 4.1 : Amounts of residues of prime PET and r-PET.

Materials	Residue at 600 °C (wt%)
Prime PET	11.2
r-PET_processed	11.7

4.1.2 Thermal properties

Thermal behaviors of the materials were carried out by using DSC analysis with heating, cooling and heating cycles. First heating, cooling and second heating curves of processed PBT and r-PET materials are shown in Figure 4.2. As stated in Table 4.2, while glass transition temperature of PBT is 66 °C, that of r-PET is 79 °C. A cold crystallization peak of r-PET was observed around 120 °C during first heating. PBT possessed faster crystallization rate and 37 % higher crystallinity than r-PET in cooling cycles. Both polymers showed double melting peak at second heating cycle, which could attributed to presence of crystals with different perfection degrees.

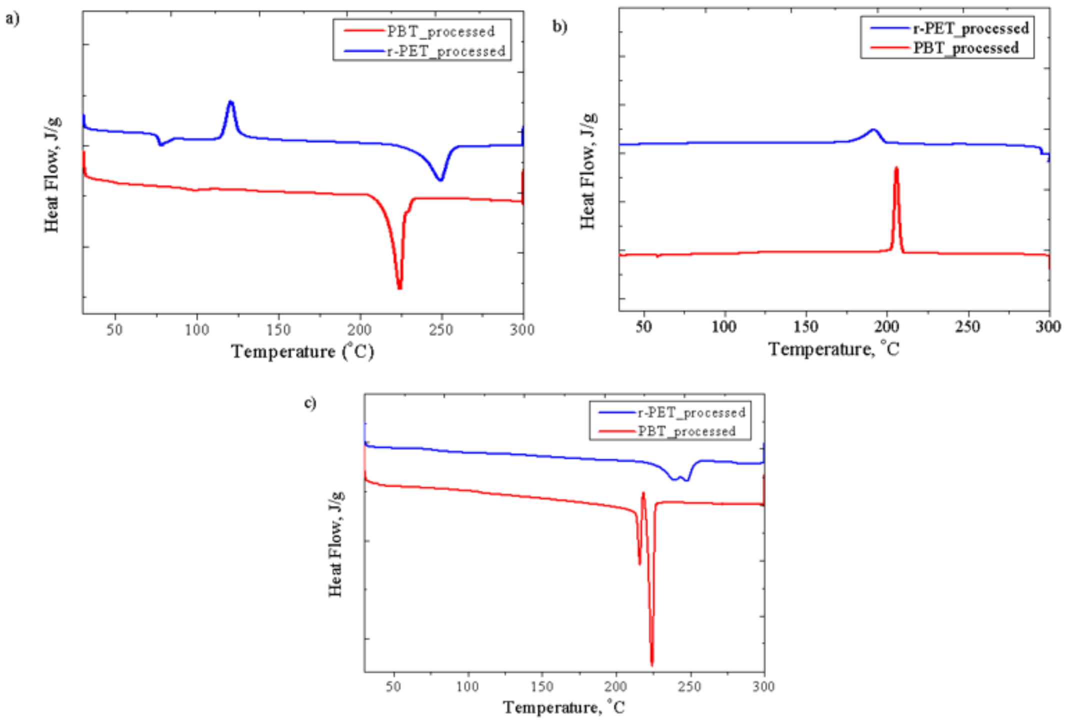


Figure 4.2 : DSC curves of processed PBT and r-PET: (a) first heating, (b) cooling, (c) second heating cycles.

Table 4.2 : Thermal properties of processed PBT and r-PET.

Materials	T_g (°C)	T_{ccr} (°C)	Tm (°C)	ΔH_m (J/g)	T_{cr} (°C)	ΔH_{cr} (J/g)	Tm_{low} (°C)	Tm_{high} (°C)	ΔH_m (J/g)
PBT_processed	66	-	224	49	201	55	215	225	53
rPET_processed	79	121	249	42	196	40	239	247	36

As stated in Figure 4.3 and Table 4.3, addition of chain extender into r-PET did not affect glass transition and melting temperatures at the first and second heating graphs.

Cooling curves of branched r-PET showed that addition of chain extender up to 0.4 wt% slightly enhanced crystallization temperature and crystallinity. It could cause by the action of branched molecular structures as nucleating points which promoted the crystallization. In highly branched r-PET sample (r-PET+CE0.80), due to the lower mobility of branched molecules, crystallization temperature and crystallinity was hindered.

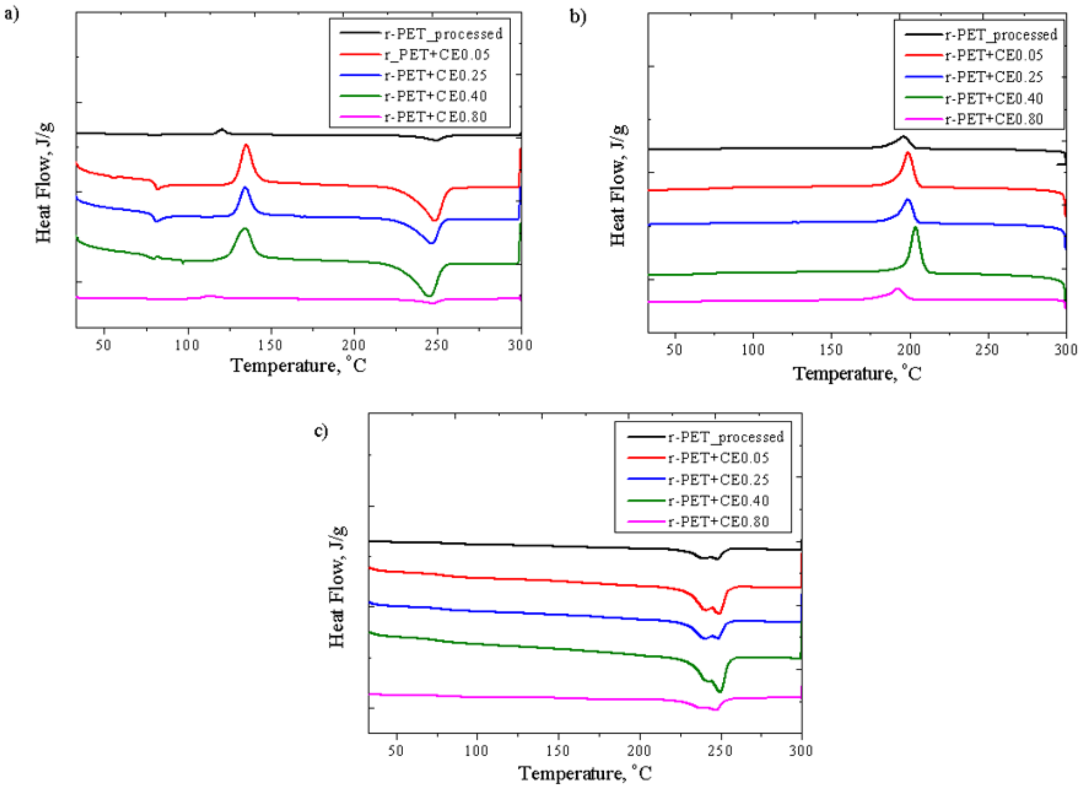


Figure 4.3 : DSC curves of branched r-PET: (a) first heating, (b) cooling, (c) second heating cycles.

Table 4.3 : Thermal properties of branched r-PET.

Materials	T_g (°C)	T_{ccr} (°C)	Tm (°C)	ΔH_m (J/g)	T_{cr} (°C)	ΔH_{cr} (J/g)	Tm_{low} (°C)	Tm_{high} (°C)	ΔH_m (J/g)
rPET_processed	79	121	249	42	196	40	239	247	36
r-PET+CE0.05	77	135	248	37	199	29	241	249	38
r-PET+CE0.25	80	134	247	38	200	31	240	249	39
r-PET+CE0.40	77	134	245	34	204	34	242	250	38
r-PET+CE0.80	75	114	248	38	192	27	239	247	34

All blends at different ratios either with or without chain extender showed a composition dependent single glass transition temperature in both first and second heating cycles. Increased composition of r-PET increased the glass transition temperature. This result signified as the literature that PBT/PET blends show miscibility at amorphous state. As seen in Figure 4.4, PBT/r-PET blends showed crystal melting temperatures of the original components. These individual melting temperatures turned out single melting peaks with some shoulders in the second heating cycle after cooling at 5 °C/min. Miscibility in crystal melting peaks in second heating was dependent on the cooling rates. Increased concentration of r-PET decreased crystallinity in cooling graphs due to lower crystallization of r-PET. DSC curves of PBT/highly branched r-PET blends were shown at Figure 4.5. Immiscible crystal melting peaks also turned out miscibility in the second heating cycle for those blends, too. While addition of 25 wt% of highly branched r-PET (P752502) decreased crystallinity, increased amounts to 50 (P505004) and 75 wt% (P257506) promoted the crystallization in comparison with A5050 and A2575. This result could be attributed to effect of branched structures as nucleating points. Thermal properties of PBT/r-PET and PBT/highly branched r-PET blends that taken from DSC analysis were recorded in Table 4.4.

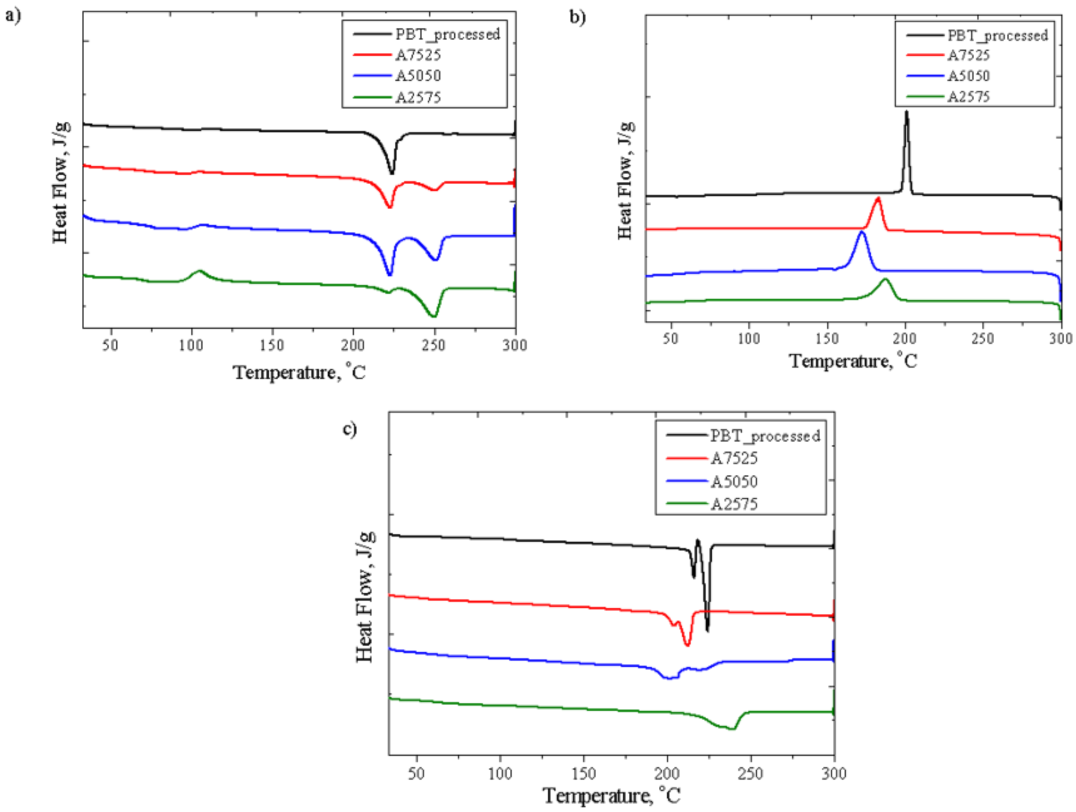


Figure 4.4 : DSC curves of PBT/r-PET blends: (a) first heating, (b) cooling, (c) second heating cycles.

Figure 4.5 :

Table 4.4 : Thermal properties of PBT/r-PET and PBT/highly branched r-PET blends.

Materials	T_g (°C)	T_{mPBT} (°C)	ΔH_{mPBT} (J/g)	$T_{mr\text{-}PET}$ (°C)	$\Delta H_{mr\text{-}PET}$ (J/g)	T_{cr} (°C)	ΔH_{cr} (J/g)	Tm_{low} (°C)	Tm_{high} (°C)	ΔH_m (J/g)
PBT_processed	66	224	49	-	-	201	55	215	225	53
A7525	66	223	32	250	11	183	42	204	212	34
A5050	73	223	19	251	25	172	37	201	207	28
A2575	73	222	4	250	35	187	36	232	239	32
P752502	63	222	19	250	6	182	26	205	214	34
P505004	71	222	17	250	21	162	39	200	220	30
P257506	73	221	2	249	29	195	39	231	238	34

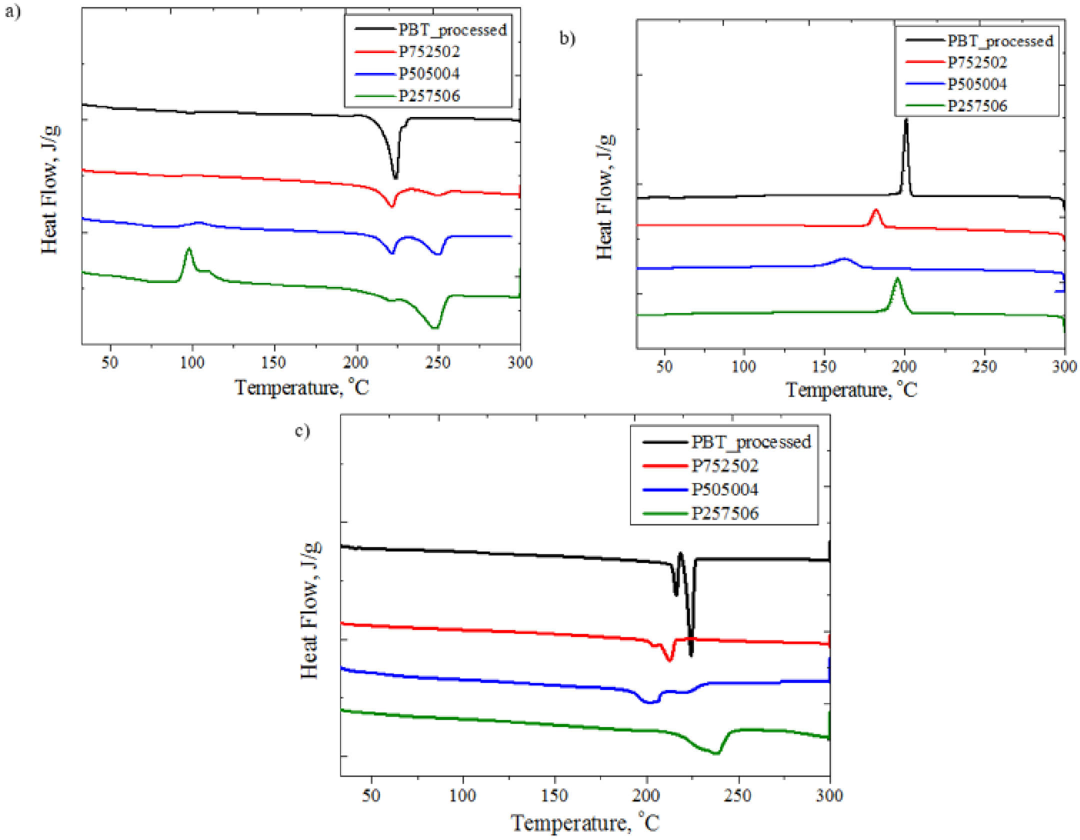


Figure 4.6 : DSC curves of PBT/highly branched r-PET blends: (a) first heating, (b) cooling, (c) second heating cycles.

At a constant chain extender concentration of 0.2 wt%, at all compositions, materials that blended by all together mixing method (A752502, A505002, A257502) showed higher crystallinity than those of blended by pre-mixing method (P752502, P505002, P257502). Low chain extender concentration could not be enough to compensate degraded properties of r-PET and prevent further degradation during pre-mixing method. Further degradation could be resulted in lower crystallinity even in presence of chain extenders in these blends. On the other hand, at higher chain extender concentrations, blends that prepared by pre-mixing method (P505004, P257506) showed higher crystallinity than those of prepared by alltogether mixing method (A505004, A257506). High chain extender concentration could compensate degradation of r-PET by increasing molecular weight in pre-mixing method. Branched molecules could act as nucleating points after blending with PBT and promote crystallization. Firs heating, cooling and second heating curves of the blends are shown in Figure 4.6, 4.7 and 4.8. Thermal properties of overall blends are listed in Table 4.5.

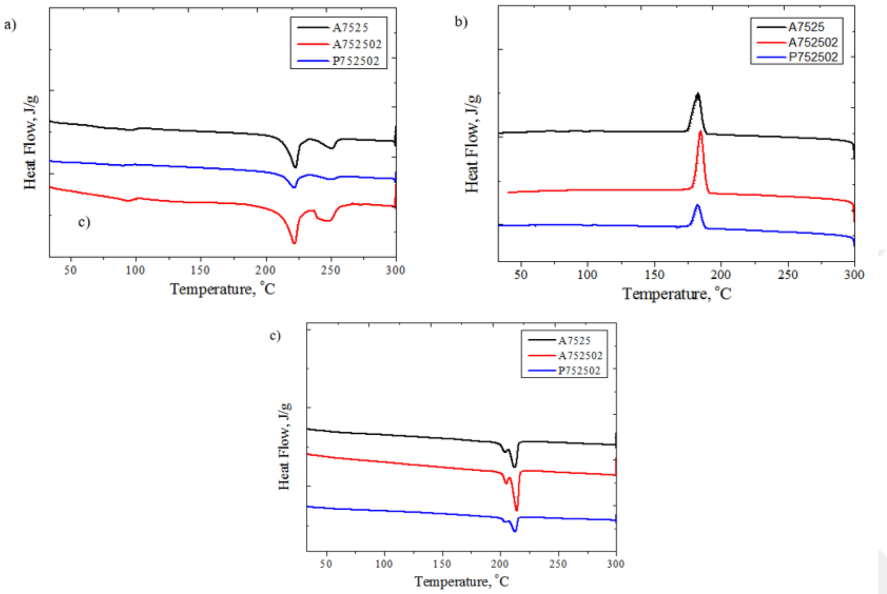


Figure 4.7 : DSC curves of A7525, A752502 and P752502 blends: (a) first heating, (b) cooling, (c) second heating cycles.

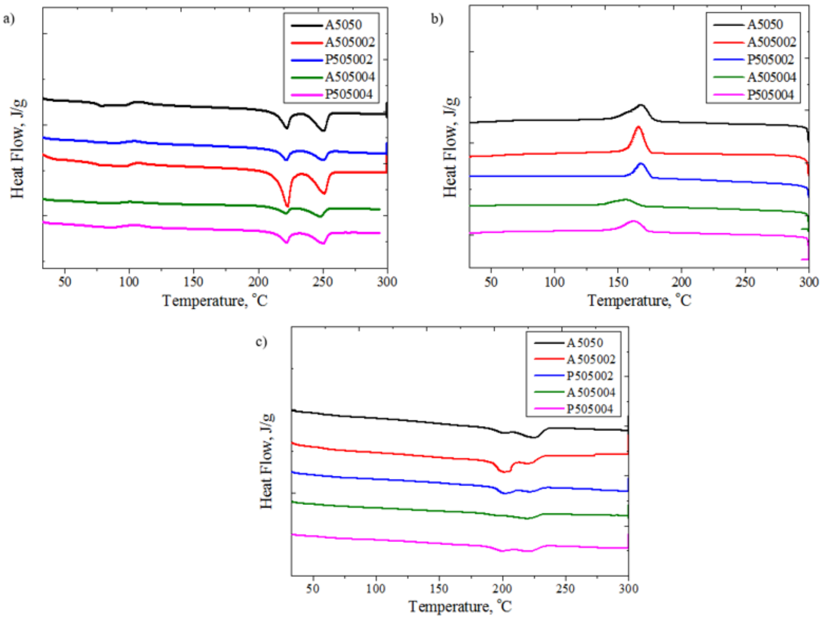


Figure 4.8 : DSC curves of A5050, A505002, P505002, A505004 and P505004 blends: (a) first heating, (b) cooling, (c) second heating cycles.

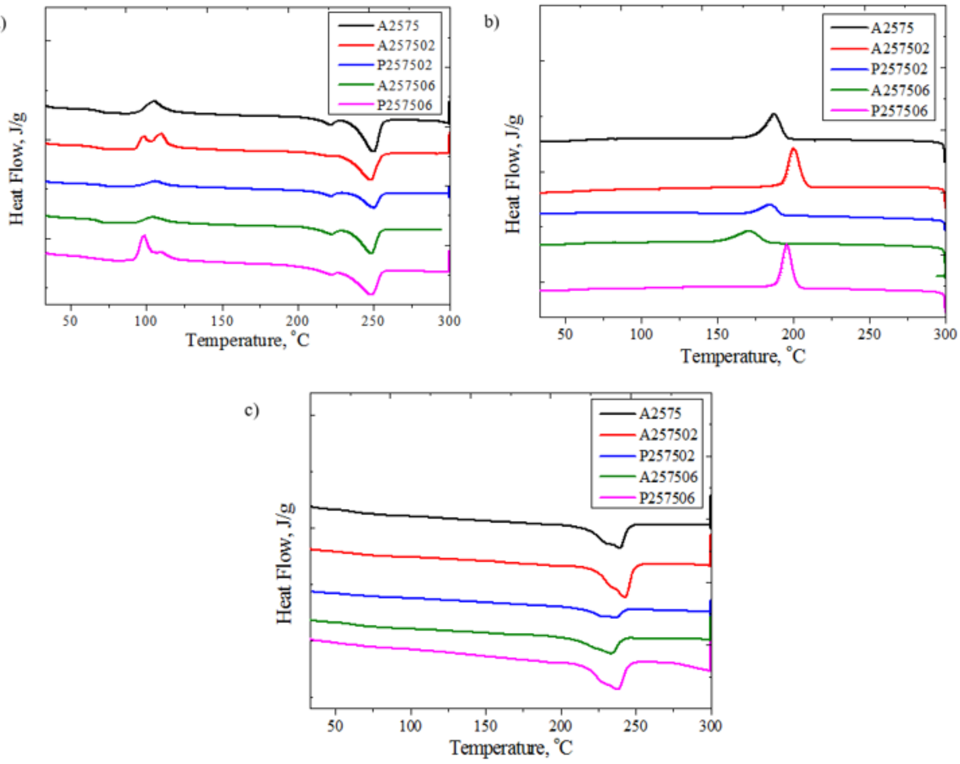


Figure 4.9 : DSC curves of A2575, A257502, P257502, A257506 and P257506 blends: (a) first heating, (b) cooling, (c) second heating cycles.

Table 4.5 : Thermal properties of overall blends.

Materials	T_g (°C)	T_{mPBT} (°C)	ΔH_{mPBT} (J/g)	$T_{mr\text{-}PET}$ (°C)	$\Delta H_{mr\text{-}PET}$ (J/g)	T_{cr} (°C)	ΔH_{cr} (J/g)	Tm_{low} (°C)	Tm_{high} (°C)	ΔH_m (J/g)
A7525	66	223	32	250	11	183	42	204	212	34
A752502	63	222	37	248	17	185	41	205	214	34
P752502	63	222	19	250	6	182	26	205	214	34
A5050	73	223	19	251	25	172	37	201	207	28
A505002	74	221	28	249	26	179	63	210	223	54
P505002	72	222	11	251	12	168	22	201	222	18
A505004	72	221	11	248	20	156	28	197	219	26
P505004	71	222	17	250	21	162	39	200	220	30
A2575	73	222	4	250	35	187	36	232	239	32
A257502	74	221	1	250	35	200	45	234	243	40
P257502	74	221	3	250	17	184	17	230	236	15
A257506	74	222	4	248	29	170	30	-	233	28
P257506	73	221	2	249	29	195	39	231	238	34

Various cooling rates of 2, 5, 10 and 20 °C/min were applied to r-PET_processed, PBT_processed, A7525, A5050, A2575, A505002 and P505002 materials. Crystallization behaviours in cooling cycles and effect of cooling rate on thermal properties in second heating cycles were investigated. Faster cooling rate resulted in decrease in crystallization temperature of r-PET_processed, PBT_processed and A7525 blend (Figure 4.9). For instance, crystallization temperature of 201 °C at 2

°C/min cooling rate (r-PET_processed_2) was postponed to 178 °C/min at 20 °C/min cooling rate (r-PET_processed_20). This result could be attributed that molecules couldn’t possess enough time to align and crystallize. On the other hand, crystallinity was not affected from differed cooling rates. In second heating cycles, double crystal melting peaks turned into single peak with increased cooling rates. Possessing a lower time for crystal growth at higher cooling rates could cause a more homogeneous crystallization with single crystal melting peak. However, in A5050, A2575, A50002 and P50502 blends, different cooling rates did not show the same sequences in crystallization and crystal melting points. Increased r-PET content in these blends could generate an unstability in thermal properties due to various degradation degrees of r-PET (Figure 4.10). Thermal properties of the materials are listed in Table 4.6.

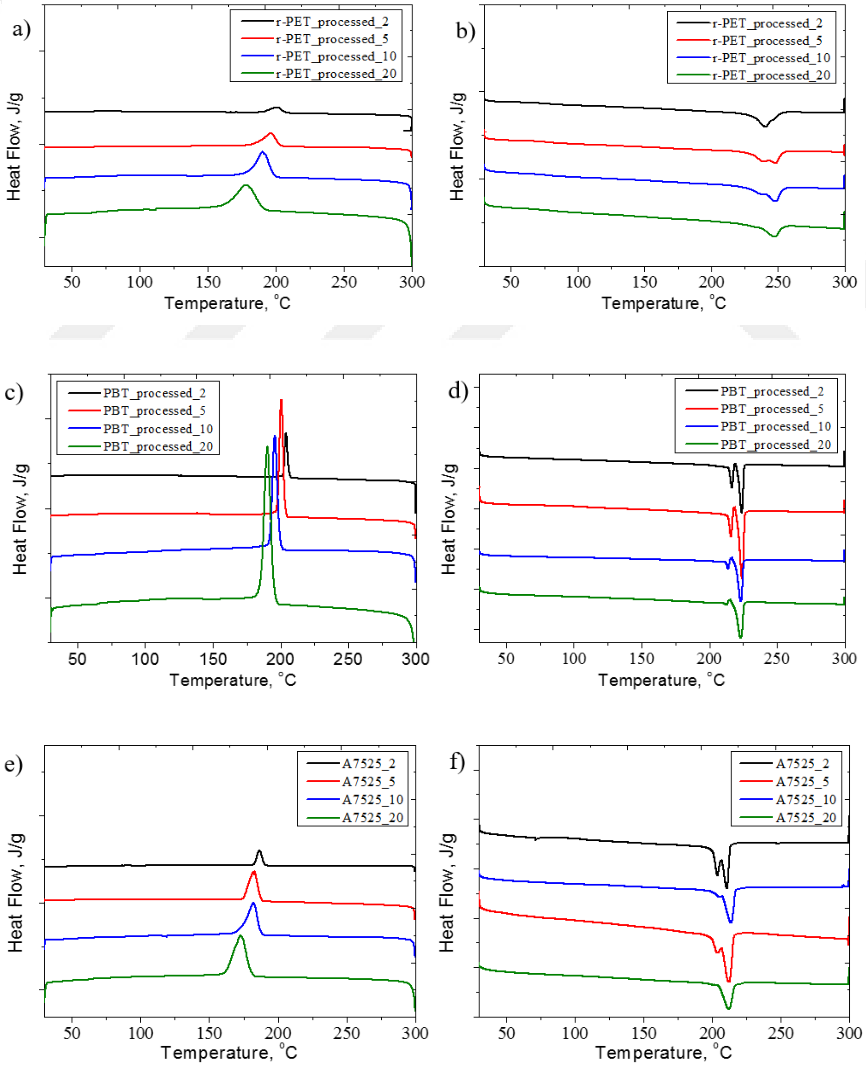


Figure 4.10 : DSC curves of (a, b) cooling, second heating cycle of r-PET_processed, (c, d) cooling, second heating cycle of PBT_processed, (e, f) cooling, second heating cycle of A7525.

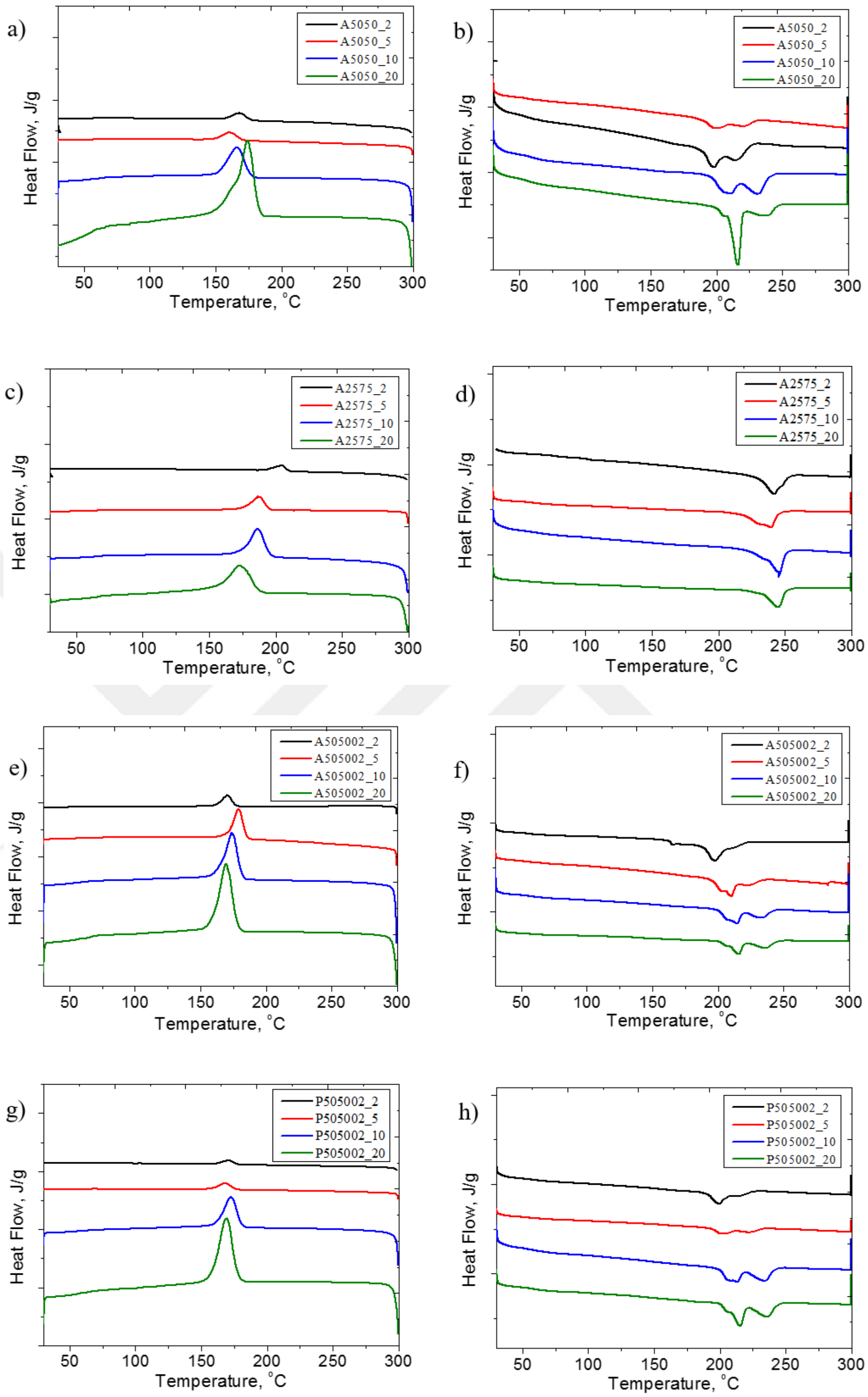


Figure 4.11 : DSC curves of (a, b) cooling, second heating cycle of A5050, (c, d) cooling, second heating cycle of A2575, (e, f) cooling, second heating cycle of A505002, (g, h) cooling, second heating cycle of P505002.

Table 4.6 : Thermal properties of materials at different cooling rates.

Materials	T_{cr} (°C)	ΔH_{cr} (J/g)	Tm_{low} (°C)	Tm_{high} (°C)	ΔH_m (J/g)
r-PET_processed_2	201	39	-	241	35
r-PET_processed_5	196	40	239	247	36
r-PET_processed_10	190	36	-	248	34
r-PET_processed_20	178	37	-	248	34
PBT_processed_2	206	52	216	224	53
PBT_processed_5	201	55	215	225	53
PBT_processed_10	196	55	214	223	53
PBT_processed_20	190	49	211	223	49
A7525_2	186	42	202	210	38
A7525_5	183	42	204	212	34
A7525_10	182	45	-	214	34
A7525_20	172	41	-	212	32
A5050_2	168	32	198	212	32
A5050_5	172	37	201	207	28
A5050_10	166	38	210	231	33
A5050_20	174	42	216	236	30
A2575_2	204	25	-	242	28
A2575_5	187	36	232	239	32
A2575_10	186	33	-	245	28
A2575_20	173	31	-	245	26
A505002_2	169	38	216	235	33
A505002_5	179	63	210	223	54
A505002_10	174	39	214	233	33
A505002_20	170	38	165	198	43
P505002_2	171	34	199	213	33
P505002_5	168	22	201	222	18
P505002_10	173	38	213	233	34
P505002_20	169	40	215	236	33

4.2 Viscoelastic Properties

4.2.1 Thermomechanical properties

Storage modulus, tan delta and complex viscosity values versus temperature was recorded in DMA analysis. Storage modulus is a measure of stored energy. Tan delta is a ratio of energy dissipation to stored energy, which could be named as damping and give information about impact resistance of the material. The temperature where tan delta give a peak clearly signifes tha glass transition temperature of the material. Lower complex viscosity could be attributed to lower melt strength of the material. DMA curves of PBT/r-PET and PBT/highly branched r-PET blends are given in Figure 4.12 and Figure 4.13, respectively. Processed PBT has storage modulus of 2088 MPa.

Addition of r-PET into PBT slightly decreased storage modulus. Increasing amount of 75 wt% of r-PET (A2575) in the blend composition decreased storage modulus at 30 °C around 10 % in comparison with PBT_processed. All blends showed lower storage modulus at rubbery state, around 130 °C. Decrease in storage modulus could be attributed to degradation in r-PET during re-processing without chain extender. Processed PBT possessed the lowest tan delta with lower energy dissipation, while A2575 had the highest. Temperature where tan delta gave a peak shifted to higher temperatures depending on r-PET concentration in the blends whether in presence of chain extender or not. Complex viscosity values also showed the same sequence as storage modulus. However, addition of highly branched r-PET at same concentrations resulted in lower decrease in storage modulus and complex viscosity in comparison with PBT/r-PET blends since degraded r-PET molecules were extended and developed by addition of chain extender. Addition of 75 wt% of highly branched r-PET (P257506) compensated the loss in storage modulus at 30 °C of A2575 around 6 %. However, at rubbery state, blends remained to show lower storage modulus in comparison with PBT_processed. While the lowest tan delta peak was possessed by PBT_processed, the highest one was of P257506. Complex viscosity values also showed the same sequence of storage modulus values. Storage modulus and complex viscosity values at 30 °C of PBT/r-PET and PBT/highly branched r-PET blends are listed in Table 4.7.

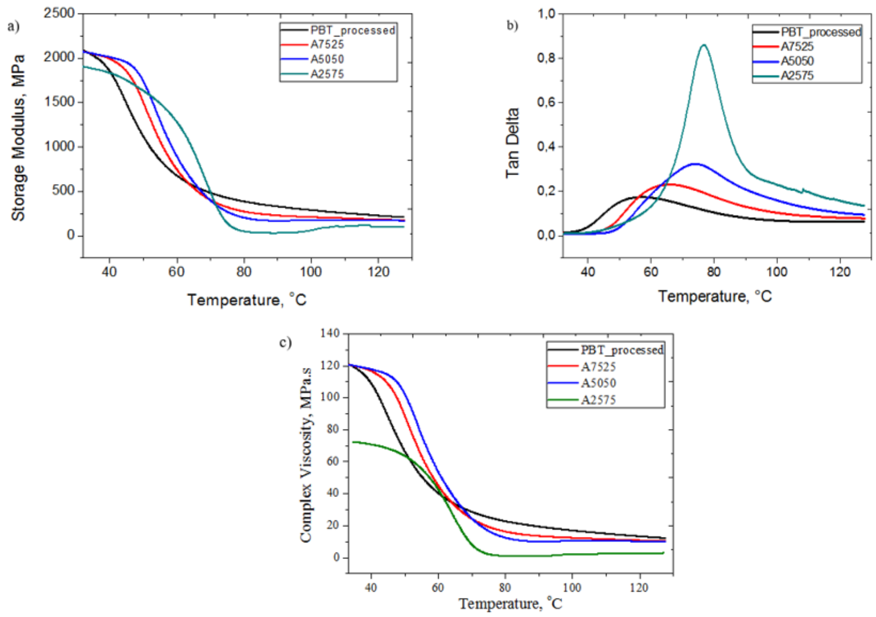


Figure 4.12 : DMA curves of PBT/r-PET blends: (a) storage modulus, (b) tan deta, (c) complex visvosity.

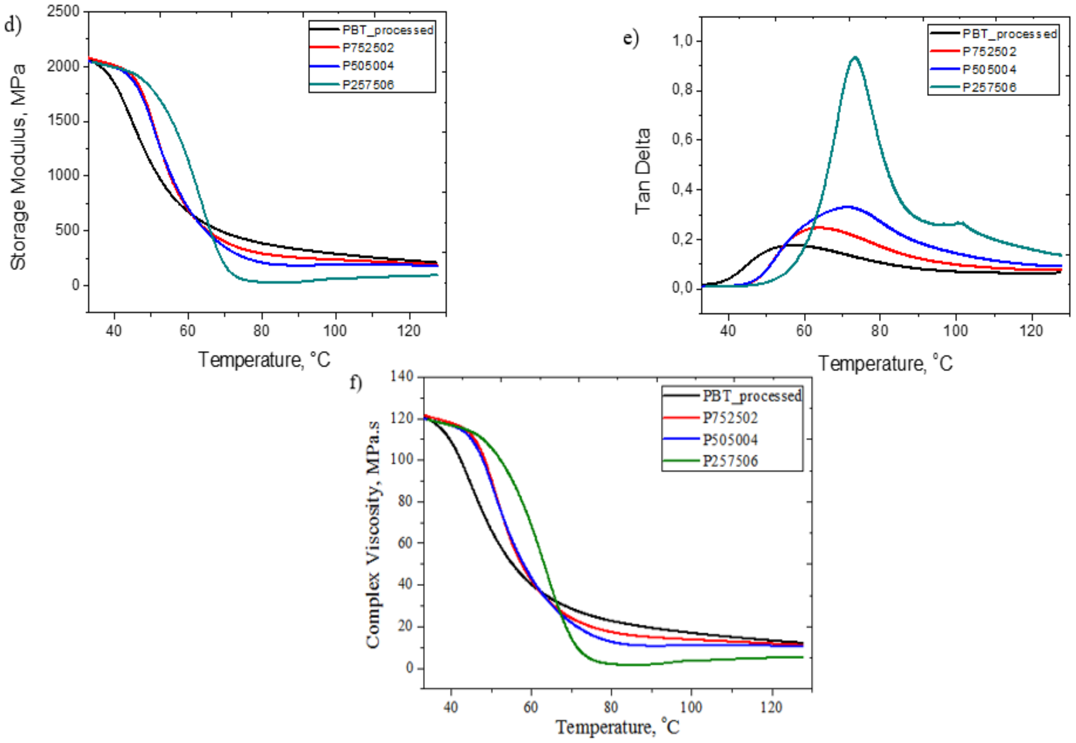


Figure 4.13 : DMA curves of PBT/highly branched r-PET blends: (a) storage modulus, (b) tan deta, (c) complex visvosity.

Table 4.7 : Storage modulus and complex viscosity values of PBT/r-PET and PBT/highly branched r-PET blends.

Materials	Storage Modulus (MPa)	Complex viscosity (MPa.s)
PBT_processed	2088	123
A7525	2077	121
A5050	2070	121
A2575	1903	72
P752502	2080	121
P505004	2056	121
P257506	2038	119

At all compositions blends that prepared by pre-mixing method showed higher storage modulus and complex viscosity in comparison with blends that prepared by all-together mixing method. Addition of chain extender decreased storage modulus and complex viscosity of the blends. However, when chain extender was added by pre-mixing method, the storage modulus and complex viscosity was increased. Addition of branched r-PET with increased molecular weight by chain extender into PBT by pre-mixing method could be resulted in higher storage modulus. On the other hand, higher number of processing of r-PET even in presence of chain extender in pre-mixing method could increase brittleness and be resulted in higher storage modulus.

At constant chain extender concentration of 0.2 wt%, increased r-PET concentration to 50 wt% (A505002) increased storage modulus of A752502 around 4%. Further increase in r-PET concentration up to 75 wt% (A257502) decreased it around 5%. Tan delta peaks was in a sequence with impact resistances of the blends in compositions of 75:25 and 50:50 PBT/r-PET. Increasing amount of r-PET to 75 wt%, the same results couldn’t be observed. Only for 25:75 PBT/r-PET blends, addition of chain extender etiher with alltogether mixing or pre-mixing method increased complex viscosity in comparison with A2575. DMA curves of 75:25, 50:50 and 25:75 ratios of PBT/r-PET blends are shown in Figure 4.14, 4.15 and 4.16, respectively. Overall storage modulus and complex viscosity values are listed in Table 4.8.

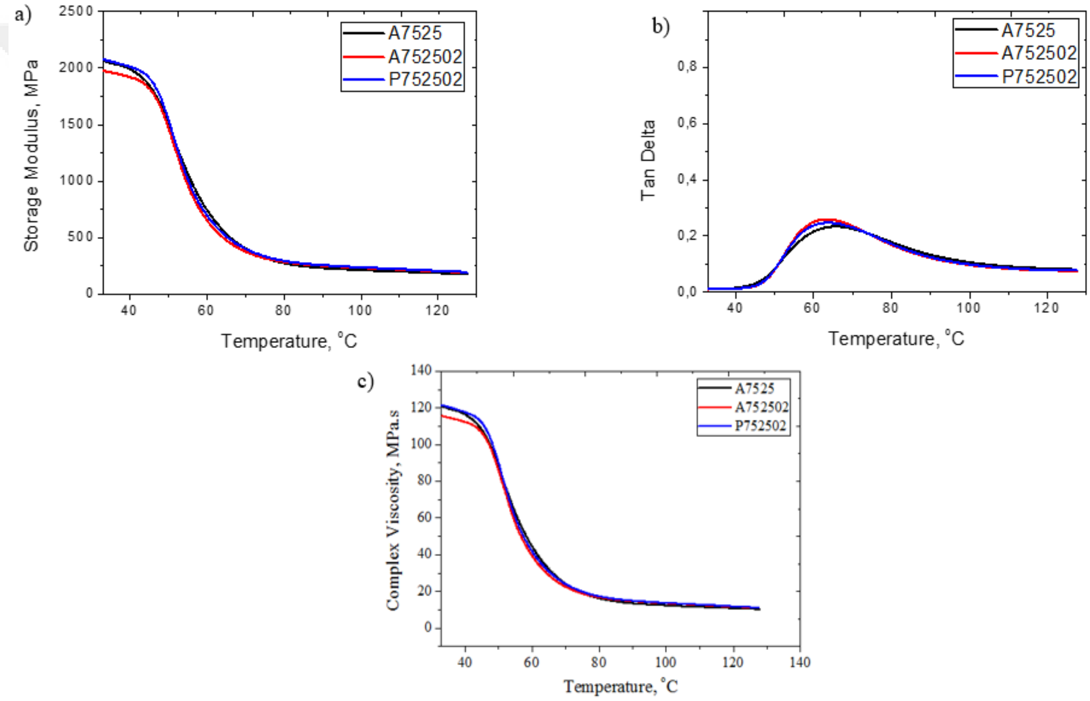


Figure 4.14 : DMA curves of A7525, A752502 and P752502 blends: (a) storage modulus, (b) tan delta, and (c) complex viscosity.

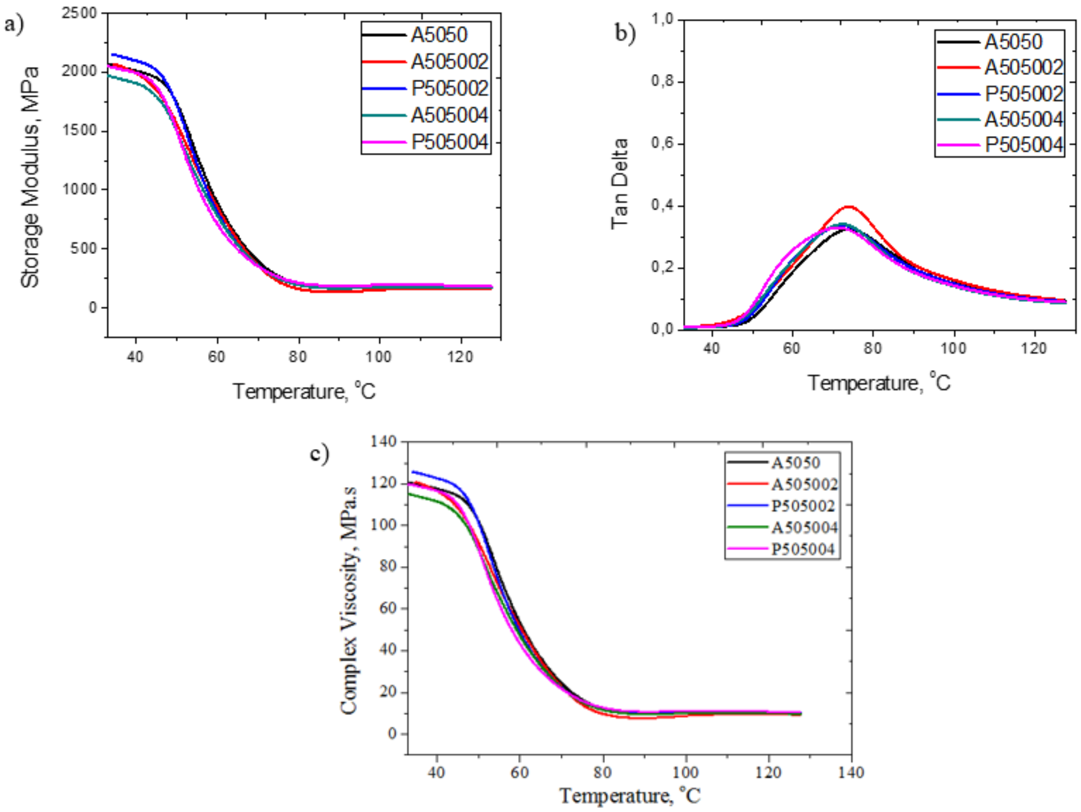


Figure 4.15 : DMA curves of A5050, A505002 and P505002, A505004, P505004 blends: (a) storage modulus, (b) tan delta, and (c) complex viscosity.

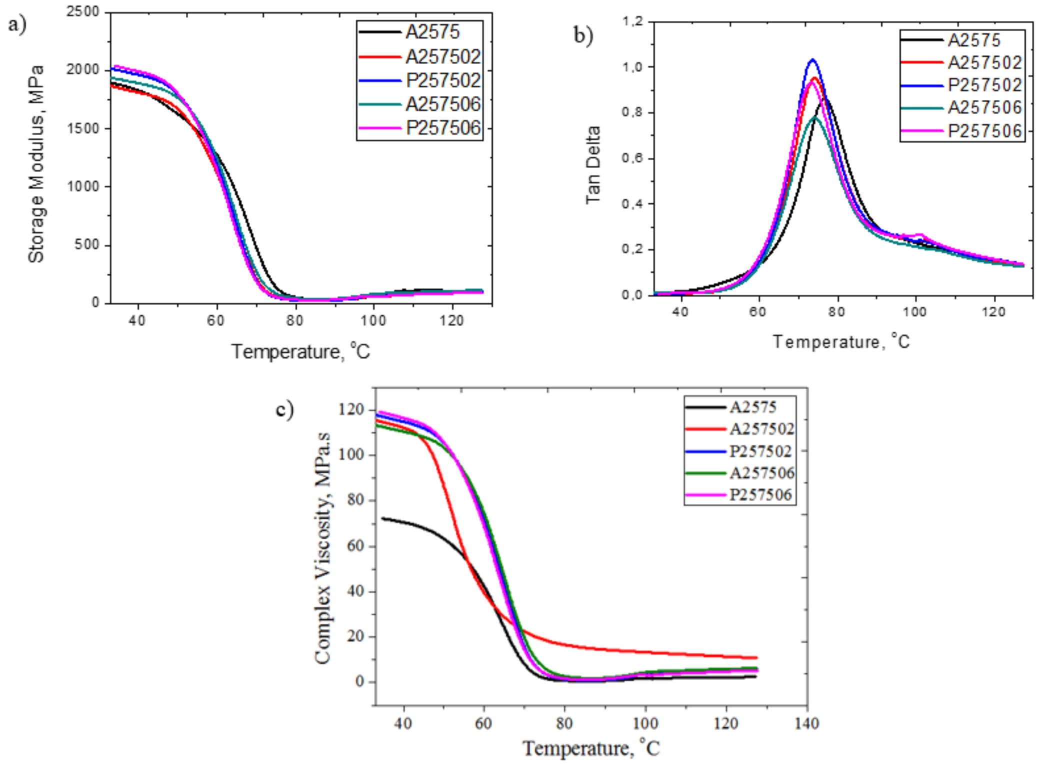


Figure 4.16 : DMA curves of A2575, A257502 and P257502, A257506, P257506 blends: (a) storage modulus, (b) tan delta, and (c) complex viscosity.

Table 4.8 : Storage modulus and complex viscosity values of overall blends.

Materials	Storage Modulus (MPa)	Complex viscosity (MPa.s)
PBT_processed	2088	123
A7525	2077	121
A752502	1991	116
P752502	2080	121
A5050	2070	121
A505002	2059	120
P505002	2147	125
A505004	1976	115
P505004	2056	121
A2575	1903	72
A257502	1886	116
P257502	2031	118
A257506	1953	114
P257506	2038	119

4.2.2 Melt flow rate

Melt flow rate (MFR) values was recorded from MFI analysis. MFR values of the samples were investigated to estimate their processabilities in extrusion process. Increasing molecular weight decreases molecular mobility with enhanced melt strength consequently processability for extrusion. Enhanced melt strength resulted in decrease in MFR values in MFI test. MFR values of PBT and r-PET before and after processing are given in Figure 4.17 and Table 4.9. As stated in literature PBT showed higher melt strength than r-PET with lower MFR value. MFR of PBT increased around 14% after processing. MFR of r-PET increased 60 % after processing. Higher increase in MFR of r-PET after processing showed its sensitivity to re-process due to further degradation.

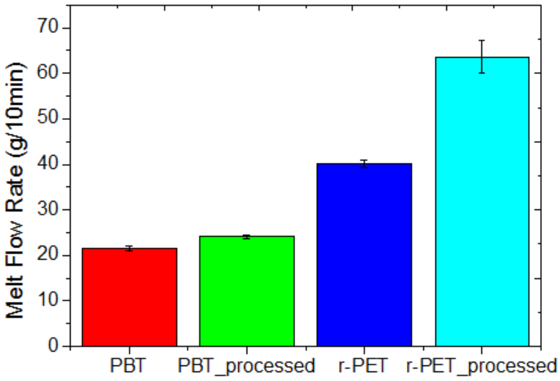


Figure 4.17 : MFR values of PBT and r-PET before and after processing.

Table 4.9 : MFR values of PBT and r-PET before and after processing.

Materials	Melt Flow Rate (g/10min)
PBT	21
PBT_processed	24
r-PET	40
r-PET_processed	64

Branching r-PET with various concentrations of chain extender enhanced the melt strength and decreased the MFR values as shown and listed in Figure 4.18 and Table 4.10, respectively. Addition of 0.25 wt% of chain extender almost compensated the melt strength loss of r-PET after processing. The lowest MFR value of 27 g/10 min was achieved by addition of 0.8 wt% chain extender into r-PET. Increase in melt strength of branched r-PET could associate with molecular weight increase due to branching reactions during extrusion, since MFR strongly depends on molecular weight of polymers.

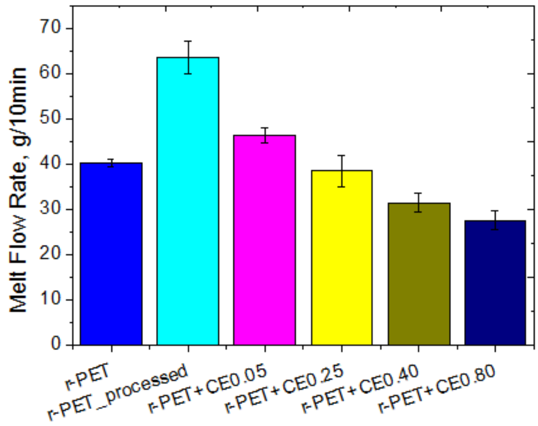


Figure 4.18 : MFR values of branched r-PET samples.

Table 4.10 : MFR values of branched r-PET samples.

Materials	Melt Flow Rate (g/10min)
r-PET	40
r-PET_processed	64
r-PET+CE0.05	46
r-PET+CE0.25	38
r-PET+CE0.40	31
r-PET+CE0.80	27

Increasing amount of r-PET into the blends resulted in higher MFR values, due to higher MFR value of r-PET itself (Figure 4.19). But still, blending r-PET with PBT compansated the melt strength loss of r-PET after processing. The lowest MFR value of 22 g/10 min was achieved in 75:25 PBT/r-PET blend (A7525). On the other hand, blending PBT with highly branched r-PET at the same ratios promoted decrease in MFR values as shown in Figure 4.20. Lower MFR values of PBT/highly branched r-PET blends in comparison with those of PBT/r-PET blends at the same ratios could attributed to a result of lower chain mobility with increased molecular weight due to branching. MFR values of PBT/r-PET and PBT/highly branched r-PET blends are listed in Table 4.11.

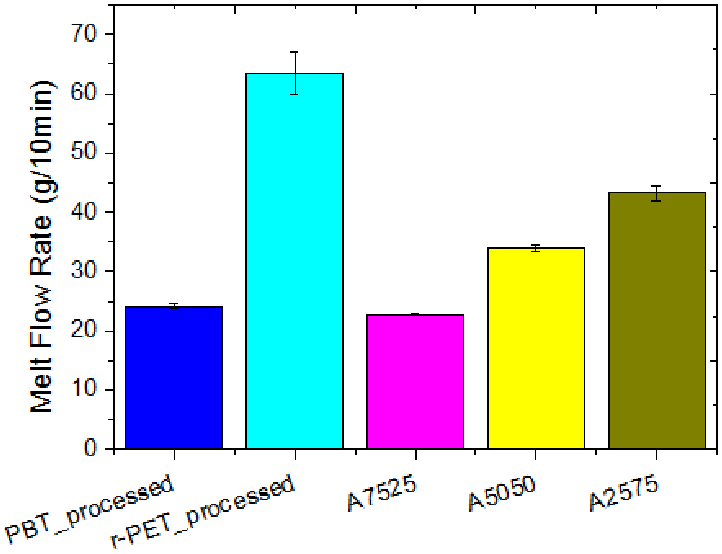


Figure 4.19 : MFR values of PBT/r-PET blends.

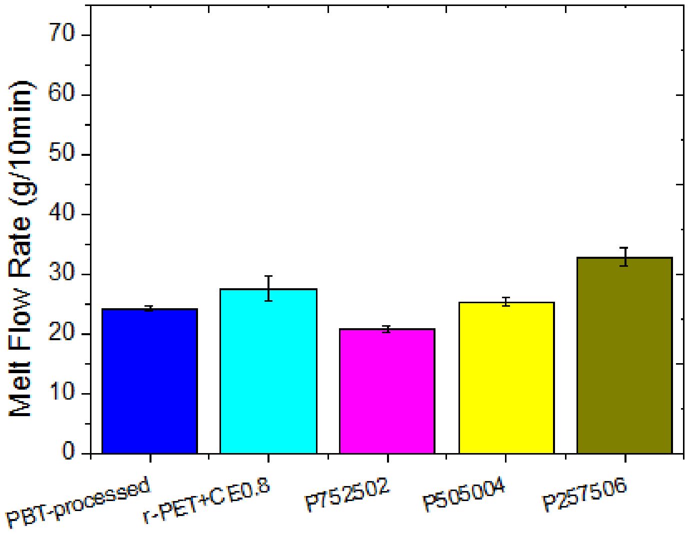


Figure 4.20 : MFR values of PBT/highly branched r-PET blends.

Table 4.11 : MFR values of PBT/r-PET and PBT/highly branched r-PET blends.

Materials	Melt Flow Rate (g/10min)
PBT_processed	24
r-PET_processed	64
r-PET + CE0.8	27
A7525	22
A5050	33
A2575	43
P752502	20
P505004	25
P257506	32

At all compositions, addition of chain extender either with alltogether or pre-mixing method decreased MFR values by branching molecules. MFR values of overall blends are shown and listed in Figure 4.21 and Table 4.12, respectively. As observed in A505002 and A505004 blends inreased chain extender concentration from 0.2 wt% to 0.4 wt% decreased MFR value from 22 to 14 g/10 min. 37 g/10 min MFR value of A257502 blend with 0.2 wt% of chain extender decreased 26 g/10 min in A257506 blend when chain extender content was increased to 0.6 wt%. In all compositions, blends that prepared by alltogether mixing method showed lower MFR than those of prepared by pre-mixing method. Branching both PBT and r-PET molecules wih functional groups of chain extender could be resulted in furher decrease in molecular mobility, as a consequence lower MFR values.

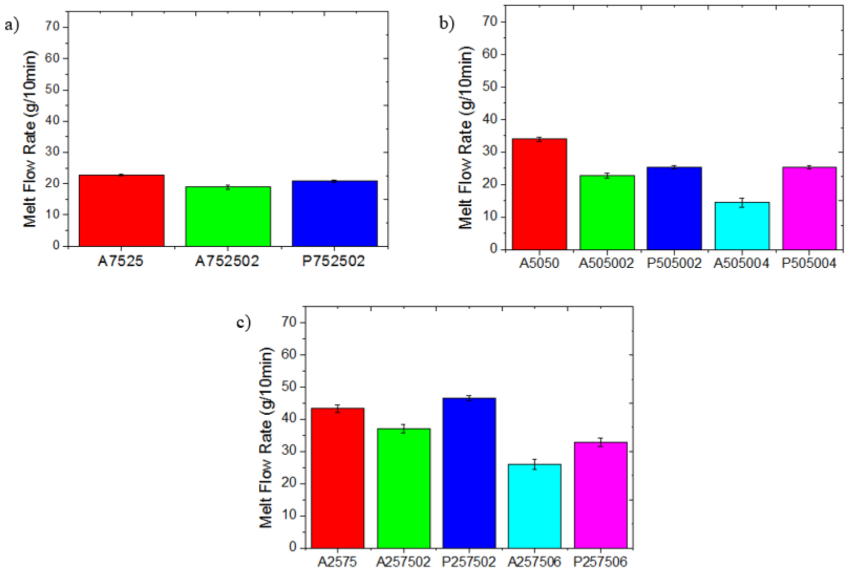


Figure 4.21 : MFR values of overall blends: (a) A7525, A752502, P752502, (b) A5050, A505002, P505002, A505004, P505004, (c) A2575, A257502, P257502, A257506, P257506.

Table 4.12 : MFR values of overall blends.

Materials	Melt Flow Rate (g/10min)
A7525	22
A752502	18
P752502	20
A5050	33
A505002	22
P505002	25
A505004	14
P505004	25
A2575	43
A257502	37
P257502	46
A257506	26
P257506	32

4.3 Mechanical Properties

4.3.1 Tensile properties

E modulus and tensile strength values of the blends were recorded from tensile test. Processed PBT showed E modulus of 2377 MPa and tensile strength of 53 MPa. The highest E modulus value was achieved in A5050 blend with 2481 MPa. Addition highly branched r-PET did not significantly affect mechanical properties of the blends. E modulus and tensile strength values of PBT/r-PET and PBT/highly branched r-PET blends are shown and listed in Figure 4.22 and Table 4.13, respectively. PBT showed average strain of around 200 %. Increasing amount of r-PET into the blends increased strain values. Stress-strain curves of processed PBT, A7525, A5050 and A2575 are given in Figure 4.23.

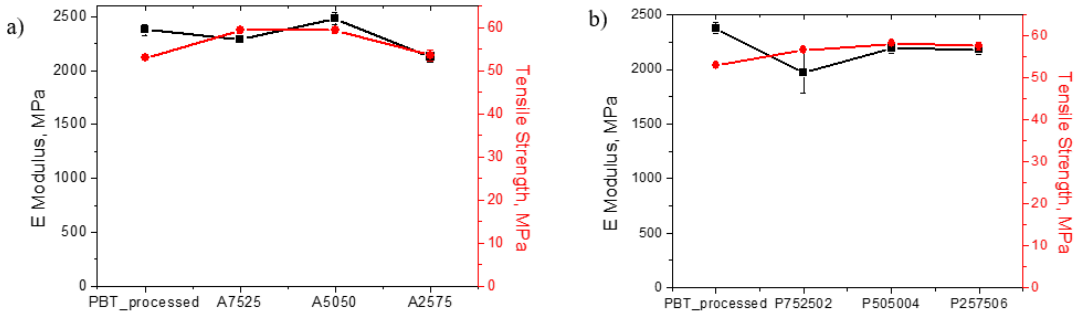


Figure 4.22 : E modulus and tensile strength values of (a) PBT/r-PET blends, (b) PBT/highly branched r-PET blends.

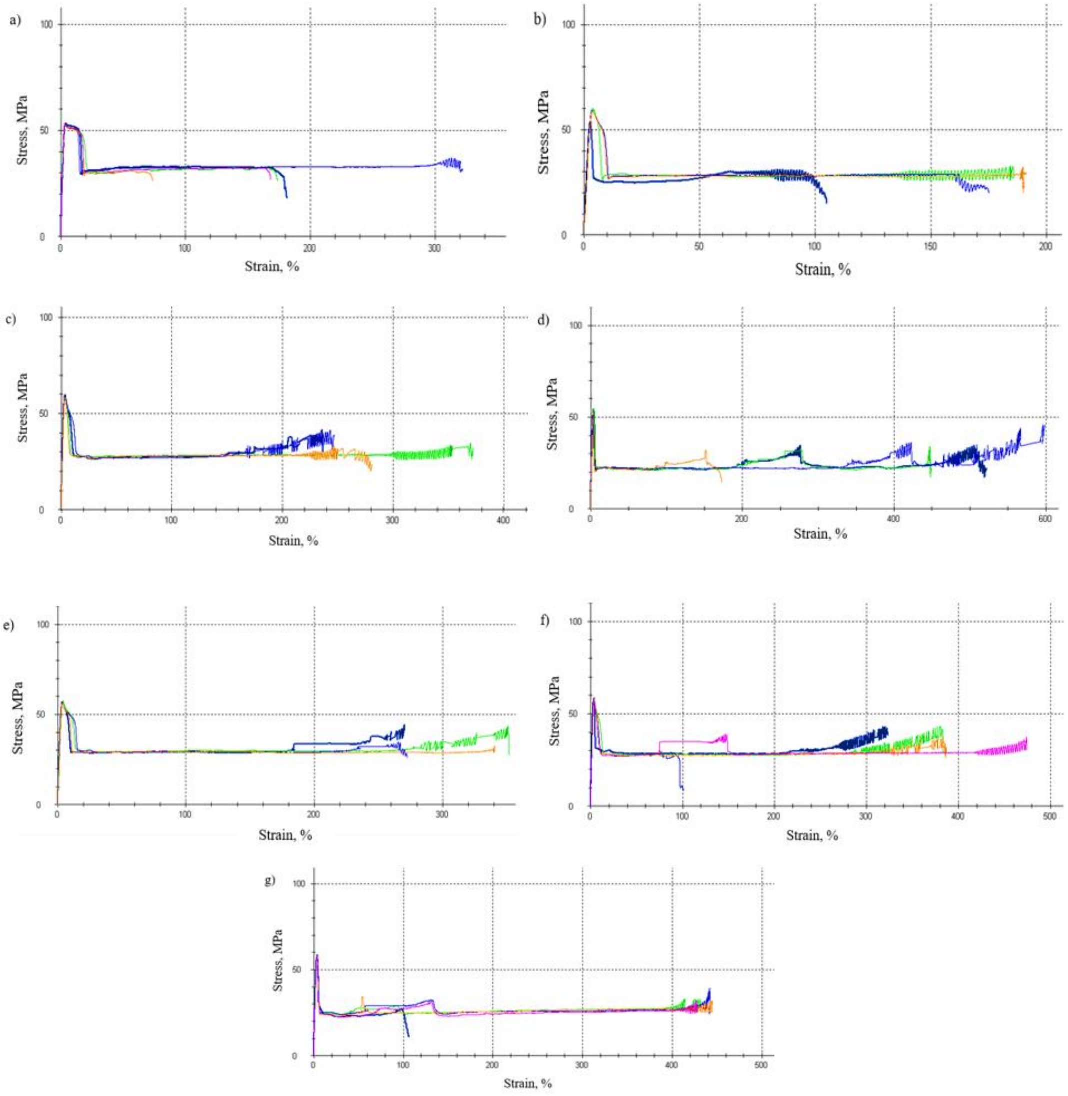


Figure 4.23 : Stress-strain curves of PBT, PBT/r-PET and PBT/highly branched r-PET blends (a) PBT_processed, (b) A7525, (c) A5050, (d) A2575, (e) P752502, (f) P505004, (g) P257506.

Table 4.13 : E modulus and tensile strength of PBT/r-PET and PBT/highly branched r-PET blends.

Materials	E Modulus (MPa)	Tensile Strength (MPa)
PBT_processed	2377	53
A7525	2292	59
A5050	2481	59
A2575	2130	53
P752502	1980	56
P505004	2195	58
P257506	2186	57

In 75:25 and 50:50 PBT/r-PET concentrations, addition of chain extender with either all together mixing or pre-mixing method slightly decreased E modulus and tensile

strength. The same sequence could not obeserved for PBT/r-PET blends in 25:75 concentrations. The highest E modulus value was achieved in P257502 blend with 2326 MPa in this composition. Tensile strength values were changed in range of 53-59 MPa for all blends. E modulus and tensile strength values of overall blends are shown and listed in Figure 4.24 and Table 4.14, respectively.

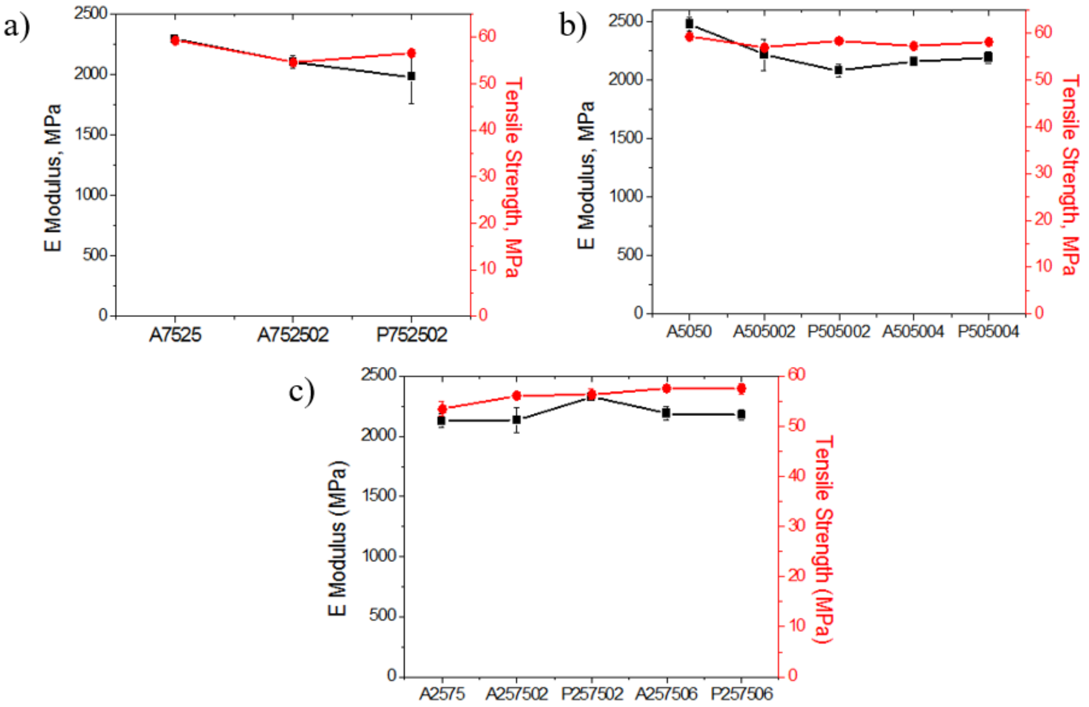


Figure 4.24 : E modulus and tensile strength values of overall blends: (a) A7525, A752502, P752502, (b) A5050, A505002, P505002, A505004, P505004, (c) A2575, A257502, P257502, A257506, P257506.

Table 4.14 : E modulus and tensile strength of overall blends.

Materials	E Modulus (MPa)	Tensile Strength (MPa)
PBT_processed	2377	53
A7525	2292	59
A752502	2105	55
P752502	1980	56
A5050	2481	59
A505002	2221	57
P505002	2028	58
A505004	2158	57
P505004	2195	58
A2575	2130	53
A257502	2205	56
P257502	2326	56
A257506	2170	57
P257506	2186	57

4.3.2 Impact properties

Impact strength of the blends were recorded from Izod notched impact test. PBT has the highest impact strength with 5.06 kJ/m^2. Addition of r-PET decreased impact strength of PBT. Only 25 wt% PBT/75 wt% of highly branched of r-PET blend showed the highest impact strength in overall PBT/r-PET blends. Impact strength values of PBT/r-PET and PBT/highly branched r-PET blends are shown and listed in Figure 4.25 and Table 4.15.

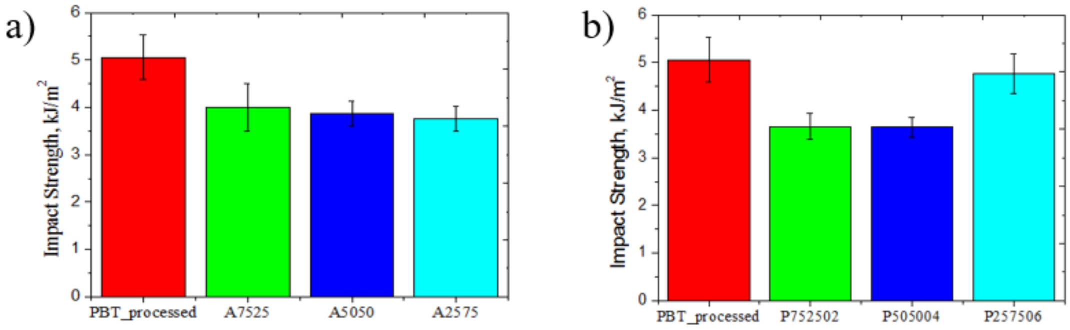


Figure 4.25 : Impact strength of PBT/r-PET and PBT/highly branched r-PET blends.

Table 4.15 : Impact strength values of PBT/r-PET and PBT/highly branched r-PET blends.

Materials	Impact Strength (kJ/m^2)
PBT_processed	5.06
A7525	3.93
A5050	3.76
A2575	3.76
P752502	3.66
P505004	3.60
P257506	4.77

At all compositions, blends that either prepared by all together or pre-mixing method showed impact strength values in the same range of error. Impact strength values of overall blends are shown and listed in Figure 4.26 and Table 4.16.

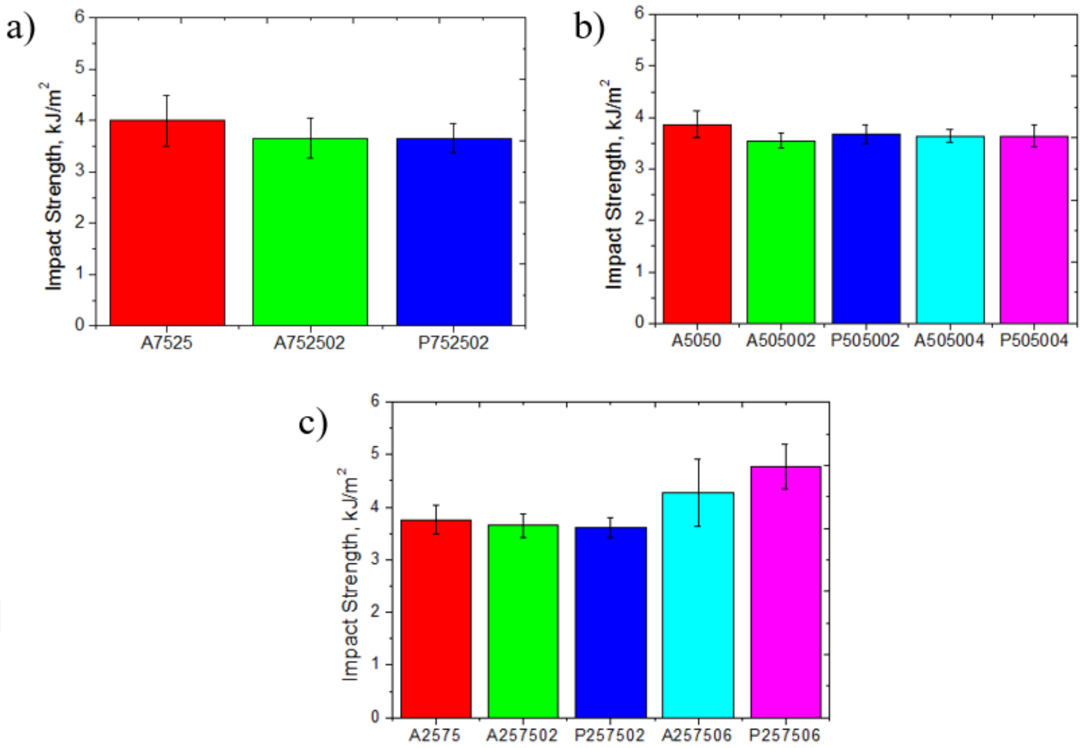


Figure 4.26 : Impact strength of overall blends: (a) A7525, A752502, P752502, (b) A5050, A505002, P505002, A505004, P505004, (c) A2575, A257502, P257502, A257506, P257506.

Table 4.16 : Impact strength values of overall blends.

Materials	Impact Strength (kJ/m^2)
PBT_processed	5.06
A7525	3.93
A752502	3.66
P752502	3.66
A5050	3.76
A505002	3.62
P505002	3.67
A505004	4.07
P505004	3.60
A2575	3.76
A257502	3.83
P257502	3.76
A257206	4.25
P257506	4.77

5. CONCLUSION

In this thesis study, PBT/r-PET binary blends at different ratios were investigated. Chain extender with a trade name of Joncryl ADR 4468® was used for compansate the degraded properties of r-PET. Addition of chain extender was carried out with two processing strategies named as all together mixing and pre-mixing method. Thermal gravimetric and crystallization properties, miscibility phenomena, thermomechanical properties, melt flow rate, tensile and impact properties of the materials were investigated.

Up to 0.4 wt% of chain extender increased crystallinity and crystallization temperature of r-PET. Chain extender could act as nucleating points and promote crystallization. On the other hand, highly branched r-PET in presence of 0.8 wt% of chain extender hindered crystallization of r-PET due to low chain mobility. In the case of PBT/r-PET blends, increased amount of r-PET decreased crystallization. Addition of 75 wt% of highly branched r-PET slightly compasante the decrease in crystallizations. All blends either with or without chain extender showed single glass transition temperature both in first and second heating cycles. As stated in literature, PBT/r-PET blends showed miscibility at amorphous state. Individual crystal melting peaks of PBT and r-PET in first heating cycle turned into single peak with some shoulders. In second heating cycles, PBT/r-PET blends showed miscibility at crystal melting state. At constant chain extender concentration, blends that prepared by all together mixing method showed higher crystallinity than those of prepared by pre-mixing method. This result could be attributed to further degradation of r-PET in pre-mixing method. At higher concentrations of chain extender, blends that prepared with pre-mixing method showed higher crystallinity in comparison with those of prepared by all together mixing method. Higher amount of chain extender could improved the degraded properties of r-PET.

Different cooling rates were applied to r-PET_processed, PBT_processed samples, A7525, A5050, A2575, A505002 and P505002 blends. Increased cooling rates was postponed crystallization temperature in r-PET_processed, PBT_processed and A7525 samples. A significant change in crystallinity could not observed.

PBT possessed the highest storage modulus and complex viscosity with lowest tan delta peak. Addition of r-PET decreased storage modulus and complex viscosity. The lowest values was obtained in A7525 blend. However, addition of 75 wt% of highly branched r-PET enhanced the decreased storage modulus and complex viscosity. This result could be associated with increased molecular weight of highly branched r-PET by branching with chain extender. All blends that prepared by pre-mixing method showed higher storage modulus and complex viscosity than those of prepared by all together mixing. Addition of chain extender decreased storage modulus and complex viscosity of the blends. However, when chain extender was added by pre-mixing method, the storage modulus and complex viscosity was increased. Addition of branched r-PET with increased molecular weight by chain extender into PBT by pre-mixing method could be resulted in higher storage modulus. On the other hand, higher number of processing of r-PET even in presence of chain extender in pre-mixing method could increase brittleness and be resulted in higher storage modulus.

Chain extender increased melt strength and processability in extrusion process by branching molecules of r-PET and PBT/r-PET blends. All blends that prepared by all together mixing method showed higher melt strength than those of prepared by pre-mixing method. Branching both PBT and r-PET molecules with functional groups of chain extender could cause a lower chain mobility and increase melt strength with lowering MFR values.

The highest E modulus was achieved in A5050 blend. In 75:25 and 50:50 PBT/r-PET concentrations, addition of chain extender with either all together mixing or pre-mixing method slightly decreased E modulus and tensile strength. The same sequence could not obeserved for PBT/r-PET blends in 25:75 concentrations. The highest E modulus value was achieved in P257502 blend in this composition. Tensile strength values were in the same range for all blends. Impact strength of blends were lower than PBT. The highest impact strength was observed in P257506 blend. This could be associated with enhanced crystallization of this blend. Chain extender was stated its efficiency in increasing processability of degraded r-PET meanwhile not affecting the tensile properties of the blends.

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PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

- **Nofar, M., Oguz, H., Kovanci C.** 2017. Development of New Manufacturing Method for Polyester Compounds Included Recycled Poly(ethylene teterphthalate). (Patent Pending)

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