

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**PRODUCTION AND CHARACTERIZATION OF
POLYESTER/POLY(METHYL METHACRYLATE) AND ACRYLONITRILE
BUTADIENE STYRENE TERBLEND S AND NANOCOMPOSITES**



Ph.D. THESIS

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Department of Polymer Science and Technology

Polymer Science and Technology Programme

MAY 2019

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MAY 2019

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**POLİESTER/POLİMETİL METAKRİLAT/AKRİLONİTRİL STİREN
BÜTADİEN ÜÇLÜ KARIŞIMLARI VE NANOKOMPOZİTLERİNİN
HAZIRLANMASI VE KARAKTERİZASYONU**

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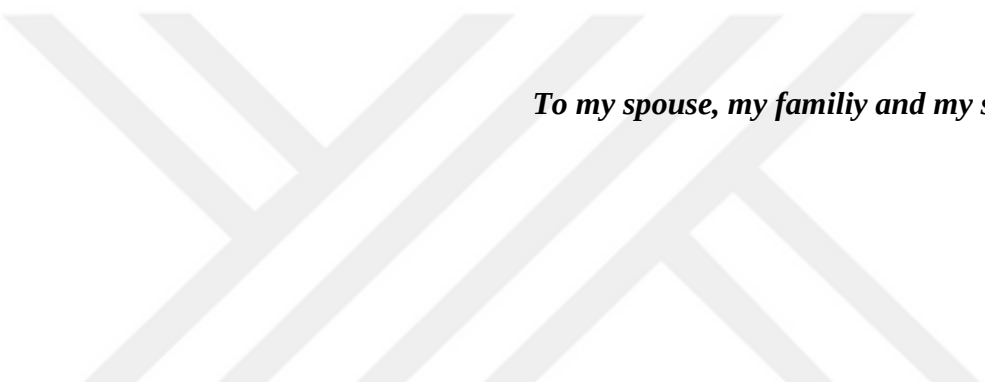
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To my spouse, my family and my son Kerem,



FOREWORD

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ABBREVIATIONS

WWII	: World War 2
ABS	: Acrylonitrile butadiene styrene
PS	: Polystyrene
PC	: Polycarbonate
PA	: Polymamide
PBT	: Polybutadiene terephthalate
PP	: Polypropylene
PE	: Polyethylene
PET	: Polyethylene Terephthalate
PMMA	: Polymethyl Methacrylate
PVC	: Polyvinyl chloride
PB	: Butadiene rubber
LDPE	: Low density polyethylene
PA11	: Polyamide 11
HDPE	: High density polyethylene
HIPS	: High impact polystyrene
CaCO₃	: Calcium carbonate
PEG	: Polyethylene glycol
PTT	: poly(trimethylene terephthalate)
PETG	: Poly(ethylene terephthalate glycol)
HDT	: Heat Deflection Temperature
E-EA-GMA	: Poly(Ethylene-ethyl acrylate-glycidyl methacrylate)
SMA	: Styrene maleic anhydride
MA-g-SEBS	: Maleic anhydride grafted styrene ethylene butylene styrene
MA-g-EP	: Maleic anhydride grafted ethylene propylene rubber
MMA-GMA	: Methyl methacrylate-co-glycidyl methacrylate
SBS	: Styrene butadiene styrene
E-BA-GMA	: Poly(Ethylene-b-butyl acrylate-b-glycidyl methacrylate)
MBS	: Poly(methyl methacrylate-g-butadiene-co-styrene)
MMT	: Montmorillonite

MFI	: Melt flow index
MFR	: Melt volume rate
SEM	: Scanning electron microscope
FD	: Flow direction
PD	: Perpendicular Direction
SAN	: Styrene acrylonitrile
SD	: Standard deviation
KOH	: Potassium hydroxide
DSC	: Differential Scanning Calorimetry
GMA	: Glycidyl methacrylate



SYMBOLS

T_g	: Glass transition temperature
T_m	: Crystalline melting temperature
T_{cc}	: Cold crystallization temperature
T_c	: Crystallization temperature
χ_c	: Crystallinity ratio
ΔH_m	: Heat of fusion during melting
H_{cc}	: Heat of fusion during cold crystallization
ΔH_m^0	: Theoretical enthalpy/heat of fusion for 100 % crystalline PET
ω_{pet}	: PET % weight ratio in the blend composition
L₀	: Initial length of the sample
L_f	: Final length of the samples after heat aging
GU	: Gloss unit
ρ	: Mixture density
ρ_{abs}	: Neat ABS density
ρ_{pet}	: Neat PET density
Φ_{abs}	: Volumetric ABS ratio
Φ_{pet}	: Volumetric PET ratio



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PRODUCTION AND CHARACTERIZATION OF POLYESTER/POLY(METHYL METHACRYLATE) AND ACRYLONITRILE BUTADIENE STYRENE TERBLENDS AND NANOCOMPOSITES

SUMMARY

Polymeric materials; because of having low cost, ease of processing and also wide range of properties, have found their way into many applications and replaced conventional materials such as metals, ceramics and wood. To eliminate disadvantages of polymeric materials or to improve the properties, many polymeric blends and composites have been developed in recent decades. Polymer blend represents very important field in developing of new materials, which has better properties in comparison with the net polymers. They are significant also from ecological and economical point of view.

ABS (acrylonitrile-butadiene-styrene) as an engineering thermoplastic material has been using for the several application which requires toughness, strength, and high surface finish quality with paintability properties in order to differentiate produced parts easily. The drawbacks of ABS are low chemical resistance, low heat deflection temperature and residual stress in final parts which causing less dimensional stability at elevated temperatures particularly in the paint curing process. The later one results in higher processing cost due to longer paint curing times at a relatively lower paint curing temperature.

The aim of this study is to investigate the combined effect of compatibilizer and nanofiller reinforcement on morphology, physical, thermal and mechanical properties of multiphase polymer blend having three immiscible organic phases, ABS (Acrylonitrile Butadiene Styrene), PET (Polyethylene Terephthalate) and PMMA (Polymethyl Methacrylate).

In order to complete these whole evaluation, at the first stage, the effect of twin screw compounding process temperature profiles on ABS were evaluated via mechanical testing and color measurement to foresee the effect of high processing temperatures on ABS during blending with PET. ABS were extruded with different twin screw extrusion temperature profiles and obtained products were investigated by focusing on mechanical nad physical properties. In that way, extrusion temperature profiles did not create noticable difference in the properties. Then, ABS/PET blends were prepared via melt blending method within the twin screw extruder and characterized by rheological, thermal and mechanical properties after injection molding process. Dimensional stability measurements after being aged at 125 °C for 48 hours was applied to correlate with injection molded part post shrinkage with blend ratio to reach a most reasonable ABS/PET blend composition ratio. From dimensional stability measurements, it was recorded that the ABS dimensional stability was improved with addition of PET. In order to investigate effect of blend ratio on viscosity of ABS and PET, rheological measurements were applied. The melt viscosity–composition curves for ABS/PET blends exhibited a trend like the rule of mixtures in which adding ABS to PET

improved the processability. Morphology of ABS/PET blends with different blend ratios were examined by Scanning Electron Microscopy (SEM) techniques. (SEM) examination revealed different morphologies depending on the composition such as dispersed, co-continuous and phase inverted, which indicated that the binary blends were immiscible and form a two-phase morphology. Glass transition, melting and crystallization behavior of prepared blends were determined by differential scanning calorimetry (DSC). In DSC analysis, no partial miscibility was observed from the PET phase melting temperature shifts as compared to those of the neat component. Also, ABS phases acted as nucleating agents due to change in PET cold crystallization temperature. Mechanical properties of blends were determined by applying tensile and impact test. Tensile properties increased with an increase in the PET content while the unnotched impact strength reached a maximum at 40 wt. % ABS content. From those measurements, optimum blend ratio was selected as ABS/PET ratio as 70/30 wt. %

Compatibilizing action of several materials like maleic anhydride grafted styrene ethylene butylene styrene (MA-g-SEBS), maleic anhydride grafted ethylene propylene rubber (MA-g-EP), polyethylene terephthalate glycol (PETG), and ethylene ethyl acrylate glycidyl methacrylate (E-EA-GMA) were evaluated for the selected ABS/PET ratio as 70/30 wt. %. Effect of the different injection molding temperature profiles were also investigated to see stability of morphologies during the final processing step. Decreased viscosities of the produced blends at high injection molding temperatures caused higher and irregularly shaped PET particulates which was also valid for compatibilized blends. This irregularity was also captured during the characterization by low mechanical properties. Improved mechanical properties were observed for the compatibilized blends and especially for E-EA-GMA best results were captured.

ABS/PMMA blends were also prepared via melt blending method by twin screw extruder and characterized by rheological, thermal and mechanical properties in order to evaluate interaction between these two. Single phase and miscible blends were obtained in which the PMMA ratios were at 50 wt. % and 75 wt. % by measured single glass transition temperature and SEM investigations.

Terblends of ABS/PET/PMMA with compatibilizers such as E-EA-GMA, E-BA-GMA (Ethylene-b-butyl acrylate-b-glycidyl methacrylate), MA-g-SEBS, and MA-g-EP and without compatibilizers were prepared by same compounding method and evaluated for the mechanical and physical properties. Since ABS solidify on the mold surface first, gloss value did not vary with the composition of terblends. E-EA-GMA as a compatibilizer in terblend was the most efficient compatibilizer with regards to mechanical properties. In compatibilized terblends, as a results of improved interaction in between immiscible phases, improvement in the tensile strength as 12 % and impact strength as 30 % were recorded.

In order to add nano calcium carbonate (CaCO_3) into terblends, a masterbatch was prepared. The carriers of masterbatch were selected as ABS and PET, alternatively. Loading level of CaCO_3 in the masterbatch was set as 10 wt. %. In the second step, two different compatibilizers, E-EA-GMA and E-BA-GMA and terblend were blended. Masterbatch containing ABS carrier showed smaller domain size and rounded PET phases compared to masterbatch containing PET carrier. When the effect of type of compatibilizer was compared, it was observed in the morphology investigation that the dispersion of PET phase was improved by addition of E-EA-GMA compared to

addition of E-BA-GMA due to having more reactive epoxide groups on E-EA-GMA. It was noted that E-EA-GMA was an effective compatibilizer.

In DSC analysis, it was observed that the glass transition temperature of PET in ABS/PET blends decreases. The decrease of glass transition temperature of PET terblends was eliminated by the introduction of both types of compatibilizer and nano filler together. The heat of fusion value at cold crystallization of PET phase was varied with type of compatibilizer. Masterbatch having PET carrier for nano CaCO_3 improved the heat of cold crystallization value and crystallization properties.

In dimensional stability measurements, it was observed that PMMA and nano filler did not contribute a spectacular improvement. From that observation, it could be claimed that main improvement in the dimensional stability was caused by the PET phase in the terblends. Addition of nano sized CaCO_3 and also compatibilizer slightly worsen the gloss properties of terblends. Any improved in mechanical properties did not record for the terblends by addition of compatibilizer. Addition of nano sized CaCO_3 was improved tensile modulus without creating a decrease in tensile strength. Usage of nanofiller masterbatch with PET carrier resin and E-EA-GMA as a compatibilizer resulted in the higher tensile modulus and tensile strength values due to the improvement of interaction between blend ingredients.

By replacing widely used commercially available ABS grades with one of already developed terblend or nano sized CaCO_3 reinforced terblend nanocomposites, higher curing temperature in paint curing process can be applicable to decrease curing time. In that way, the curing process costs of painted products can be decreased due to increase in the throughput of the process and more cost competitive products with improved mechanical, physical properties as well as dimensionally stable at elevated temperature can be launched to the market.



POLİESTER/POLİMETİL METAKRİLAT/AKRİLONİTRİL STİREN BÜTADİEN ÜÇLÜ KARIŞIMLARI VE NANOKOMPOZİTLERİNİN HAZIRLANMASI VE KARAKTERİZASYONU

ÖZET

Polimerik malzemeler; düşük maliyeti, kolay işlenmesi ve ayrıca çok çeşitli özellikleri nedeniyle birçok uygulamaya girmiş; metal, seramik ve ahşap gibi geleneksel malzemeler yerini almıştır. Polimerik malzemelerin dezavantajlarını ortadan kaldırmak veya özelliklerini güçlendirmek amacıyla son yıllarda birçok polimerik karışım ve kompozit geliştirilmiştir. Polimerik karışımlar, modifiye edilmemiş polimerlere kıyasla daha iyi özelliklere sahip olan yeni malzemelerin işlenmesinde çok önemli bir alanı temsil eder. Bunlar ekolojik ve ekonomik açıdan da önemlidir.

Bir mühendislik termoplastik malzemesi olarak ABS (akrilonitril-bütadien-stiren), tokluk, mukavemet ve sıcaklık direnci ve yüksek yüzey kalitesi gerek duyulan çeşitli uygulamalarda üretilen parçaları kolayca farklılaştırmak için kullanılır. ABS'in en büyük dezavantajları olarak düşük kimyasal dayanım, düşük sıcaklıklarda deformasyon ve özellikle final parçalarda düşük boyutsal kararlılığa neden olan kalıntı gerilmesi ile, göreceli olarak sıcaklık dayanımı gerektiren yapısal parçalardaki uygulamaları yada 75 ° C gibi düşük sıcaklıkta uzun süreli kürlenme süreleri nedeni ile oluşan yüksek maliyetlerden ötürü sınırlamalar yaratır.

Bu çalışmanın amacı; uyumlaştırıcı ve nano dolgu malzemesi takviyesinin üç karışmaz organik faza sahip olan ABS (Akrilonitril Bütadien Stiren), PET (Poli(etilen tereftalat)) ve PMMA (Polimetil Metakrilat) karışımlarına morfolojik, fiziksel, termal ve mekanik özellikleri üzerindeki birleşik etkisini araştırmaktır.

Tüm bu değerlendirmeyi tamamlamak için, ilk önce ABS ile PET'in karıştırılabileceği yüksek sıcaklıkların etkisini öngörmek amacıyla, çift vidalı ekstrüzyon işlem sıcaklıklarının ABS üzerindeki etkisi, mekanik testler ve renk değişiklikleri ile değerlendirilmiştir. ABS, farklı çift vidalı ekstrüzyon sıcaklıklarında ekstrüde edildi ve elde edilen ürünlere etkileri araştırılmıştır. Olası sıcaklık profillerinin ABS özelliklerinde gözle görülür bir fark yaratmadığı sonucuna varılmıştır. Bundan noktadan sonra, ABS / PET karışımları eriyik harmanlama yöntemiyle çift vidalı ekstruder ile hazırlanarak enjeksiyon kalıplama işleminden sonra reolojik, termal ve mekanik özellikler ile karakterize edilmiştir. Özellikle yüksek sıcaklıklara dirençli uygulamalar için optimum ABS / PET karışım oranının belirlenmesi için enjeksiyon proseseinden sonraki boyutsal kararlılığını incelemeleri 125 ° C'de boyutsal kararlılık incelemesi ile yapılmıştır. ABS / PET karışımları için eriyik viskozitesi-bileşim eğrileri, PET'e ABS eklenmesinin işlenebilirliği geliştirdiği ve bu ilişkinin karışımlar kuralına benzeyen bir eğilim sergilediği belirlenmiştir. Taramalı Elektron Mikroskopu (SEM) incelemesinde, ikili karışımların karışmadığını ve iki fazlı bir yapının bileşim oranına göre dağılmıştan sürekli yapıya kadar farklı morfolojiler sergilediği tespit edilmiştir. Çekme özellikleri, PET içeriğindeki artışla artarken, çentiksiz darbe dayanımının ağırlıkça % 40 PET içeren bileşimlerde maksimuma ulaştığı tespit edilmiştir. Diferansiyel taramalı kalorimetre ölçümlerinde, PET fazının erime

sıcaklığının düz PET'e göre değişmemesi nedeniyle fazlar arasında kısmi çözünürlük gözlenmemiştir. Ayrıca, ABS fazlarının PET fazlarının soğuk kristallenme sürecinde değiştirerek çekirdeklendirme etkisi göstermiştir. Isıl yaşlandırma ile yapılan boyutsal kararlılık ölçümlerinde ABS'in boyutsal kararlılığın PET ilavesi ile iyileştirildiği görülmüştür.

MA-g-SEBS, MA-g-EP, PETG ve E-EA-GMA gibi çeşitli malzemelerin uyumluluk etkisi, seçilen ağırlıkça % 70/30 ABS / PET oranı için farklı enjeksiyon kalıplama sıcaklık profilleri için değerlendirilmiştir. Yüksek enjeksiyon kalıplama sıcaklıklarında üretilen karışımların azalan viskoziteleri nedeni ile, düzensiz şekilli PET parçacıklarına neden olduğu ve bunun uyumlaştırılmış karışımlar için de geçerli olduğu tespit edilmiştir. Bu düzensiz ve büyük PET fazları karakterizasyon sırasında düşük mekanik özelliklerle de tespit edilmiştir. Özellikle E-EA-GMA ile uyumlaştırılmış karışımlarda iyileştirilmiş mekanik özellikler görülmüştür.

Öte yandan, ABS/PMMA karışımları eriyik harmanlama yöntemiyle çift vidalı ekstruder ile hazırlanmış ve bu ikisi arasındaki etkileşimi değerlendirmek için, termal ve mekanik özellikler ile karakterizasyon yapılmıştır. PMMA oranlarının ağırlıkça % 50 ve ağırlıkça % 75 olduğu karışımlarda iki fazın çözünmesi ile tek faz camı geçiş sıcaklığı elde edilmiş ve taramalı elektron mikroskobu incelemesinde faz ayrımı gözlenmemiştir.

Bu noktadan sonra, ABS/PET/PMMA üçlü karışımları ile uyumlulaştırıcı içeren ve içermeyen karışımlar mekanik ve fiziksel özellikler açısından değerlendirilmiştir. ABS ile kaplanmış parça yüzeyleri nedeniyle parlaklık değerlerinin değişmediği ve üçlü karışımdaki E-EA-GMA uyumlulaştırıcının fazlar arasındaki iyileştirilmiş etkileşim nedeni ile gerilme mukavemetini % 12 ve darbe özelliklerini % 30'luk arttırmada en etkili olduğu tespit edilmiştir.

Üçlü karışımlara nano kalsiyum karbonat eklenmesi için, ilk adım olarak ABS ve PET olarak iki farklı taşıyıcı reçine kullanılan konsantre karışımlar üretilmiş ve ikinci aşamada iki farklı uyumlulaştırıcının E-EA-GMA ve E-BA-GMA etkileri nano CaCO_3 içeren konsantreler ile beraber incelenmiştir. E-BA-GMA'ya kıyasla üzerinde daha reaktif epoksit grubu olması nedeniyle E-EA-GMA ile geliştirilmiş karışımlarda iyileştirilmiş PET dispersiyonu tespit edilmiştir.

Nano dolgu maddesinin taşıyıcı reçinesi için, ABS taşıyıcı sistemin PET taşıyıcı konsantrelere göre kıyasla daha küçük ve yuvarlak boyutu PET fazları içerdiği ve bunun nano boyutlu CaCO_3 'ün seçici bir lokalizasyon eğilimi göstermesinden ötürü olabileceği tespit edilmiştir.

PET fazlarının camı geçiş sıcaklığında uyumlulaştırıcı ve nano dolgu kullanımı nedeni ile düşüşün olmadığı gözlenmemiştir. Kullanılan uyumlulaştırıcıya bağlı olarak PET fazların soğuk kristallenme sıcaklığının değişkenlik gösterdiği ve ayrıca PET reçine taşıyıcı konsantreli nano malzeme ile bu değerin iyileştirildiği tespit edilmiştir.

125 ° C'deki boyutsal stabilite ölçümlerinde, PMMA ve nano dolgu maddesi bir çok belirgin bir iyileşme yaratmamıştır. Boyutsal kararlılıktaki ana iyileşme karışımdaki PET fazından kaynaklanmıştır.

Nano boyutlu CaCO_3 ve uyumlulaştırıcı ilavesi, karışımların parlaklık özelliklerini biraz daha kötüleştirilmiş fakat yine de uygun aralıkta bulunduğu tespit edilmektedir.

Uyumlulaştırıcı ilavesiyle iyileştirilmiş mekanikler gözlenmemiştir. Nano boyutlu CaCO_3 , gerilme kuvvetlerinde bir azalma yaratmadan gerilme modülünü geliştirmiştir.

PET taşıyıcı reçineli nano dolgu konsantresi ve uyumlulaştırıcı E-EA-GMA kullanımı ile daha yüksek gerilme modülü ve gerilme dayanımı değeri elde edilmiştir.

Yeni geliştirilen üçlü karışım veya üçlü karışım nanokompozitlerinin kurlenme sıcaklığının arttırılabileceği ve böylelikle kurlenme süresinin kısaltılabilmesiyle ABS yerine kullanımı mümkün olabilecektir. Sıcaklığın arttırılmasına bağlı olarak kısaltılmış kurlenme süresiyle boyalı ürünlerin maliyetleri azaltılabilir ve nihayetinde daha rekabetçi ürünler piyasaya sürülebilecektir.





1. INTRODUCTION

For the last century, polymeric materials have been gathered more attention even though having incredibly short history after the entrance of the term of polymer in 1832. Bakelite™ in 1909 (phenol-formaldehyde) was the first commercialized product as thermoset material and the first thermoplastic polystyrene with trade name of Trolitul™ was served to market six years later [1]. During the World War II (WWII), global scarcity of material availability increased and so the development of polymeric material gained more importance with resulting replacement of other materials by polymers such as nylon replaced silk, vinyl replaced leathers etc...[2]. Especially after the WWII, increased knowledge and technology of polymeric materials conducted an increase in usage polymeric materials due to their easy formability, light weight, low cost, resistance to various chemical materials, low electrical conductivity, ability to be transparent and to be colored and low cost[3,4].

In some cases, polymeric materials could not respond all the needed or critical properties of existing materials. As a result of increase in application areas of the polymeric materials have lead new research topics and gained speed the developments of the polymeric materials and its composites with the mixing of different polymers and/or addition of fillers such as talc, mica, calcite, fibers, nanomaterials etc...[5–7]. The new area of polymeric blends and composites have been improved by the addition of the fillers or blending with different polymers.

One of the first attempt to adjust the property of polymeric materials has been to add some filler or reinforcing agent into the matrix, which could easily improve the mechanical properties. Different type of fillers and different filler loadings showed totally different effects on the properties of polymeric composites [8–16]. The effects of filler on the composite properties mainly depended on the particle shape, particle size, volume fraction in the matrix and compatibility with matrix. Composites with high strength fillers such as glass fibers usually have strength to weight ratios that exceed better values compared to metals and their alloys [17]. This property makes polymer matrix composites ideal for structural applications. On the other hand recent

developments in nanomaterial reinforced composites which can show higher mechanicals as a result of higher aspect ratio and higher interaction with polymeric matrices has been gaining more importance[10,18–23]. The researches in thermoplastic composites is a still growing area because of the processing and cost advantages but sometimes it may not be enough to reach target properties by just adding filler or reinforcing agents into a polymer and in this case blend based solutions may be proper way of solving the problem [5,6,10,24–26].

The polymeric blends; which are defined as a mixture of at least two different macromolecular substances in which one component is above 2 wt.% like polymers or copolymers, play an important role in widening application windows due to their ability to produce new products with tailor-made properties with minimal investment, thereby creating attention from both academy and industry[24,27]. In the mixture of polymeric materials, which is, most usually resulting an immiscible system can be results of coarsening, alternating morphology, poor adhesion between phases and irreproducible results. These mixtures can have large domains in the dispersed phases and poor interaction in between them[1]. Alloys and blends of polymeric materials are most usually confusing terms; alloy can be described as polymer blend with a distinct phase morphology[24] or with stabilized morphologies [28]. The aim of blending has been evolved time after time by the increased knowledge on polymeric materials. Blending due to impact modification was the one of first application starting in 1960s and it was followed by diluting of expensive resin with a commodity resin for decreasing the cost. By the entrance of high temperature polymers into the market in 1990s, blending was applied to improve processability, decrease the cost and now blending has been used to secure set of properties which are critical for final applications[29].

The properties of polymeric components defines the performance of the blends related with the arrangement of ingredients in the space. The thermodynamics and flow-imposed morphology is controlling the spatial arrangements. Mostly miscibility of blends are measured and controlled by the thermodynamic measurements, but it has more widen use for scientist. The glass transition temperature (T_g); that is relatively simple to measure, is the most widely used tool for the detection miscibility. For the miscible polymer blends, T_g is expected to have single value but it still contains some uncertain situations. Such as, when the one component is lower or around 10 wt. % in

the blend and when Tg's are occurring at similar temperatures. Moreover, it should not be used when the ingredients of blends have the Tg values differing from each other 10 °C from each other [1].

In order to achieve synergistic property improvement of individual parent components, like better processability, higher influence on strength, better chemical resistance. Many commercial polymer blends have been developed using an extrusion-compounding process[5,6,10,29–35]. One of the most important issue in polymeric blend development is the polymer miscibility of different phases which directly affecting the final product properties. Polymeric blends are either miscible or immiscible with regards to the sign of the free energy of mixing[1,24]. Generally, as explained by Ajji[1] “the polymer/polymer miscibility does not exist — it is always limited to a “miscibility window” (p.295) range of independent variables, such as composition, molecular weight, temperature, pressure, etc.”. When a blend is out of miscibility window, this immiscibility of polymers causes phase separation and low interaction between two phases resulting in undesired mechanical properties[25,36–38] and vice versa miscible phases can improve the mechanicals[5,27,32,34,39–44].

In order to reach required combination of properties and processability; development of either polymers or blends; especially by the introduction and the development of different compatibilizers. Whether they are reinforced or non-reinforced is to be very famous for the last decades. In order to improve performance of immiscible or partly miscible blends; compatibilization action is required, which can be applied in three aspects: (1) Decreasing the interfacial tension to improve fine dispersion, (2) Improving the morphology stability during the high stress and/or strain creating conditions and process like (e.g., during extrusion, injection molding etc..) or, and (3) Improvement of adhesion between the phases in the solid state. By the addition of compatibilizers, polymer or generation of compatibilizers during the reactive extrusion of blends can be carried out to achieve miscible structures. There are several theories for the compatibilization of polymer blends by the addition of a compatibilizer such as follows: (i) interface, (ii) interphase, and (iii) compatibilization process[1]. These theories can be supported by several actions; (i) addition of copolymer (AB) into blends of A and B polymer which has selectively miscible in phases related with structure, (ii) addition of solvent like phase to obtain totally miscible structure or addition of cosolvent in polymeric nature to miscible in both phases to create interface, (iii)

addition of large amount of (25-35 wt.%) core-shell copolymer acting like impact modifier, (iv) reactive compatibilization by compounding with a reactant, (v) blending mechano-chemical way in which chains are broken and recombined as a generation of copolymer [1,5,24,25,29].

The main objective of blending has been always reach to favorable properties from each ingredients. In Figure 1.1[1] points out the expected property combination of blends depending on the miscibility. In miscible blends, it is expected to obtain an average property depending on the ratio of each components such as Tg of blend will increase or decrease depending on the ratio as a single value. In case of having an immiscible blend, due to heterogeneous morphology and insufficient structural unity with poor heat stability, properties are expected to be worse than individual components. In case of having a compatibilized immiscible polymer, synergistic improvements in the final property like rubber-toughened polyamide, which is immiscible rubber phase (to improve impact property), integrated thermoplastic (to enhance heat stability) by compatibilization. Another example can be the blend of semi crystalline thermoplastics with amorphous materials to obtain high chemical resistant tough materials [1,45].

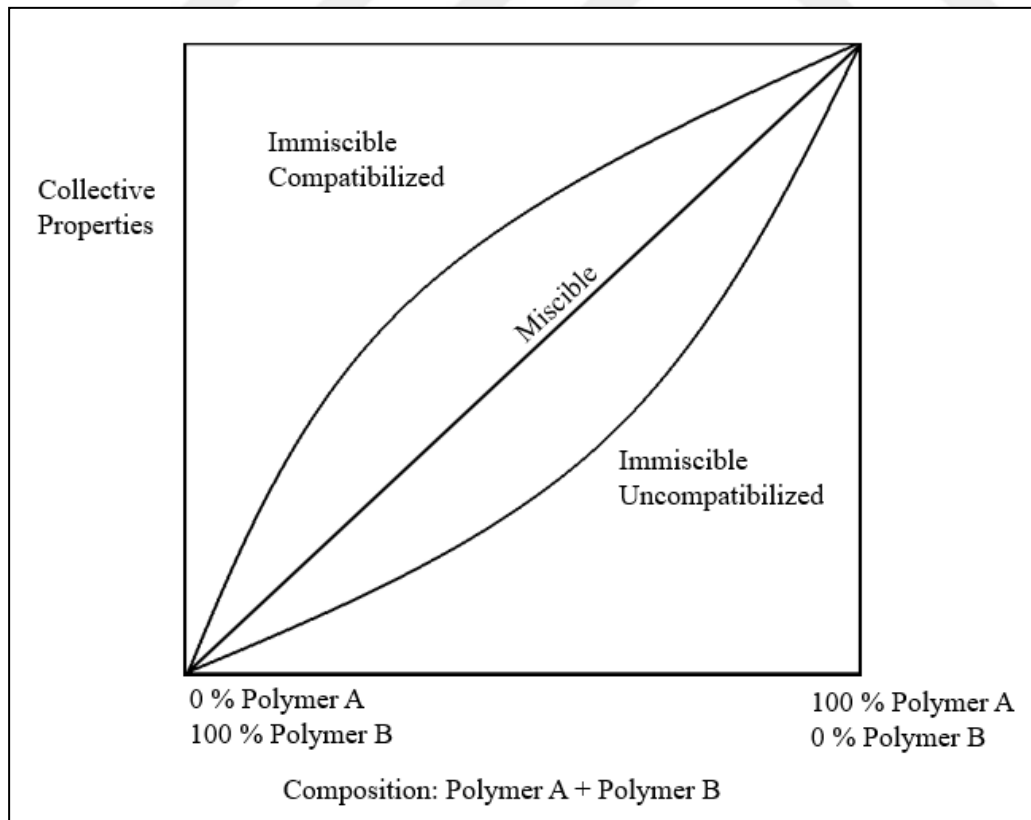


Figure 1.1 : Polymer blend properties versus composition regarding to compatibility and miscibility.

In tailor made product development targets, morphology plays an important role to define final properties of blends [1,45–47]. In miscible and partially miscible blends, fine morphology can be observed in which small quantity polymer is dispersed in major phase. These results satisfactory properties related with particle size and distance between of minor phase droplets such as the impact absorbance property of blends strongly varied with by the dispersed particle size, the ligament thickness, and the interfacial adhesion. When the morphology is disturbed during the processing or usage the performance will be varied if not stabilized properly[1]. In immiscible blends, morphology can be varied such as; (i) dispersed minor phase, (ii) two phase morphology as co-continuous. This morphological structure is mainly varied with regards to blend components, ratios, the viscosity and the viscosity ratio of ingredient polymers, blending parameters like temperature, pressure etc...[45]. This is mostly related with difficulty of mixing at molecular level, due to immiscibility and phase separation of most polymer blends. Also, when the phase separation occurs, the physical properties strongly depend on the phase-separated morphology[1,45,48].

Most of the compatibilizer developments have been done for the blend of amorphous and semi crystalline polymer in order to obtain a stabilized and compatibilized morphology. Blended amorphous materials like ABS (acrylonitrile-butadiene-styrene), Polystyrene (PS) or Polycarbonate (PC) and crystalline materials like Polyamide (PA), Polybutadiene terephthalate (PBT), Polypropylene (PP), Polyethylene (PE) and Poly(ethylene terephthalate) (PET) have been studied in last few decades to overcome difficulties in compatibilization and to combine desirable features of both polymers[6,29,49–55]. On the other hand, for applications requiring good surface quality and higher temperature resistance than neat ABS, ABS/PC blends have been investigated but for several applications these blends were cost prohibitive [5,6,22,31,50,56–59].

ABS (acrylonitrile-butadiene-styrene) is an engineering thermoplastic that finds extensive applications in home appliances, electronic equipment, and automobile parts because it has good balance of properties, toughness, strength, and temperature resistance, coupled with its ease of molding and high surface finish quality, as well as low mold shrinkage properties[60]. Because grades can be tailored to the application property requirements and the availability of electropaintability, ABS is often used in automotive interior and exterior trim components[61,62]. Its drawbacks, such as low-

heat-deflection temperature, residual stress in final parts, and dimensional stability at elevated temperatures that is required especially during a paint curing process creates limitations for its applications in structural parts or causes higher processing costs due to long paint curing times at a relatively lower [80°C] paint curing temperature[12,63–65].

1.1 Purpose of Thesis

The main objective of this study is to develop a material, which can withstand the higher process temperatures subjected during the paint curing process by improving dimensional stability while maintaining visual properties with reasonable price to shorten the painting process cycle time by replacing the neat ABS material for the visual applications.

As a first step, effect of high temperature processing conditions during compounding on neat ABS material were investigated by optical, mechanical and physical properties. In the second step, effect of ABS/PET ratio on rheological, morphological, thermal and mechanical properties with dimensional stability. In the third step; effect of different types of compatibilizers were evaluated on morphological, thermal and mechanical properties of selected ABS/PET blends with the investigation of different injection molding temperature process profiles. Effects of Polymethyl Methacrylate (PMMA) ratio on ABS were investigated by prepared blends in the thermal, mechanical and morphological properties with fixed processing conditions.

In the following step, addition of PMMA into selected ABS/PET blend with different compatibilizers were investigated. In the final stage, addition of nano sized calcium carbonate with different carrier resin as ABS and PET into ABS/PET/PMMA matrix were investigated by morphological, thermal, optical, physical and mechanical properties with dimensional properties.

1.2 Literature Review

Acrylonitrile–Butadiene–Styrene copolymer (ABS) is the most commonly used engineering thermoplastic because it has a competitive price/performance ratio and there have been several attempts to improve ABS properties such as; chemical resistance and mechanical properties[5,22,60,66–73,25,30,32,33,43,44,58,59]. In

order to achieve a good combination of properties and processability of ABS, several companies have commercialized different blends with different polymers as given in Table 1.1[1,6,24]. The most preferred blend is containing ABS and PC. For this kind of blends ABS has been added to improve processability of PC with satisfactory mechanical properties and surface gloss[31,46,56,57,74]. In addition, there are some other ABS based blends with polyvinyl chloride (PVC) to improve impact strength, flammability, processability and hot tear strength. In addition lately some commercial products based on ABS/PET has been launched the market due to improved chemical resistance and increased cost of ABS related with shortage on butadiene rubber (BR). Even though there are some several industrial applications and products are available there have been several researches on going to improve ABS blends with several reasons starting from price to some technical limitations[6].

Table 1.1 : Commercial ABS blends.

Polymer A	Polymer B	Trade Name	Company	Key Properties / Reason of Blending
ABS	PVC	Cycovin Kaf	B.F. Goodrich	impact strength, processability, flammability, hot tear strength
ABS	PVC	Kaneka Enplex	Kanegafuchi	
ABS	PC	Cycology	Sabic	impact strength, processability, good mechanical, properties, high dimensional stability
ABS	PC	Bayblend	Bayer	
ABS	PC	Triax	Ineos	
ABS	PC	Pulse	Dow	
ABS	PA6	Terblend	Basf	reduced moisture sensitivity, improved toughness, reduced shrinkage
ABS	PA6	Triax	Ineos	
ABS	TPU	Prevail	Dow	high impact strength, paintability without primer
ABS	ASA	Terblend	Basf	good weather resistance
ABS	PET/PBT	Strex	Samsung	good chemical resistance, high toughness, reduced moisture sensitivity
ABS	PET/PBT	Novalloy	Daicel	
ABS	PET/PBT	Techniace	Nippon	
ABS	PET/PBT	Makroblend	Bayer	

Polymers; due to being a carbon based organic material, the degradation of polymeric materials can be observed as the all possible types of ageing effects faced during the life cycle of application and also degradation in material and part manufacturing processes[75]. When the polymeric materials faced several circumstances from processing to usage like shear stress, heat, light, air, water, mechanical loading and chemicals, some unwanted reactions may start which can be described as degradation.

Degradation is leading the change of length of chains with result of appearance and mechanical properties[76]. Even the ABS has the combination of several polymer properties like; tensile strength and chemical resistance from acrylonitrile, toughness and low temperature properties from butadiene and gloss with processability from polystyrene[77], it has low stability performance in open environment conditions and also during the processing [24,62,78,79]. This degradation sensitive behaviour of ABS can be explained by the grafted polybutadiene phases which is really sensitive the environmental conditions due to unstable double bond in the structure[80–82]. The instable structure during the life cycle of product or processing can result a decrease in the impact strength with crosslinking, cracks on the surface and more brittle structure in final application. Several researches have been done to improve several properties like, outdoor performance[78] and processing[56,62,75,80].

Most of the compatibilizer developments have been done for the blends of amorphous and semi crystalline polymer. Blended amorphous materials like ABS (acrylonitrile-butadiene-styrene), Polystyrene (PS), Polyethylene Terephthalate Glycol (PETG) or Polycarbonate (PC) and crystalline materials like PA (Polyamide), PBT (Polybutadiene terephthalate), Polypropylene (PP), Polyethylene (PE), poly(trimethylene terephthalate) (PTT) and Poly(ethylene terephthalate) (PET) have been studied in last few decades to overcome difficulties in compatibilization and to combine desirable features of both polymers[6,29,49–55,83]. Some of the selected researches for ABS with polyesters are summarized in Table 1.2.

There are several compatibilizers like; styrene maleic anhydride (SMA)[68], maleic anhydride grafted styrene ethylene butylene styrene (MA-g-SEBS)[84,85], ethylene ethyl acrylate glycidyl methacrylate E-EA-GMA[67,70], poly(methyl methacrylate-co-glycidyl methacrylate) (PMMA-GMA)[49], styrene butadiene styrene (SBS)[30] and ethylene-b-butyl acrylate-b-glycidyl methacrylate (E-BA-GMA)[86] used in the researches for ABS based blends.

As a semi crystalline thermoplastic polymer, Poly (ethylene terephthalate) (PET) is a common polyester resin with good physical and chemical properties for applications such as; textiles, packaging, and films. In addition, glass fiber filled PET compounds also find engineering applications[36,87]. However, unmodified PET is not suitable for injection molding due to its slow crystallization rate and the embrittlement tendency upon crystallization in addition to narrow processing windows[87].

In order to improve several properties PET has been blended with several products. When blended with PMMA; the improvement thermal stability the electronic applications which is requiring conductivity with the addition of carbon black[88,89]. PET blended with PC; in order to combine toughness of PC[90] with chemical resistance of PET and PBT for better processability with better crystallization[87] and impact modifiers to improve toughness[48,73,91]. This kind of examples can be widened for several polymer PS[92], PP[35,36], PE[93], PA[94], PLA[34,95] etc...[1,96]. Some of the selected researches for ABS with PET are summarized in Table 1.3.

Nanocomposites; which is based on nanoparticle usage in the polymeric matrices, has been gaining more and more importance due to having high surface area which can interact with matrix to improve modulus, strength, toughness, chemical resistance, gas permeability resistance, thermal stability, and dimensional stability even though low loading around 5wt.% [97]. One of the difficulty of nanoparticle usage is the dispersion problems due to tendency of agglomerate to create bigger particles. The most of properties of composites are mostly related with good distribution, dispersion and proper interaction with the matrix[14].

Fillers in nano dimensions can help to improve modulus and hardness they cannot change the tensile strength properties with improved impact performances up to a certain loading levels. Also, nano filler can be used when the light transmittance is needed with smooth surface [13,50,60,98–100].

Mostly used nanoparticles with different purposes are clay, calcite, carbon nanotubes, zeolite, zirconia, silver, silicone, aluminium oxide etc... [14]. Each nano filler has been used for different purposes like; clay for mechanical improvement due to high aspect ratio and compatibilizing action in low density polyethylene/polyamide 11 (LDPE/PA11) blends [99] or high density polyethylene/polyamide 6 (HDPE/PA6) blend[101] or clay for improvement of flammability as investigated by Zheng et al[102] for PMMA clay nanocomposite in PS, ABS, PP, PE and high impact polystyrene (HIPS).

Mineral based nanofillers like clay, calcium carbonate (CaCO_3) and aluminium oxides are the mostly used nano fillers due to availability in nature and low cost. In one of the research by Jiang et al[98], effect of nano and micron sized CaCO_3 on ABS were

investigated. As result; micron sized CaCO_3 improved the modulus with slight decrease in tensile strength and impact properties but on contrary, nano sized CaCO_3 did not decrease the impact property and also improved the tensile properties due to having large surface area means more interaction with the matrice. Chen et al[103] investigated the effect of polyethylene Glycol (PEG) coated nano CaCO_3 on PET and pointed out that; nanofiller improved the thermal stability with better crystal growth. Di Lorenzo et al[104] used uncoated and steric acid coated nano calcite during the polymerization of PET and it was shown that with surface coated nano filler, better dispersion and superior crystallization obtained.

In the research of Razak et al[10], the effect of 1 to 5 wt. % nano montmorillonite (MMT) on the properties of ABS and recycled PET blends for the composition of 30:70 and 70:30 wt.% were investigated. At 3 wt. % of MMT incorporation to blends, modulus values reached to maximum even though tensile and flexural strength values were reaching maximum at 1 wt. % loading. However, impact properties decreased around 45% at 5 wt. nano MMT loading due to reduction of chain movements by nano particulates resulting an fragile structure by limited their ability to adapt the deformation[10]. Poor impact strength of the nanocomposites can be related with the lack of the crack deflection and cavitation[105].

However, ABS blend dimensional stability at higher temperatures which is an important parameter during the paint curing process to shorten curing time with increased productivity[12,63,64] have attracted little attention. Weakly-Bollin[65], described that , thermal stress relaxation of ABS starts around 75-80 °C in which the residual stresses imposed during the injection molding release with the increased temperature and might cause the dimensional instability. Also Boldizar et al[75] mentioned about the shrinkage of ABS material after aging in 110 °C silicone oil around 6%. In view of this, the paint curing processes were usually operated below that temperature with longer curing periods, such as 40 to 90 minutes depending on the part geometry. In order to addresses this well-known industrial problem, high temperature resistant materials were combined with low temperature curing paints[106,107]. PC/ABS blends were one possible solution, but their high cost and relatively low chemical resistance of amorphous components limited their usage[1].

Table 1.2 : Selected researches for ABS with polyesters.

Polymer A	Polymer B	Compatibilizer	Research Area	Reference
ABS	PBT	E-EA-GMA	The effect of screw profiles and process conditions on PBT/ABS (70/30 wt. %) with/without compatibilizer on the crystallization of the blends. It was reported that compatibilizer inhibited melt crystallization and low feeding rates improved the degradation of PBT.	Ambrósio et al[67]
ABS	PBT	E-EA-GMA	Effect of compatibilization and ABS type on properties of PBT/ABS (70/30 wt.%) blends were investigated with morphological and impact measurements. Process limited miscibility window expanded by compatibilizer. ABS having the highest flowability was reported to be superior for optimizing morphology and impact properties of PBT.	Hale et al[70]
ABS	PBT	E-EA-GMA	Effect of compatibilization on properties of PBT/ABS (70/30 wt.%) blends were investigated with morphological and impact measurements. Unstabilized structure of uncompatibilized blends were observed. The reaction between the carboxyl end groups of PBT and the epoxide groups of compatibilizer extrusion to form a graft copolymer is presented.	Hale et al[71]
ABS	PBT	SMA	Optimum Styrene maleic anhydride (SMA) ratio on ABS/PBT (30/70 wt.%) blend were investigated and 5 wt.% was reported as optimum ratio.	Basu et al[68]
ABS	PTT	MA-g-SEBS glycidyl end-capped epoxy resin	The effect of compatibilizer on blends were investigated via morphology and rheology measurements and reported that compatibilizer improved the dispersion and viscosities are epoxide ratio dependent.	Xue et al[39]
ABS	PTT	MA-g-SEBS glycidyl end-capped epoxy resin	The effect of compatibilizer on blends were investigated via thermal measurements. Two Tg were reported with effected cold crystallization peak of PTT. The crystallization of PTT were compatibilization ratio dependent.	Xue et al[84]
ABS	PA6 PET / PBT PC / SAN	SMA PMMA-GMA	Effect of several semi-crystalline polymers on ABS investigated via mechanical and morphology investigations. Co-continuous structures and improvements in mechanicals via compatibilizers reported.	Liu et al[49]

Table 1.3 : Selected researches for ABS with PET.

Polymer A	Polymer B	Compatibilizer or Nano Filler	Research Area	Reference
ABS	PET		Two different ABS type with PET evaluated and resulted an immiscible structure. Co-continuous structure reported at 30 wt.% to 70 wt.% PET content with improved mechanicals.	Cook et al[44]
ABS	PET	MA-g-SEBS	Effect of processing condition on compatibilized blend were investigated. Effect of processing condition on PET degradation and morphology change reported.	Cook et al[33]
ABS	PET	SMA	Waste PET in ABS was added and effect of SMA investigated with mechanicals and HDT. Improvements in heat deflection temperature (HDT) and mechanicals reported.	Paul et al[42]
ABS	HIPS /PETG	SBS	The effect of SBS on blends were investigated. HIPS/PETG blend showed worse mechanicals like uncompatibilized immiscible blends. Phase separation in ABS/PETG also reported.	Focke et al[69]
ABS	PETG	SBS	The effect of ABS/PETG ratio with/without SBS were evaluated with morphology and mechanical measurements. Ratio depended morphology reported and addition of SBS was creating finer dispersion.	Joseph et al[30]
ABS	PET	nano MMT	The effect of different surface treated nano MMT were used in ABS/PET blends to investigate on rheological properties. Topology and rheological change concerning surface treatment reported.	Kracalik et al[19]
ABS	PET	nano SiO ₂ AES	In PET/ABS/AES (55/40/5) blends effect of nano-SiO ₂ particles on the morphology and mechanical properties of blends. The uniform dispersion of the nano-SiO ₂ components and the two-continuous phase of rPET/ABS was with improved mechanicals reported.	Shi et al[108]
ABS	PET	nano MMT SMA	The effect of nano MMT on mechanical, morphological and rheological properties of ABS/PET (70/30 wt.%) were investigated. Maximum tensile strength was obtained for 1 wt.% nano MMT with a good dispersion. At higher loadings modulus increased but impact decreased.	Razak et al[10]
ABS	PET	SMA ABS-HGP	The effect SMA and ABS high glue powder on ABS/PET (70/30 wt.%) were investigated via mechanical, thermal, rheological and morphological properties. As a results SMA was effective as a compatibilizer and amount was increasing the impact. ABS and SMA effected to crystallization peak of PET.	Zhao et al[43]

1.3 Hypothesis

The driving force for blending ABS with PET is that; PET has lower price compared to ABS and low water absorption, better chemical resistance with high dimensional stability but limited processing window. On the other hand, ABS has good processability, and high impact strength with limited dimensional stability above 75 °C, which is inhibiting the higher paint curing process temperatures for visual application as well its application is limited for production of part subjected to high temperature during its service life. By combining PET with ABS, the drawbacks of both components can be eliminated, and the resulting blend has outstanding performance. However, PET and ABS have poor compatibility. By incorporating of various compatibilizers can improve the compatibility but also decrease the certain mechanical properties such as stiffness. Addition of nano-sized filler can help to improve stiffness with slightly affecting the surface properties of blend. In addition, incorporation of PMMA into ABS matrix can be used to improve surface properties like gloss.

This study aimed to provide a compatibilized, nano sized CaCO_3 reinforced ABS/PET/PMMA blend which might be an ideal material where high surface quality, colourfastness, easier injection molding process, and higher dimensional stability at elevated service or process temperature are required.



2. MATERIALS AND METHODS

2.1 Materials

In the studies, industrial grades of polymers, compatibilizers and nano-sized filler from different suppliers were used. ABS was selected as main matrix polymer from Ineos Styrolution Corporation with grade name Terluran GP35 (~71 wt. % styrene-acrylonitrile copolymer as a hard phase, 29 wt. % particulate butadiene graft rubber with intrinsic viscosity (IV) = 64 ml/g) having the density of 1,04 g/cm³ and melt flow index = 34 g/10 min. (at 220 °C 10 kg).

PET was selected from Sasa Corporation with the grade name of Sasa Advanite 14006 PET having the density of 1.38 g/cm³ and intrinsic viscosity (IV) = 0,65 ml/g.

PMMA was selected from Arkema Corporation with the trade name of Altuglass VML 100 having the density of 1,18 g/cm³ and melt flow index = 14,5 g/10 min. (at 230 °C 3,8 kg).

Different types of compatibilizers varying in chemical structures and functionalities were selected.

Two types of compatibilizers having styrenic structure were selected as maleic anhydride grafted styrene ethylene butylene styrene block copolymer (MA-g-SEBS) with different maleic anhydride ratio as given in the Table 2.1 from Kraton Corporation with trade name of FG1901G and FG1294G.

Table 2.1 : Properties of used MA-g-SEBS as compatibilizer.

Type	Trade Name	
	Kraton FG1901G Linear SEBS + 1,4 to 2,0 % maleic anhydride	Kraton FG1294G Linear SEBS + 0,7 to 1,3 % maleic anhydride
Polystyrene Content (%)	30	13
Diblock Content (%)	-	30
Tensile Strength (MPa)	34	24
Elongation at Break (%)	500	750
Hardness, Shore A, 30s	75	65
Melt Flow Index (g/10 min) (at 230 °C, 5 kg)	22	40

Maleic anhydride (MA) grafted ethylene propylene copolymer was supplied from DuPont with the trade name of Fusabond N493 (Ethylene propylene copolymer grafted with 0,9 wt. % MA having a melting point at 50 °C with melt flow index=1,6 g/10 min. at 190 °C at 2,16 kg).

Amorphous PET named as PETG as a compatibilizer was supplied from Eastman Corporation with the trade name of Eastar Copolyester 6763, which is a transparent material with glass transition temperature (T_g) of 80 °C.

E–EA–GMA as compatibilizer from Arkema with trade name Lotader AX8900 was selected as a random terpolymer of ethylene, acrylic ester and glycidyl methacrylate (density of 0,94 g/cm³ and 65 °C melting point as 6 g/10 min. melt flow index at 190 °C 2,16 kg load). Acrylic ester group which brings the softness, polarity and high thermal stability as ratio of 24 wt. % . In addition, acrylic ester gives the high flexibility and high impact behaviour. 8 wt. % content of glycidyl methacrylate are expected to give reactivity versus OH, COOH and NH₂ groups to reach optimal dispersion during processing. High content of ethylene gives ability to disperse easily in all PE based products.

Elvaloy PTW as a compatibilizer from DuPont was selected for Ethylene/N-Butyl Acrylate/Glycidyl Methacrylate Copolymer with a density of 0,94 g/cm³ and 12 g/10 min. melt flow index at 190 °C 2,16 kg loading having a melting point of 75 °C as the ratios of E–BA–GMA respectively 63:31:6 wt.%. Excellent adhesion to the PET matrix expected due to epoxy functionality of terpolymer.

As filler and mechanical property modifier nano sized calcium carbonate was supplied from Shiraishi – Omya GmbH with trade name of Hakuenka® CCR-S10; which is a precipitated calcium carbonate coated with fatty acids with 70 nm average particle size.

2.1.1 Formulations and sample codes for investigation of extrusion processing parameters on ABS

In this section of study, due to having higher melting point of PET around 260 °C, it was aimed to observe the effects of processing conditions on ABS in twin-screw extruder. Industrial grade of ABS (Terluran GP35) were used as 100 % wt. at different processing conditions and coded as given in Table 2.2.

Table 2.2 : Twin-screw extrusion temperature profiles to investigate effect of processing conditions (°C).

Sample Code	Barrel 1	Barrel 2	Barrel 3	Barrel 4	Barrel 5	Barrel 6	Barrel 7	Die
ABS_Injection	Just injection molding without any extrusion process							
ABS_170-190	20	170	175	180	180	185	190	190
ABS_190-210	20	190	195	200	200	205	210	210
ABS_210-250	20	210	215	220	220	230	240	250
ABS_250-290	20	250	255	260	260	270	280	290

2.1.2 Formulations and sample codes for investigation of effect of ABS/PET blends ration on properties

Table 2.3 shows the sample codes and ABS, PET concentration used in this section to investigate effect of ABS/PET ratio on several properties.

Table 2.3 : Compositions and sample codes for ABS/PET blends.

Sample Code	weight ratio, %	
	ABS	PET
A000-P100	0	100
A020-P080	20	80
A030-P070	30	70
A040-P060	40	60
A050-P050	50	50
A060-P040	60	40
A070-P030	70	30
A080-P020	80	20
A100-P000	100	0

2.1.3 Formulations and sample codes for investigation of processing conditions and compatibilizers on selected ABS/PET blend

In order to investigate the effect of compatibilizer and injection molding processing conditions several formulations prepared and sample codes were given Table 2.4.

Table 2.4 : Blend compositions and sample codes for compatibilized blends.

Sample Code	weight ratio, %					
	ABS	PET	FG-1901X	FG-1924X	MA-g-EP	PETG
A070-P030	70	30				
A070-P030-M3	67	30	3			
A070-P030-Z3	67	30		3		
A070-P030-E3	67	30			3	
A070-P030-P3	67	30				3

2.1.4 Formulations and sample codes for investigation of ABS/PMMA ratio

In order to investigate the effect of PMMA ration on ABS conditions several formulations prepared and sample codes were given Table 2.5.

Table 2.5 : Prepared formulations for ABS/PMMA.

Sample Code	weight ratio, %	
	ABS	PMMA
A100-PM000	100	0
A095-PM005	95	5
A090-PM010	90	10
A075-PM025	75	25
A050-PM050	50	50
A025-PM075	25	75
A000-PM100	0	100

2.1.5 Formulations and sample codes for investigation of effects of different compatibilizers on ABS/PET/PMMA blends

In order to investigate the effect of different compatibilizers on ABS/PET/PMMA terblends several formulations prepared and sample codes were given Table 2.6.

Table 2.6 : Blend compositions and sample codes for compatibilized blends for ABS/PET/PMMA.

Sample Code	weight ratio, %						
	ABS	PET	PMMA	E-EA-GMA	E-BA-GMA	MA-g-SEBS	MA-g-EP
A070-P027-PM03	68	27	5				
A065-P027-PM03-L3	65	27	5	3			
A065-P027-PM03-P3	65	27	5		3		
A065-P027-PM03-M3	65	27	5			3	
A065-P027-PM03-E3	65	27	5				3

2.1.6 Formulations and sample codes for investigation of effects of nano calcium carbonate on ABS/PET/PMMA blends

In order to investigate the combined effect of different compatibilizers and nano CaCO_3 filler concerning carrier material as ABS or PET on ABS/PET/PMMA terblends properties different formulations were prepared as given in Table 2.7. At first 10 wt. % nano CaCO_3 filler reinforced materials with ABS or PET resin carriers were produced after drying the masterbatch resins were used in the production of terblends.

Table 2.7 : Prepared Blend compositions and sample codes for nano CaCO_3 reinforced ABS/PET/PMMA terblends.

Sample Code	weight ratio, %							
	ABS	PET	PMMA	CCR-S10	E-EA-GMA	E-BA-GMA	Nano ABS	Nano PET
Nano ABS	90			10				
Nano PET		90		10				
Terblend-L	65	27	5		3			
Terblend-L-A	38	27	5		3		27	
Terblend-L-P	65		5		3			27
Terblend-PTW	65	27	5			3		
Terblend-PTW-A	38	27	5			3	27	
Terblend-PTW-P	65		5			3		27

2.2 Sample Production Methods

2.2.1 Twin screw extrusion

In order to obtain well-mixed compounds, an intermeshing, co-rotating twin-screw extruder (24 mm, 28:1 L/D, PRISM TSE24 IIC with a degassing port connected to the Edwards rotary vacuum pump, water bath and fixed length pelletizer) were used. Hence, twin screw extrusion temperature profiles and screw design were kept constant to eliminate processing condition affects as Cook et al[33] reported that PET/ABS blend properties were strongly dependent on processing conditions[30,42,95]. Screw speed and motor torque were set to 500 rpm and 75-80 % respectively. Table 2.8 gives the temperature profile used during the investigation of extrusion process profile on neat ABS.

Table 2.8 : Extrusion temperature profile for neat ABS (°C).

Sample Code	Barrel 1	Barrel 2	Barrel 3	Barrel 4	Barrel 5	Barrel 6	Barrel 7	Die
ABS_170-190	20	170	175	180	180	185	190	190
ABS_190-210	20	190	195	200	200	205	210	210
ABS_210-250	20	210	215	220	220	230	240	250
ABS_250-290	20	250	255	260	260	270	280	290

Table 2.9 shows the extrusion temperature profile for prepared ABS/PET, ABS/PMMA and ABS/PET/PMMA blends on several properties.

Table 2.9 : Extrusion temperature profile for prepared blends (°C).

Extrusion Temperature Profile for prepared blends								
Unit (°C)	Barrel 1	Barrel 2	Barrel 3	Barrel 4	Barrel 5	Barrel 6	Barrel 7	Die
	20	250	260	260	270	270	280	265

The extruder screw profile was configured to achieve good melting and mixing of polymers by high shear, proper residence time in the reaction zones, and venting close to the outlet of the extruder as shown schematically in the Figure 2.1. moreover, properties of the twin-screw extruder were given in Table 2.10.

The screws of the extruder were designed to be six zones:

1. raw material intake and solid conveying zone
2. plasticizing zone (first kneading block)
3. melt conveying zone
4. further homogenization zone (second kneading block)
5. degassing zone
6. pressure built up zone

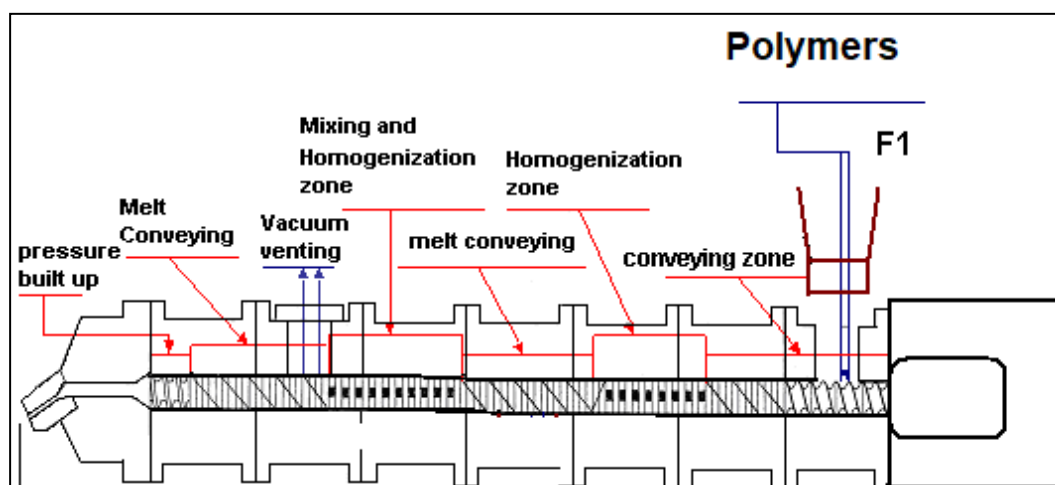
**Figure 2.1 :** Extruder screw design and schematic illustration of compounding process.

Table 2.10 : Prism TSE 24 Twin screw extruder properties.

	Units	PRISM TSE24
Screw diameter	mm	24
Maximum screw speed	rpm	1000
L/D (shaft length/screw diameter)	-	28 / 1
Channel depth	mm	5,15
Screw diameter/channel depth	-	4,66
Screw/barrel clearance	mm	0,2
Shaft center line distance	mm	18,75
Shaft center line/radius ratio	-	1,5625
Total Area	cm ²	8,5
Screw area	cm ²	4,7
Free area	cm ²	3,8
Total volume	cm ³	511
Free volume	cm ³	228
Barrel peripheral surface area	cm ²	830
Surface area/total volume	m ² /liter	0,14
Surface area/Free volume	m ² /liter	0,31
Max. channel shear rate @ 1000 rpm	s ⁻¹	244
Max. power	kW	9
Max. torque/shaft	Nm	43
Max. torque/Free volume	Nm/cm ³	0,16

Compatibilizers and PET are humidity sensitive materials with the humidity they can lose their efficiency. Compatibilizers and polymers were dried for 4 hours at 80 °C in a drying oven. Ingredients of each formulations were premixed before feeding the main feeder. Nano calcium carbonate (CaCO₃) were feed from the side feeder after the calibration of gravimetric feeder.

After the twin-screw extrusion process, granulated materials were obtained and these materials were used for rheology, melt flow index (MFI) measurements and raw material for sample bar production in injection molding process.

2.2.2 Injection molding

Injection molding is defined as a process where melted plastic material forced into a mold cavity and cooled down in it by taking its shape. When the plastic material cooled in the mold pins can eject it. The process is based on the ability of the thermoplastics to be softened by heat and to harden when cooled. This process is usually used for

mass production. Injection molding machines are mainly divided into 3 parts. These are mold, clamping unit and injection unit (Figure 2.2).

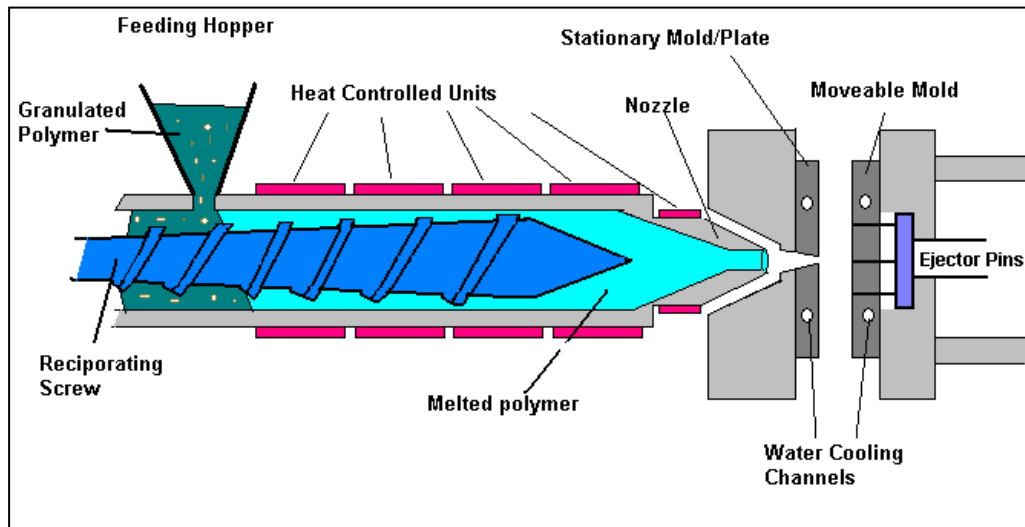


Figure 2.2 : Schematic illustration of injection molding process.

The clamping unit is designed to keep mold parts under pressure during injection of molten plastic and cooling time. Injection unit consists hopper; heat controlled barrels-cylinder, screw and motor. Mold is the place where the melted polymeric material shaped by cooling down. During the injection process polymeric materials in the form of pellets, are loaded into a hopper on top of the injection unit. The pellets feed into the cylinder by the reciprocating movement of the screw and heated until they melt. When the melted plastic is accumulated in front of the screw, injection process begins. The speed controlled forward movement of screw forces molten plastic into mold cavity and then holds the force for a while to minimize the shrinkage of molded part. After finishing injection and holding the pressure, the mold is kept closed to cool down the melted plastic and shape it. When the cooling is completed, mold opens and the ejectors force the molded-shaped parts out.

Arburg Allrounder 320 C injection molding machine was used to produce plates, tensile and Izod impact test specimens according to ISO R 527 and ISO 180 standards. The Arburg Allrounder 320C injection machine's specifications are given below in Table 2.11.

Table 2.11 : Arburg Allrounder 320C Injection machine specifications.

	units	Arburg Allrounder 320C
Screw diameter	mm	30
Max. injection pressure	bar	2000
Max. volumetric displacement	cm ³	144
Hydraulic motor power	W	1500
Max. clamping force	tones	50
Max. screw speed	rpm	154
Screw back pressure	bar	350

Injection processing temperatures were given in tables from feeding hopper to nozzle, respectively to inject all compounds and the neat ABS, except the neat PET, which used a different profile. Process parameters like injection speed, time and pressure for all specimens were kept constant to eliminate process parameter affects. Mold temperature during the injection molding process was kept constant as 80°C. The mold (Figure2.3.) was cooled to room temperature with a Piovani ST092 water-cooling chiller.

During the investigation the effect of extrusion processing profile on ABS material, used injection molding profile during sample production was given in Table 2.12.

Table 2.12 : Injection molding temperature profile of ABS materials and blends (°C).

	Barrel 1	Barrel 2	Barrel 3	Barrel 4	Nozzle
Temperature (°C)	230	235	245	250	245

Mentioned injection molding temperature profile (Table 2.12) and injection speed was not applicable to PET, it was experimentally observed that, at high temperatures above 260°C, PET behaved unpredictable and uncontrollable. Which might be explained by Sudden PET solidification either in the injection molding machine nozzle or in the mold runner caused short shots and occasionally complete failures to inject the PET melt into the mold. So, for PET experiments, the temperature profile of injection molding machine was modified[27] as given in the Table 2.13.

Table 2.13 : Injection molding temperatures of ABS/PET blends and neat polymers (°C).

Sample code	Barrel 1	Barrel 2	Barrel 3	Barrel 4	Nozzle
ABS-PET Blends	240	250	260	280	260
A100-P000	240	250	260	280	260
A000-P100	250	240	240	260	250

In order to investigate effect of injection molding parameters on blend properties, two different processing conditions were used as given in Table 2.14. This different temperature profile were used for the blends containing 70% ABS, 30% PET and with/without several compatibilizers.

Table 2.14 : Injection molding temperatures of selected blends to investigate effect of processing conditions (°C) on compatibilized blends.

Profile code	Barrel 1	Barrel 2	Barrel 3	Barrel 4	Nozzle
Profile A	230	235	245	250	245
Profile B	240	260	270	280	265

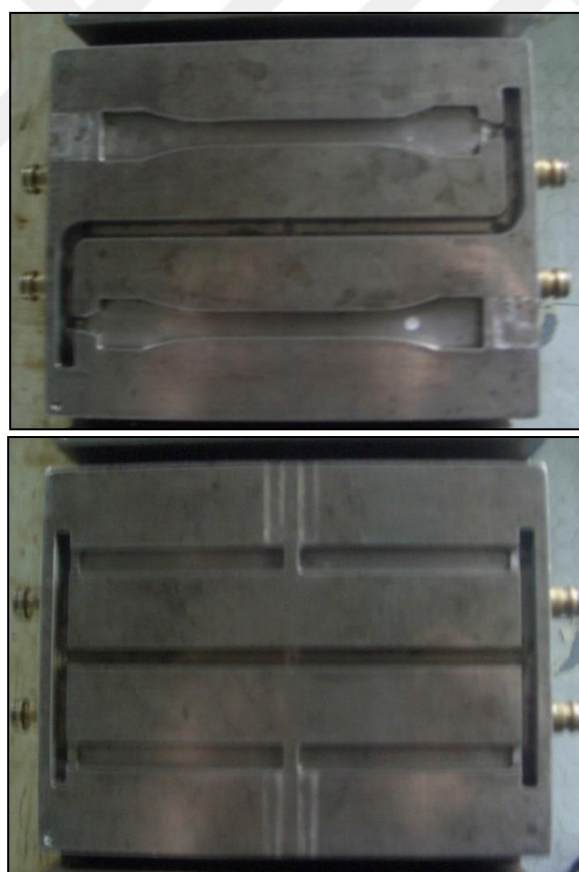


Figure 2.3 : Selected injection molding molds.

2.3 Characterization Methods

In the experimental part of thesis, different type of characterization methods were used concerning measurement system and type of the materials to be measured. Prepared granulates were predried in oven for 3 hour at 80 °C prior to any measurements. Injected test specimens were conditioned in a temperature-controlled air circulation cabinet for at least 48 hours at 23±2 °C to eliminate the post crystallization affects or physical aging.

2.3.1 Rheology measurements

Rheological properties of all blends and neat polymers were measured by using the Dynisco LCR 7000/7001 capillary rheometer using CZ394-20 die (Capillary diameter 1.0 mm, capillary cone 180°, capillary length 20.0 mm). The samples were dried for 2 hours at 80 °C before loading into the piston chamber and heated to the measurement temperature in 360 seconds. Polymer melt viscosity vs. shear rate was then determined for several temperatures to characterize flow characteristics.

2.3.2 Melt flow index measurements

To define flow properties of melt polymers Melt flow index (MFI) or melt flow rate (MFR) is applied according to ISO 1133 test standard[4]. The test is very similar to an extrusion plastometer operating at a fixed temperature and under load. According to the polymer, load and temperature is predefined. The testing device consists of heating cylinder, temperature control equipment, piston, die and the loading unit.

At least six gr test samples in pellet form were fed into the preheated cylinder, after cleaning of the cylinder and piston. While the charging, the material was compressed by hand pressure to ensure the charge is free from air. After charging, 1 kg preload was applied via the piston for 4 minutes and then 2.16 kg test weight was applied. The molten polymeric material was forced out of the die. The rate of extruded material was measured by cutting off the extrudate at suitable time interval; i.e., 30 second. At least three cut-off were weighed with balance having 0.001 grams accuracy. The melt flow rate expressed in grams per the reference time (10 minute) is given by the equation (2.1):

$$\text{MFI (220}^{\circ}\text{C, 10 kg)} = (S \times M) / t \quad (2.1)$$

Where S is the reference time in second, i.e., 600 second; M is the average mass of the cut-offs, in grams; and t is the cut-off time interval, i.e., 30 seconds.

2.3.3 Morphology

The morphology observations were performed with JEOL JSM-7100F scanning electron microscope (SEM). A 20kV accelerating voltage was used after the notched samples were submerged within liquid nitrogen for 2 hours and fractured. Fractured surfaces were coated with thin gold film to avoid charge built up due to their low conductivity. Images were taken from the center of fractured surfaces and for the surface investigation, mold surface of injection-molded bars were analysed as given in Figure 2.4.

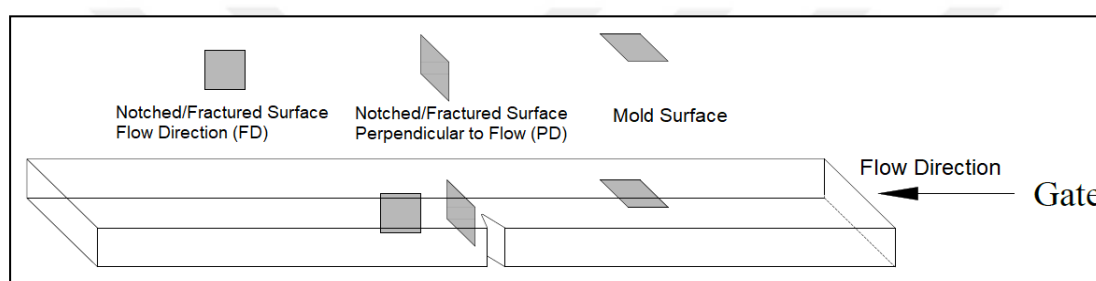


Figure 2.4 : Schematics of the SEM investigation areas on injection molded samples.

To etch the PET phase from the blends; 10 wt.% potassium hydroxide (KOH) in ethanol was used. To etch ABS phase, acetone was used. Freeze fractured surfaces were placed in the solvent for selective etching for 12 hours and an ultrasonic bath was used to assist etching. Then samples were washed carefully with deionized water and dried for 12 hours.

In ABS/PMMA blends, 5 seconds etching was applied with acetone and after that etched samples were washed carefully with deionized water and dried for 12 hours.

2.3.4 Thermal measurements

Glass transition temperature (T_g), crystalline melting point (T_m), and heat of fusion of the specimens were determined by TA Instruments Q20 differential scanning calorimeter. The temperature was increased linearly from 0 °C to 300 °C at 10 °C/min and decreased at the same rate from 300 °C to 0 °C after deleting the thermal history. % Crystallinity ratio (χ_c) for the PET phase in blends was calculated from (Equation (2.2)):

$$\chi_c(\text{wt. \%}) = 100 \frac{\Delta H_m - |\Delta H_{cc}|}{\Delta H_m^0 \cdot \omega_{pet}} \quad (2.2)$$

- ΔH_m = heat of fusion during melting
 H_{cc} = heat of fusion during cold crystallization and melting during heating
 ΔH_m^0 = theoretical enthalpy for 100 % crystalline PET taken as 135.8 J/g[109]
 ω_{pet} = PET % weight ratio in the blend composition.

2.3.5 Dimensional stability measurements

To evaluate dimensional stability, an aging test was performed to simulate the paint curing process in an air-circulated oven at 125 °C for 48 hours. Aging temperature was determined as the maximum possible temperature for a shorter curing time. To determine dimensional stability, sample lengthwise dimension was measured by a low force electronic digital caliper before and after the heat aging and the percentage change in the dimensions was calculated as from (Equation (2.3)):

$$\text{Dimensional change \%} = 100 \frac{(L_0 - L_F)}{L_0} \quad (2.3)$$

- L_0 = initial length of the sample
 L_F = final length of the samples after heat aging

2.3.6 Gloss measurements

Gloss; which is the measurement of reflected visible light from a surface in comparison to black glass surface was determined according to ASTM D-523-14[110]. After injection molding, two sets of preconditioned plates were used for this measurement and values were recorded via Konica Minolta Multi Gloss 268 Plus after calibration. Since the gloss values were higher than 70 gloss units (GU), the measurement angles were selected as 20° and 60°.

2.3.7 Color measurements

By the spectral distribution of reflected light from the surface, color measurements can be done with several different methodologies [111]. Color change according to processing parameters were determined from injection molded plates from 5 different points by Minolta CR-300 color measuring device in which the color is calculated as 3 vectoral values; L* defines lightness, a* denotes the red/green value and b* the blue/yellow value according to ASTM D2244[112].

2.3.8 Density measurements

Density measurements were performed according to the procedure described in ISO1183-3[113] as Pyknometer method. In this method, specimen was first weighted in the air with an electronic balance with 0.001 grams sensitivity and then placed in the Accpro 1330 Pyknometer. The machine calculated the volume by first evacuating the air in the measuring vessel and then filling up the vessel with nitrogen. To compare measured values with theoretical values, the equation given below was used to calculate theoretical density based on rule of mixtures (Equation (2.4)):

$$\rho = \Phi_{abs} \rho_{abs} + \Phi_{pet} \rho_{pet} \quad (2.4)$$

Where;

$$\begin{aligned} \rho &= \text{mixture density} \\ \rho_{abs} &= \text{neat ABS density} \\ \rho_{pet} &= \text{neat PET density} \\ \Phi_{abs} &= \text{ABS volumetric ratio} \\ \Phi_{pet} &= \text{PET volumetric ratio} \end{aligned}$$

2.3.9 Mechanical measurements

2.3.9.1 Tensile testing

Instron universal tensile testing machine 3367 equipped with 30 kN load cell and type AutoX 750 mechanical long stroke extensometer was used to measure tensile properties. Testing speed was 5 mm/min at standard condition, i.e., 23 ± 2 °C and 50 % humidity. 5 samples from each group were tested according to ISO 527-2[114].

2.3.9.2 Izod and Charpy impact testing

Notched Izod impact strengths were determined according to ISO 180[115]. Similar to tensile test specimens, injection molded test bars [4 ± 0.2 mm, 10 ± 0.2 mm, 80 ± 0.2 mm] were conditioned at 23 ± 2 °C and 50 % relative humidity for at least 48 hours to standardize post crystallization or physical aging effects. 2 mm notch with notch base radius 0.25 ± 0.05 mm was machined at the specimen mid-span. Unnotched Charpy impact strength was determined without applying any notch to the samples according to ISO 179[116]. The testing machine used was Zwick HIT5.5P Impact

Tester equipped with 5 J impact capacity pendulum, and 10 samples were evaluated from each group.





3. RESULTS AND DISCUSSIONS

3.1 Effects of Twin-Screw Extrusion Processing Conditions on ABS Polymer

In this section of study, it was aimed to observe the effects of processing conditions on ABS in twin-screw extruder. Process temperature windows for ABS can be specified as 180- 200⁰C. On the other hand, process temperature profile of PET is above 260 °C. To prepare an ABS/PET blend, process temperature profile should be higher than the process temperature profile of PET. However, at such elevated temperature, ABS may subject to degradation resulting in color change or loss in mechanical properties. Before the blending process of ABS with PET, different twin-screw extrusion process profile were set as given in Table 2.8.

As mentioned in the Chapter 2.1, industrial grade of ABS (Terluran GP35) were used after drying in the air-circulating oven for 4 hours at 80 °C. ABS was loaded into twin-screw extruder as described in Chapter 2.2.1. In order to just see the effect of twin-screw extrusion process, ABS sample without any extrusion process (ABS_Injection) were also injection molded as given temperature profile in Table 2.12.

After the injection molding process as described in Chapter 2.2.2, produced samples were conditioned at 23 ± 2 °C and 50 % relative humidity for at least 48 hours.

After the process of extrusion, melt flow index measurements were applied as described in Chapter 2.3.2. As seen in Figure 3.1, In contrary of work of Boldizar et al[75], a slight decrease in the melt flow index values are observed even though processing just once in a different temperatures. This decrease might be related with thermo-oxidative behaviour of polybutadiene (PB), is more at higher temperatures leading a crosslinking reaction and so creating bigger molecules obstacle the movement of melted ABS material[79]. On the other hand, all the measurement results are in line with ± 10 % error bands, which means the effect of high processing temperature is not drastically changing the flow behaviour.

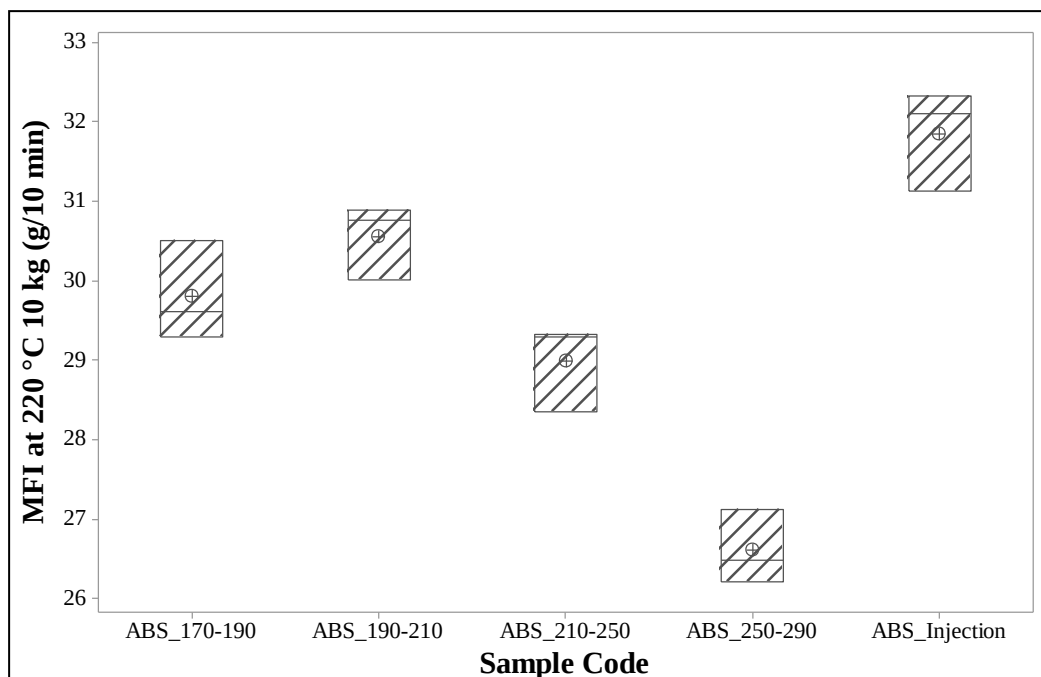


Figure 3.1 : Melt Flow Index (MFI) values of neat ABS after different extrusion processing conditions.

After conditioning the injection molded plates, gloss and color change were measured as described in Chapter 2.3.6 and Chapter 2.3.7 to investigate effect of extrusion process on the visual properties of material. Due to having glossy surface, 85° gloss measurements were neglected as suggested by ASTM D523 standard[110] with regards to not showing any reasonable differences in the measured values. As observed in Figure 3.2, there was no difference in the gloss values of ABS material concerning different processing temperature. As it was pointed out that; gloss of ABS polymer is related with the styrene acrylonitrile (SAN) phases and also domain size of PB[1] and mainly it is the reflective nature of objects surface. It was assumed that; even though twin-screw extruder results in better kneading performance compared to injection molding; samples did not show any reasonable difference in the size of polybutadiene sizes and distributions.

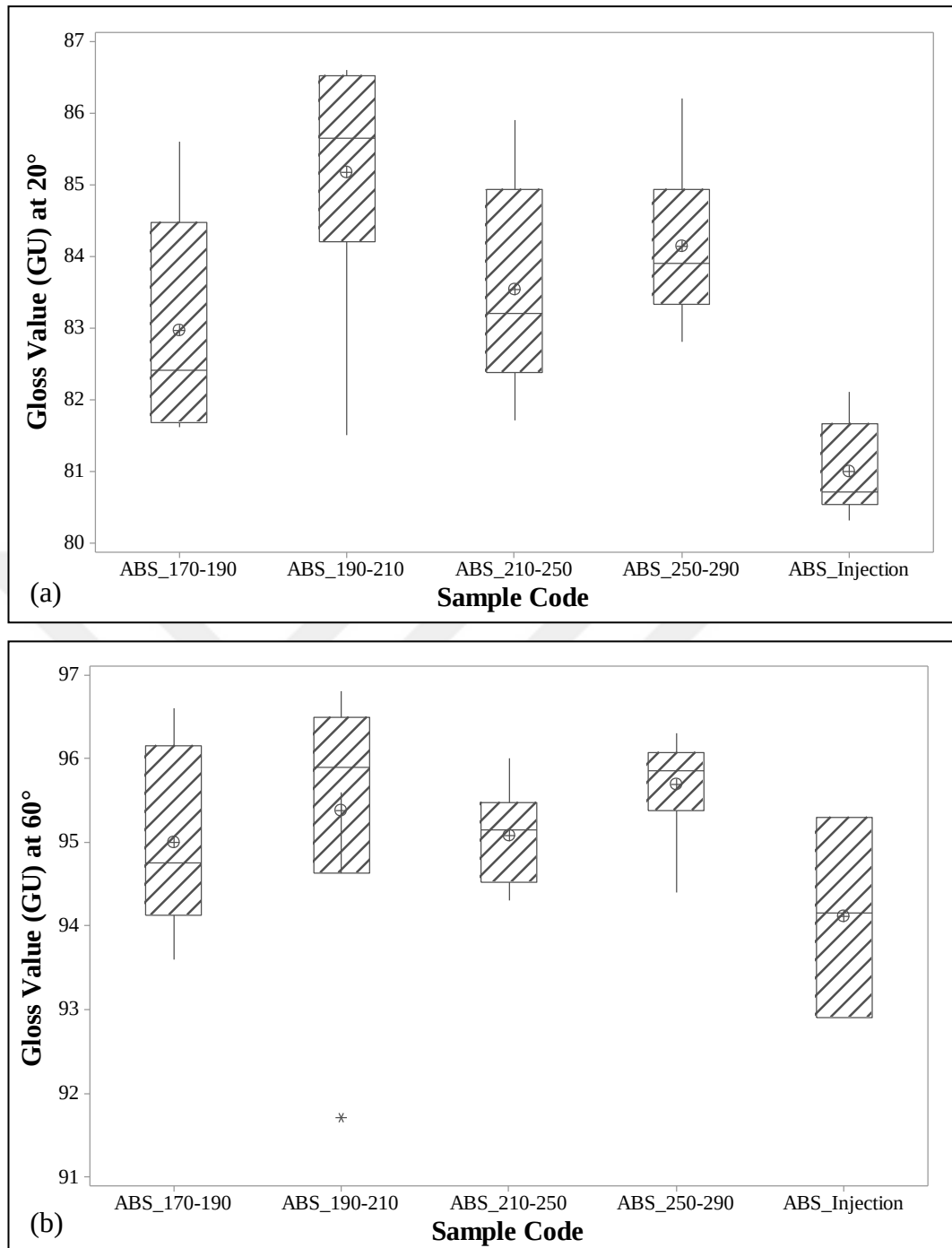


Figure 3.2 : Gloss values of neat ABS after different extrusion processing conditions.

In the color measurements, special attention was paid to change of yellowness (change in “b” value) which is an indication of degradation caused by processing [1,64,117]. Comparison of color measurement of samples from extruded and then injected molded samples with only injected molded samples were done. In Figure 3.3, it was seen that the total color change (ΔE) was coming from the change in b value (yellowness). This

behaviour is an evidence of some degradation related with the processing conditions. At higher processing condition more yellowness were measured as expected.

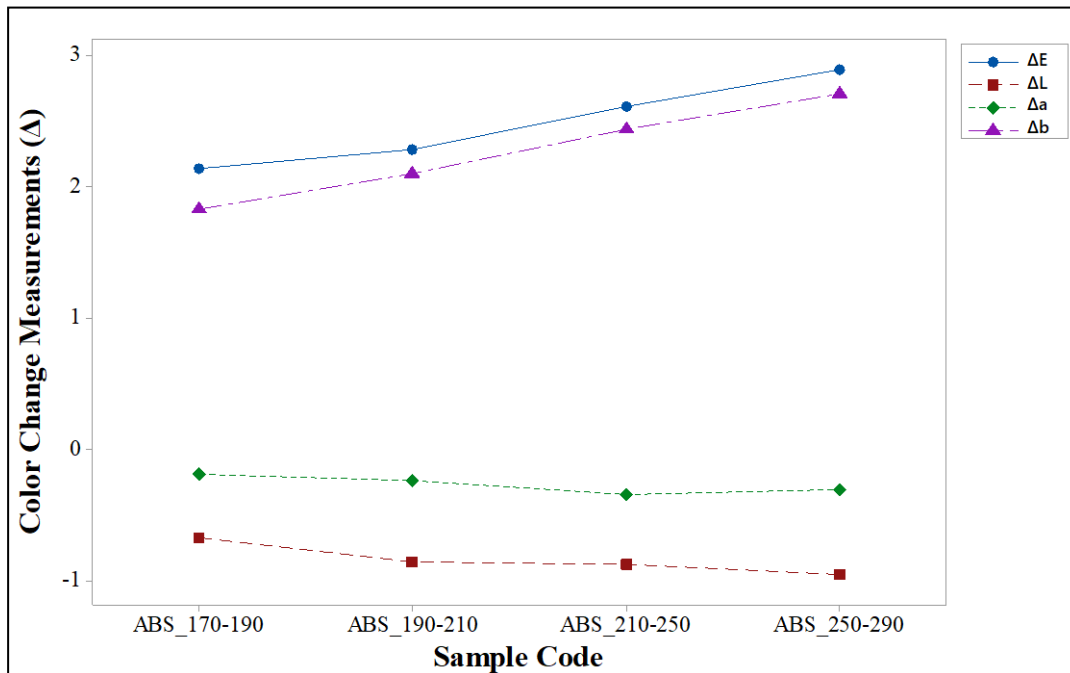


Figure 3.3 : Color change of neat ABS after different extrusion processing conditions.

Figure 3.4 plots the effect of extrusion processing conditions on neat ABS by performing the tensile test as explained in Chapter 2.3.9.1. Tensile modulus, tensile strength and strain at tensile strength values were used for characterization. All the measurement results obtained from 5 samples were shared in box-plot graphs.

Tensile modulus values were detected as not effected by the extrusion process profiles. As it described in ISO 527-2[114], this value is calculated as a slope of stress-strain curve for the strain values as 0,05-0,25% and so it was not expected to be influenced by any kind of degradation. However, strain at tensile strength values were directly affected by extrusion processing conditions with the increased temperature caused a decrease from 2,59 % to 2,24 % that might be related with the degradation of polybutadiene phases, which gives the flexibility to the main matrix. This value with combination of modulus is important factor for the plastic part designer especially for the snap fit applications.

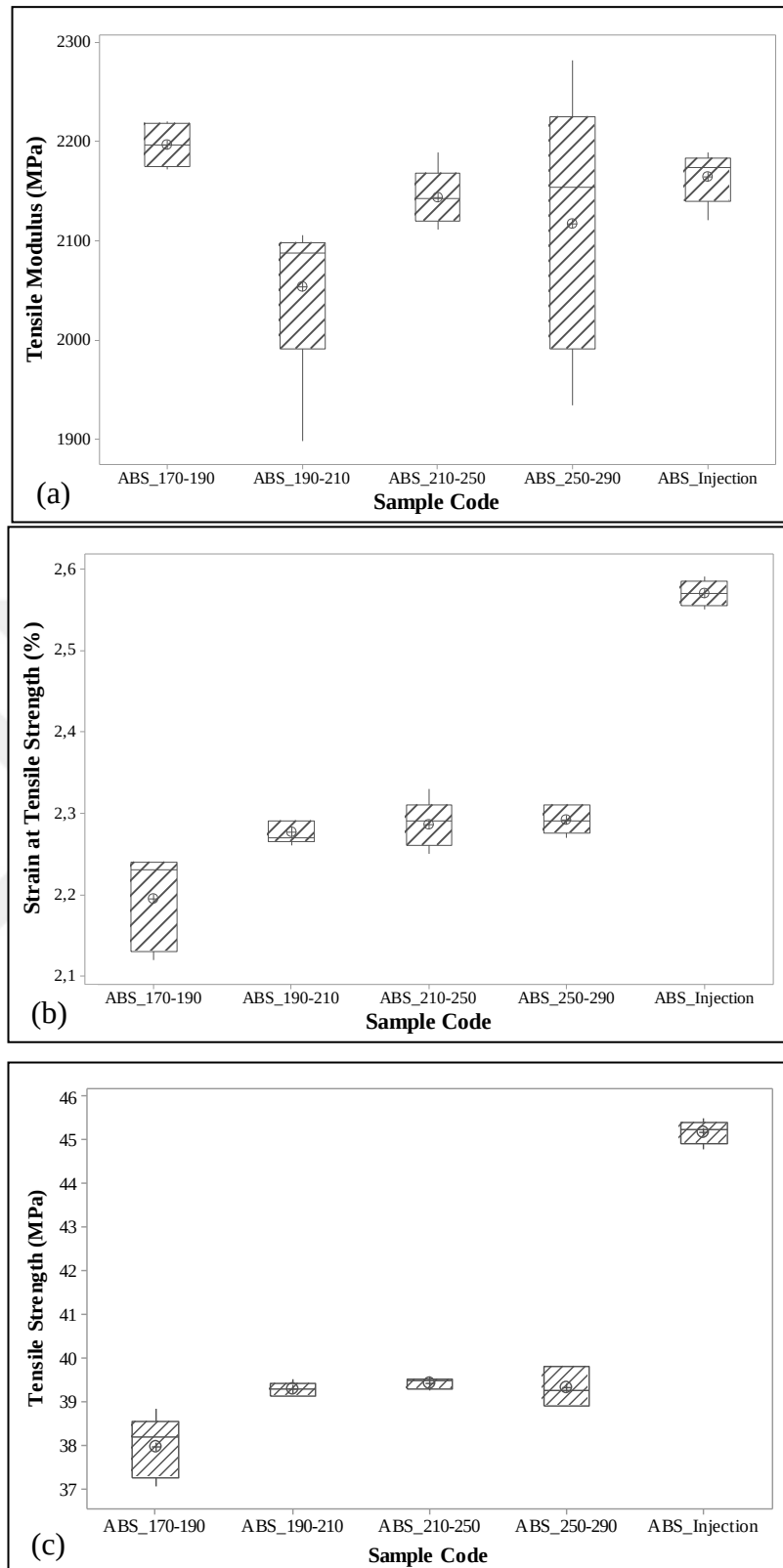


Figure 3.4 : The effect of extrusion processing conditions on the tensile properties of neat ABS.

On contrary, tensile strength values were decreased with the extrusion process up to 16%. One possible explanation to this decrease might be the degradation of acrylonitrile phases [5,75].

Notched impact strength measurements were performed as described in Chapter 2.3.9.2 to investigate the energy absorption at high-speed deformations. Plotted graph given in Figure 3.5 was indicated that, twin-screw extrusion process was improving the rubbery phase distribution more homogenously as explained by Boldizar et al[75]. Due to that, variance of the notched Izod impact values were decreasing. ABS which was not processed in the twin-screw extruder (ABS_Injection) had a mean value as 14,89 kJ/m^2 with a standard deviation (SD) of 1,67. The notched impact strength of ABS material processed at extrusion process profile (ABS_190-210) was 14,35 kJ/m^2 with standard deviation of 0,32.

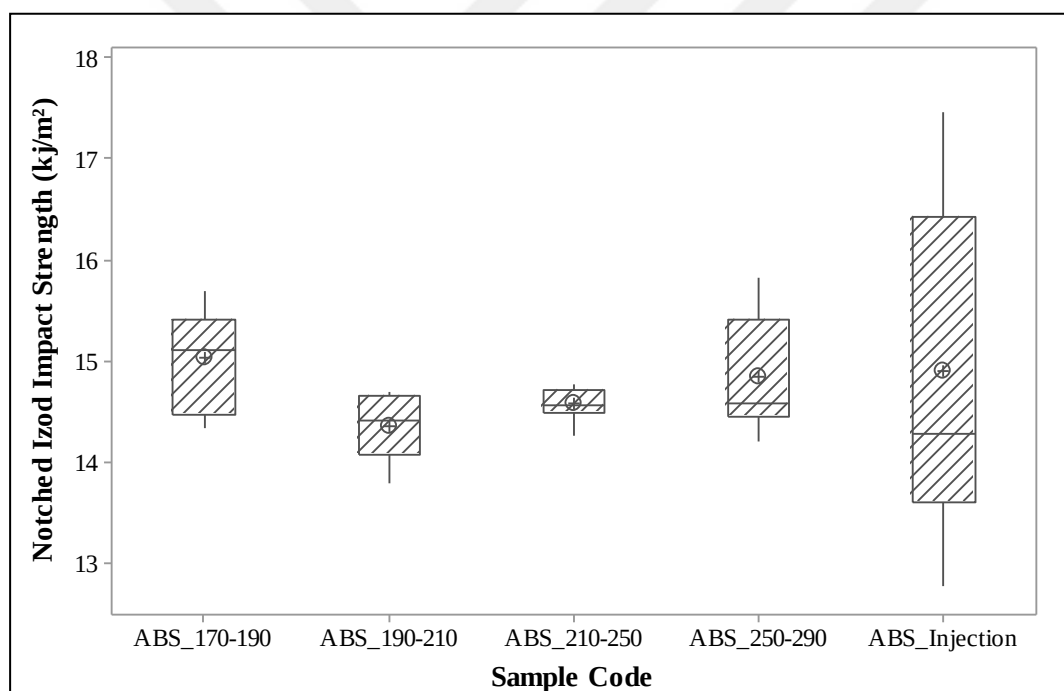


Figure 3.5 : The effect of extrusion processing conditions on the impact properties of neat ABS.

One of the first conclusion can be drawn from this section is that; the twin-screw extrusion temperature process profile is not drastically effecting the final properties of ABS material. Observed slight decrease in the melt flow index values is in line with $\pm 10\%$ error bands. This was one of the evidence of no net effect of extrusion process to properties of ABS. Similarly, gloss values, tensile modulus and strain values was not affected, seriously. On the other hand, twin-screw extrusion process helped to

improve the rubbery phase distribution more homogenously resulting in decrease the variance of impact values. Evidence of slight degradation as thermo-oxidative behaviour of polybutadiene was measured in color changes. Possible degradation behaviour of AN resulted in decrease in tensile strength by 16% for extrusion temperature profile of 170-190⁰C compare to only injection molded sample. However, the difference in tensile strength of extruded samples were not significant. Due to this fact, it is concluded that the effect of twin-screw extrusion process profile can be neglected for the next step of this study. The extrusion temperature profile was selected as 250-290⁰C and was kept constant for the rest of the study.

3.2 Effect of Acrylonitrile-Butadiene-Styrene (ABS)/ Poly (ethylene terephthalate) (PET) Blends on, Morphological, Physical and Mechanical Properties and Dimensional Stability After Aging at Elevated Temperature

This section of thesis, it is aimed to develop an ABS/PET blend; which might be an ideal material where high surface quality, colorfastness, easier injection molding process, and higher dimensional stability at elevated service or process temperature were required.

In the trials, ABS (Terluran GP35) and PET (Sasa Advanite 14006) were used as explained in Chapter 2.1. Table 2.3 shows the sample codes and ABS, PET concentration used in this section.

All the blends were prepared via twin-screw extruder as explained in Chapter 2.2.1 and 3.1 with fixed processing conditions. Hence, twin-screw extrusion temperature profiles and screw design were kept constant to eliminate processing condition affects. Temperature profile for twin-screw extrusion was given in Table 2.9.

Neat ABS (A100-P000) and neat PET (A000-P100) were not extruded, just used in injection molding process to get samples. Injection processing temperatures were given in Table 2.12 to inject all compounds and the neat ABS, except the neat PET, which used a different profile. It was experimentally observed that, at high temperatures above 260⁰C, PET behaved unpredictable and uncontrollable. Which might be explained by sudden PET solidification either in the injection molding machine nozzle or in the mold runner caused short shots and occasionally complete failures to inject the PET melt into the mold. So, for PET experiments, the temperature

profile of injection molding machine was modified as given in Table 2.13. Process parameters like injection speed, time and pressure for all specimens were kept constant to eliminate process parameter affects.

Rheological properties of all blends and neat polymers were measured by using capillary rheometer as explained in Chapter 2.3.1. Figure 3.6 shows the apparent shear viscosity versus shear rate for selected specimens at 260, 270, 280, and 290 °C.

The viscosity of ABS decreased slightly with increased temperature as expected for non-Newtonian blends [95,118]. It is noteworthy that, PET showed an unstable behaviour by not varying the viscosity with increased shear rate as near Newtonian behaviour similar to poly(trimethylene terephthalate) (PTT)[39,41] with regard to increased temperature and shear rate as given in Figure 3.7. In addition, the difference in viscosities of neat ABS and PET was quite large for all the temperatures and shear rates.

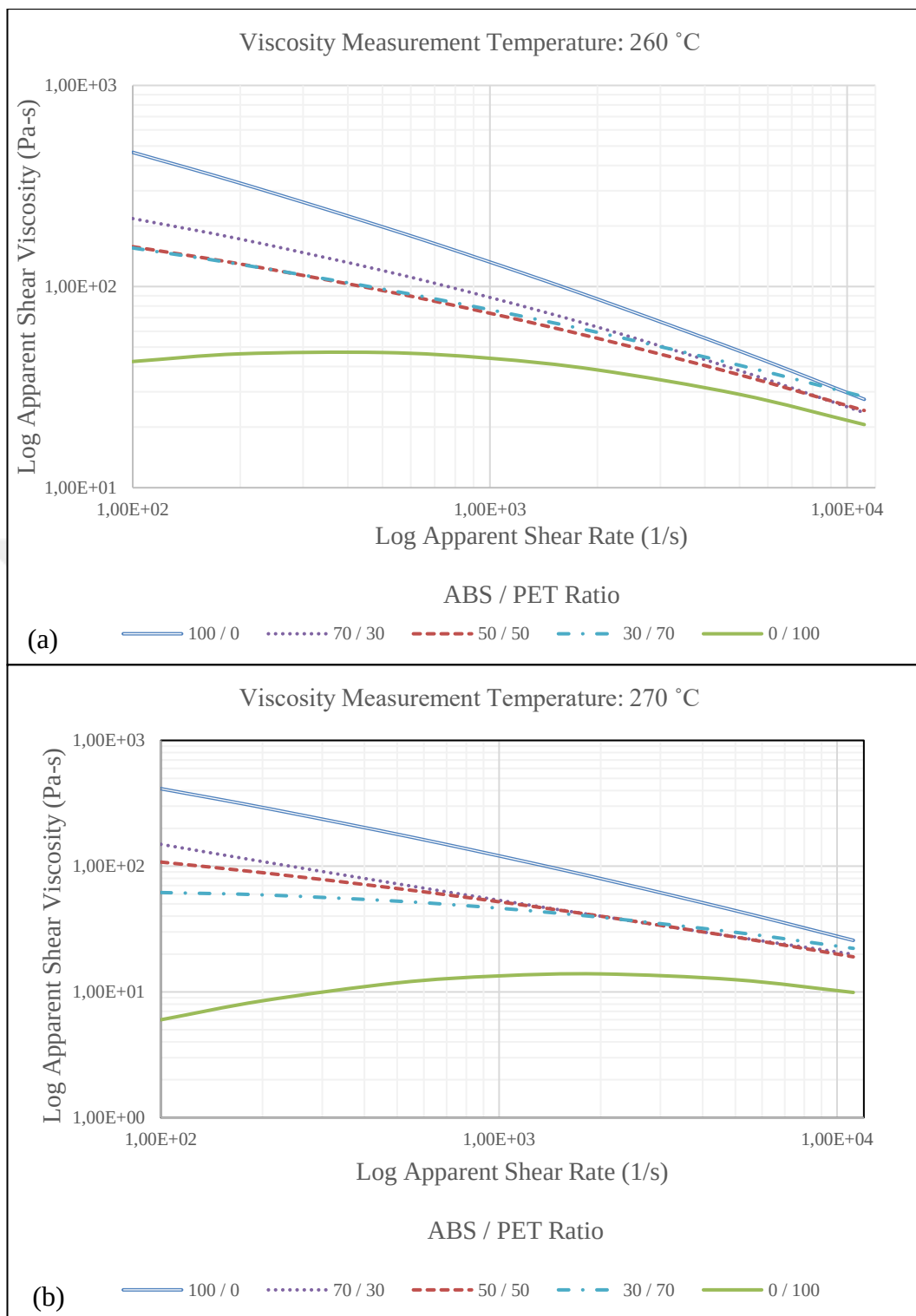


Figure 3.6 : Viscosity versus Shear Rate for ABS, PET and 3 intermediate blends at a) 260, b) 270, c) 280 and d) 290 °C.

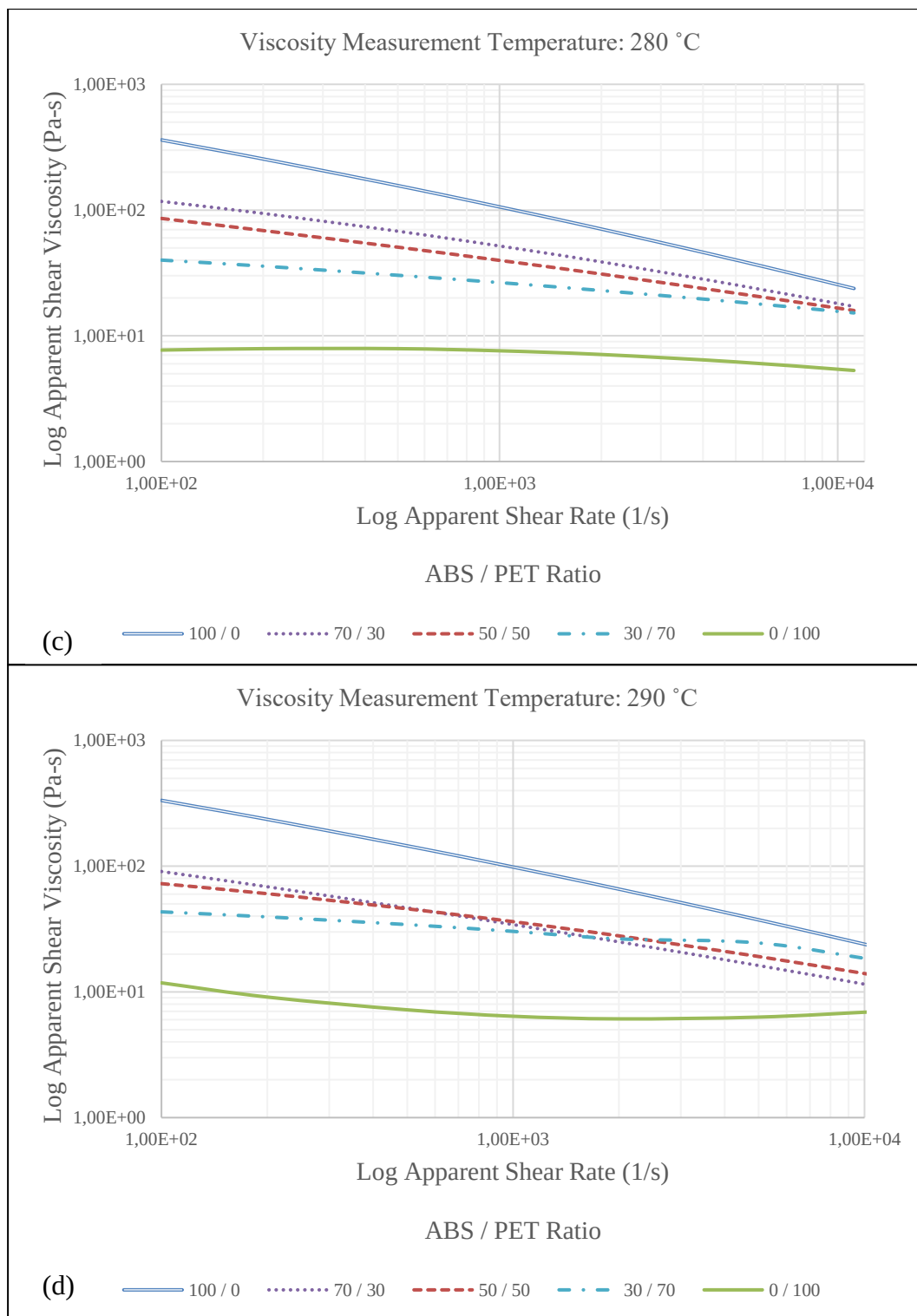


Figure 3.6 (continued): Viscosity versus Shear Rate for ABS, PET and 3 intermediate blends at a) 260, b) 270, c) 280 and d) 290 °C.

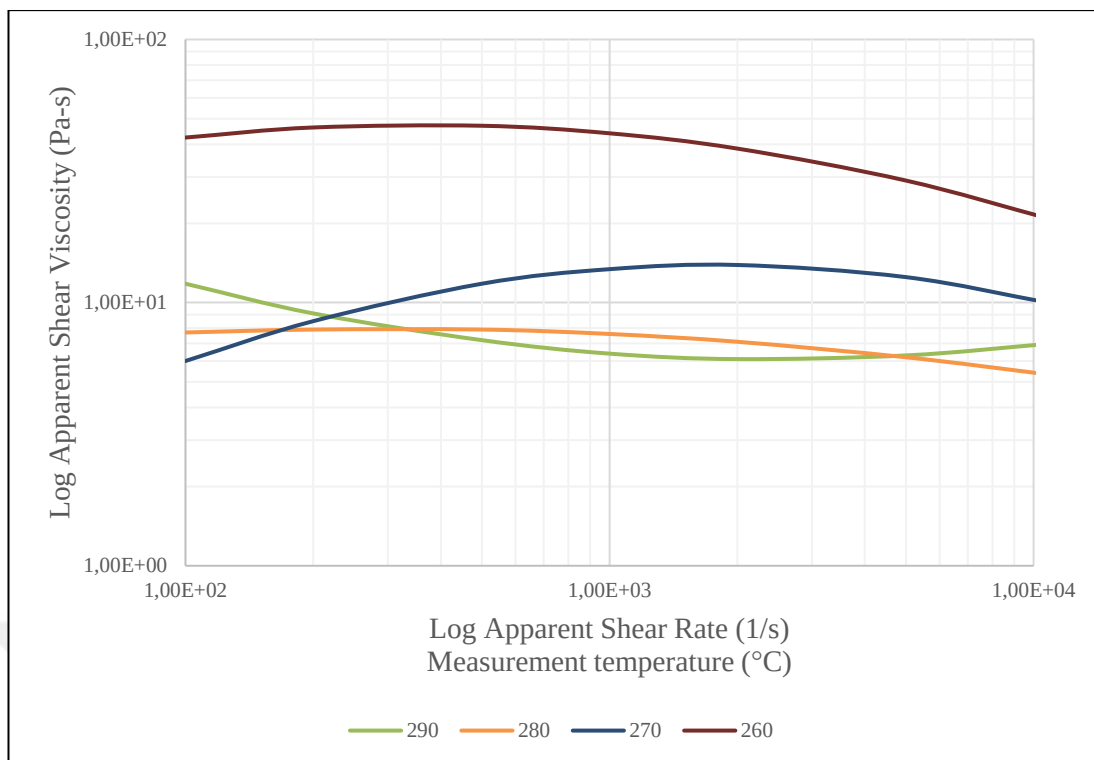


Figure 3.7 : Viscosity versus Shear Rate for neat PET (A000-P100) at 260, 270, 280 and 290 °C.

Likewise, for all ABS/PET blends, the shear viscosity decreased with increasing shear rate. This is typical shear-thinning behaviour improved processability by increasing the blend viscosity and rendering it non-Newtonian viscosity behaviour, which resulted in more stable processing conditions. Addition of ABS improves PET processability. These blends presented viscosities between those of neat ABS and PET components, which might also suggest that there was no chemical interaction between them as reported by several researchers previously for incompatible blends [19, 38, and 94].

Morphology investigation of the fracture surfaces were characterized as described in chapter 2.3.3. In Figure 3.8 show a weak phase contrast and no clear morphology due to the biphasic morphology of ABS. Figure 3.9 shows SEM images of blends with selectively etched surfaces.

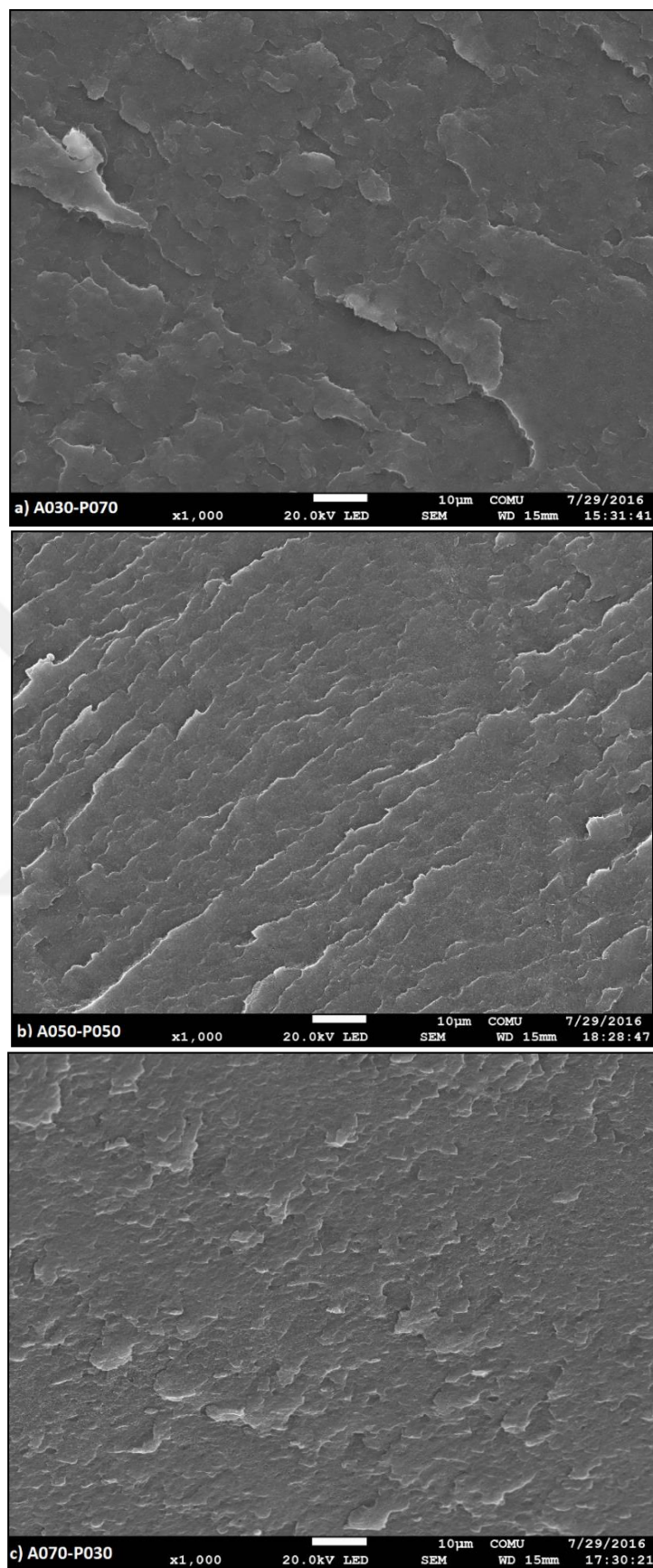


Figure 3.8 : SEM images, notched surfaces without etching: a) ABS/PET 30/70, b) ABS/PET 50/50, c) ABS/PET 70/30.

These SEM images given in Figure 3.9 showed that acetone dissolved the ABS phase from the mold surfaces selectively. Although 10 wt. % potassium hydroxide (KOH) in ethanol solution was used for A050-P050 and A070-P030 blends, almost no PET phase was dissolved from the mold surface of blends. For ABS loadings greater than 30%, mold surface was mostly occupied by ABS even though the main phase was PET. Because of this, PET phase could not be dissolved by 10 wt. % KOH in ethanol at the surface. This case might be explained as follows; during cooling in the mold cavity, PET was expected to solidify much earlier than the ABS phase due to the sudden crystallization while ABS was still in molten state. This crystallization behaviour combined with potential shear induced migration of components in immiscible polymer blends under high shear processing such as injection molding resulted in the similar morphologies observed by Kato et al[119].

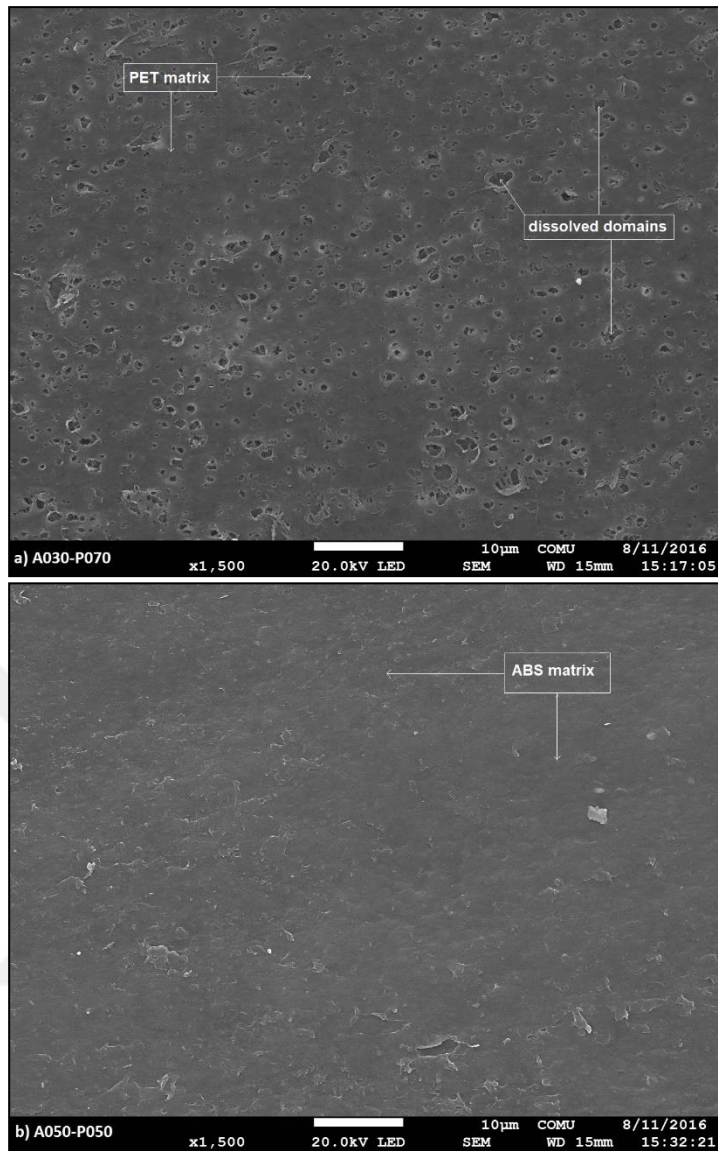


Figure 3.9 : SEM images of selected blends at mold surfaces after etching process: a) ABS/PET 30/70 acetone etching of ABS phase, b) ABS/PET 50/50 10 wt. % KOH in ethanol etching of PET phase, c) ABS/PET 50/50 acetone etching of ABS phase, d) ABS/PET 70/30 10 wt. % KOH in ethanol etching of PET phase.

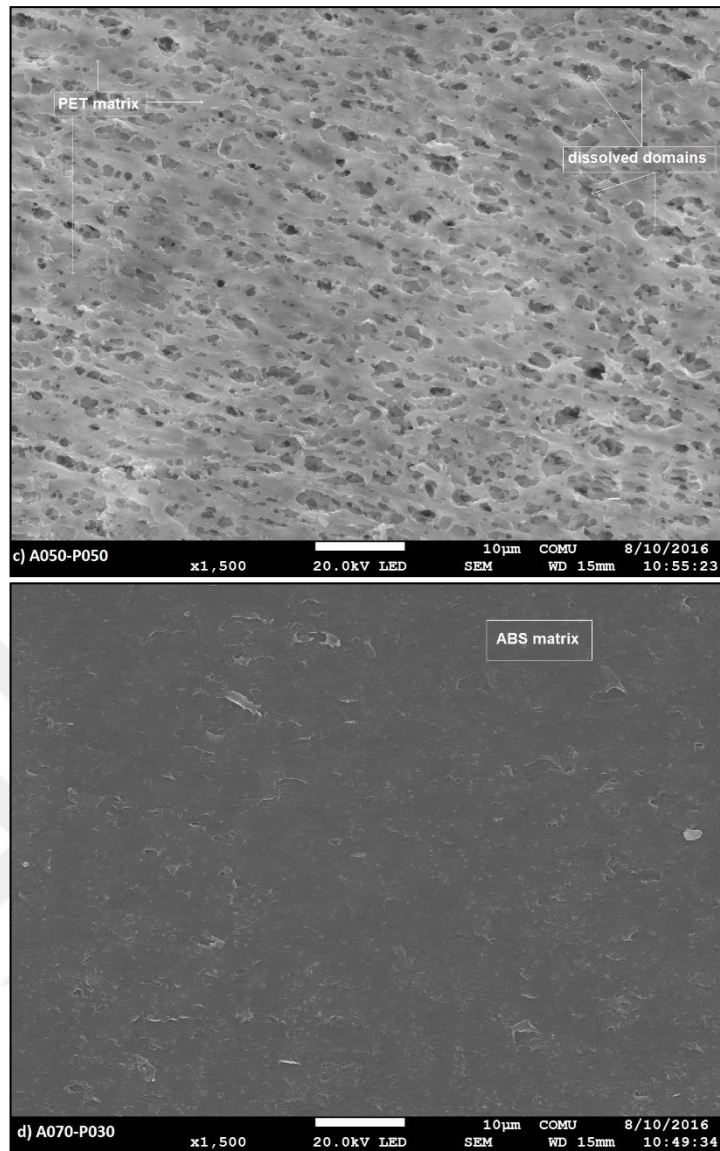


Figure 3.9 (continued): SEM images of selected blends at mold surfaces after etching process: a) ABS/PET 30/70 acetone etching of ABS phase, b) ABS/PET 50/50 10 wt. % KOH in ethanol etching of PET phase, c) ABS/PET 50/50 acetone etching of ABS phase, d) ABS/PET 70/30 10 wt. % KOH in ethanol etching of PET phase.

Figure 3.10 shows that for 20 wt. % ABS in the PET matrix there was a typical island/sea structure due to incompatibility. 20 wt. % PET in the ABS matrix showed island/sea structure as fibrils due to large viscosity difference the PET phase experienced some unstable elongation along the flow direction (FD). W. Hale et-al. [70] reported similar observations for the PBT/SAN blend and Liu et al.[49] for ABS/PBT blends. This observation might be related to the fact that large droplets of one of the ingredients can deform and elongate in parallel to the flow direction resulting in fibrils forming throughout the compounding process. Accordingly, the

elongated component may break down into small droplets (the Raleigh disturbance) [49].

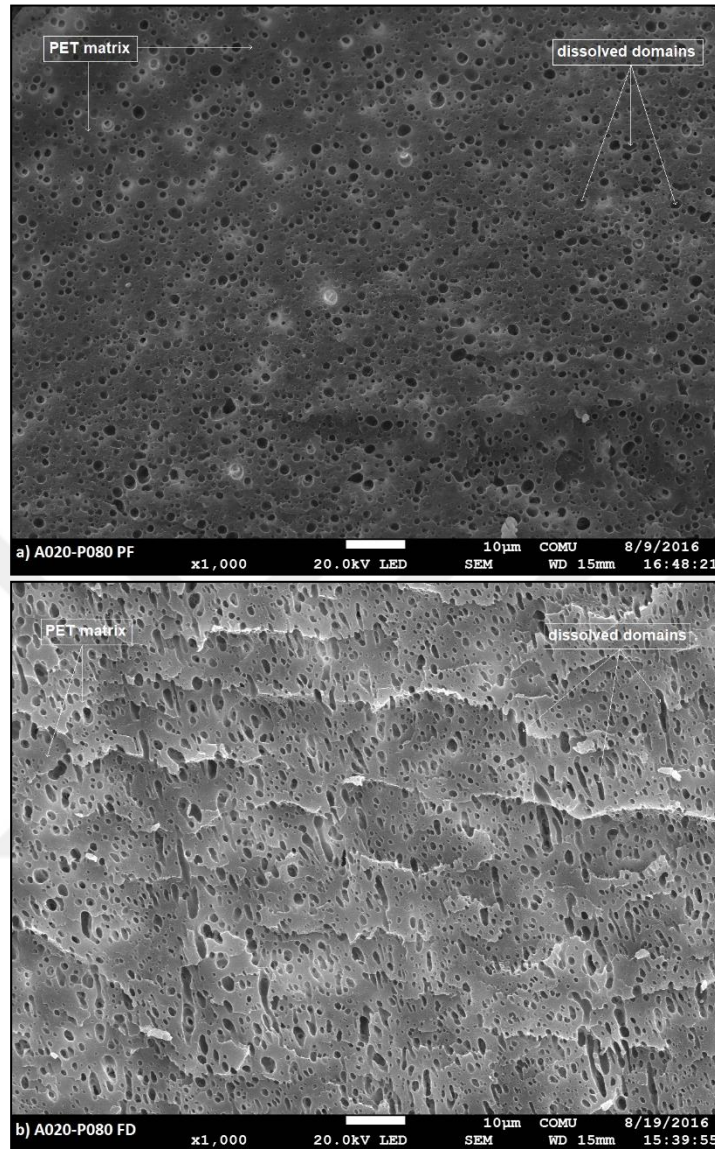


Figure 3.10 : Selected SEM images in the perpendicular to flow (PF) direction and in the flow direction (FD) of samples after selective etching of ABS phase via acetone or PET phase via 10 wt. % KOH in ethanol from fractured surfaces: a) ABS/PET 20/80 perpendicular to flow direction (PF), b) ABS/PET 20/80 flow direction (FD), c) ABS/PET 80/20 perpendicular to flow direction (PF), d) ABS/PET 80/20 flow direction (FD)

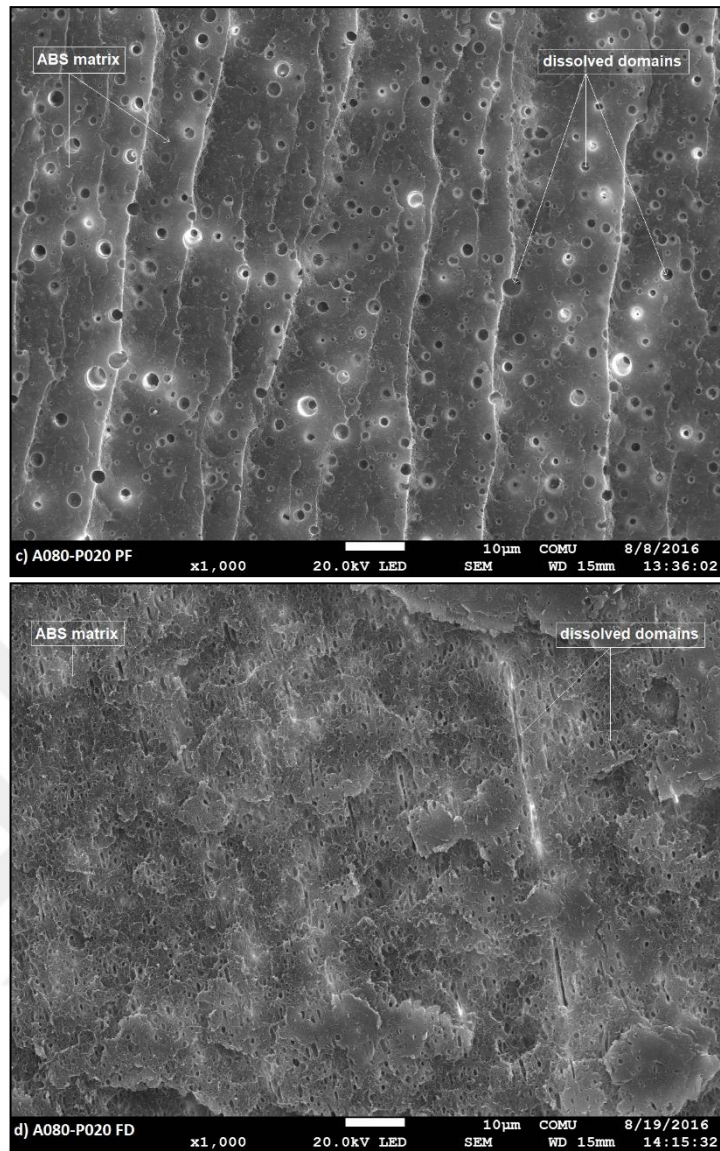


Figure 3.10 (continued): Selected SEM images in the perpendicular to flow (PF) direction and in the flow direction (FD) of samples after selective etching of ABS phase via acetone or PET phase via 10 wt. % KOH in ethanol from fractured surfaces: a) ABS/PET 20/80 perpendicular to flow direction (PF), b) ABS/PET 20/80 flow direction (FD), c) ABS/PET 80/20 perpendicular to flow direction (PF), d) ABS/PET 80/20 flow direction (FD)

The ABS/PET 50/50 SEM images (Figure 3.11) show a continuous morphology with finer PET phase dispersion, The ABS/PET 30/70 and ABS/PET 70/30 SEM images (Figure 3.12) show a semi-continuous morphology.

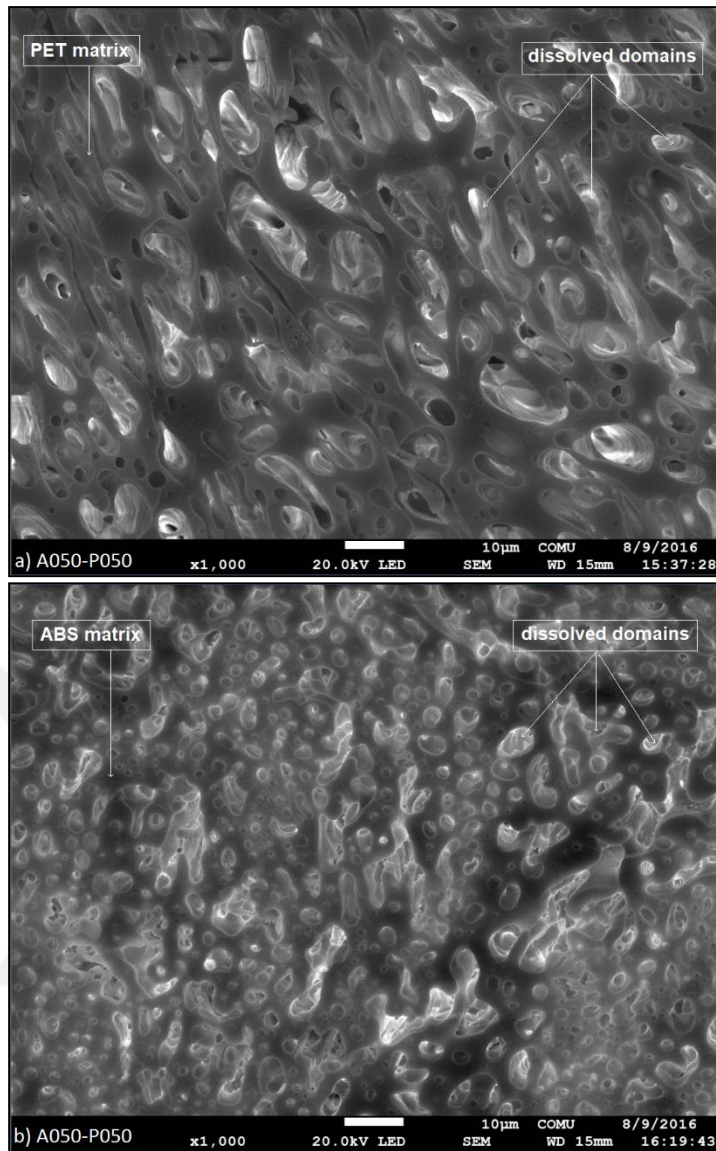


Figure 3.11 : SEM pictures of cyro-fractured A050-P050 blend a) after ABS phase etching with acetone and b) PET phase etching with 10 wt. % KOH in ethanol.

The phase morphology of melt-mixed ABS / PET blends depended on the blend ratio. A sea/island dispersed morphology exists up to 30 wt. % ABS or a PET level beyond which a co-continuous to continuous morphology was observed similar to ABS/PP blend as reported by Hom et al[16].

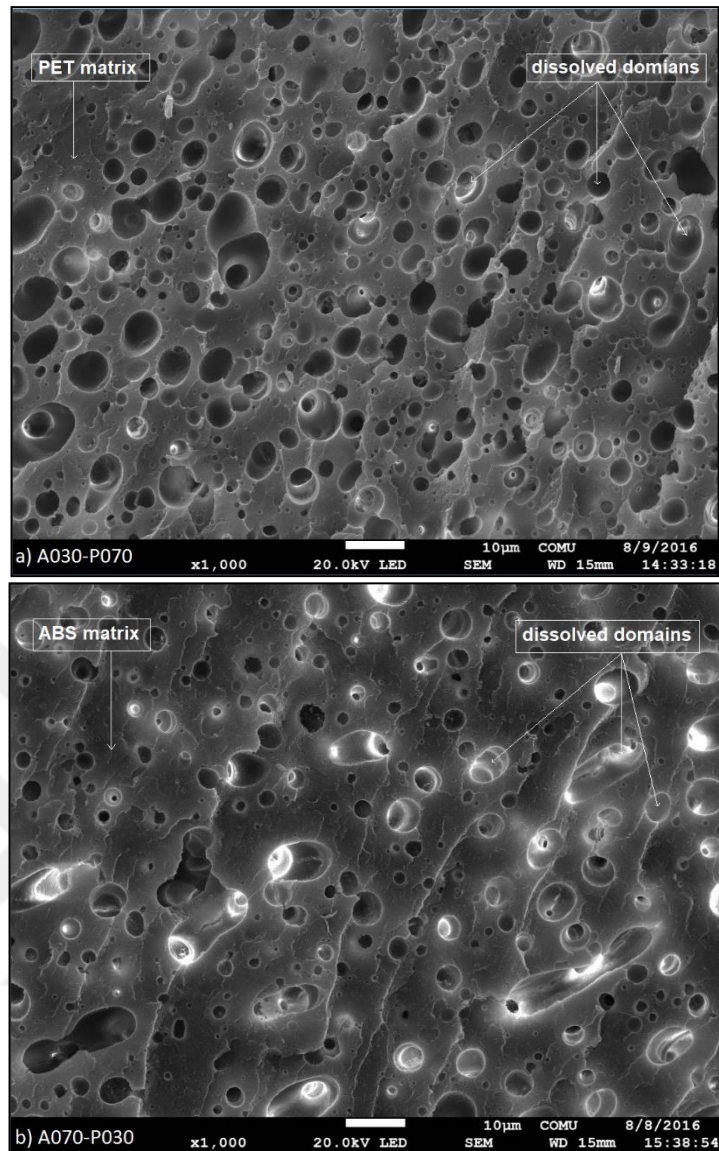


Figure 3.12 : SEM images of ABS/PET 30/70 and 70/30 blends after selective etching of ABS phase (a) and PET phase (b).

Figure 3.13 shows the PET Cold crystallization temperature versus PET concentration and Figure 3.14 shows the Differential Scanning Calorimetry (DSC) graphs for ABS, PET for a 50/50 blend. Table 3.1 summarizes these results. The T_g of SAN phase in the ABS and recrystallization exotherm (known as cold crystallization) of PET during heating were overlapped.

The PET cold crystallization peak temperature decreased as ABS content increased which could be explained due to frozen PET chains in domains. During heating, frozen chains might reach a critical mobility and frozen structures may reorganize as explained by several researchers [19,39,42,95,109,118].

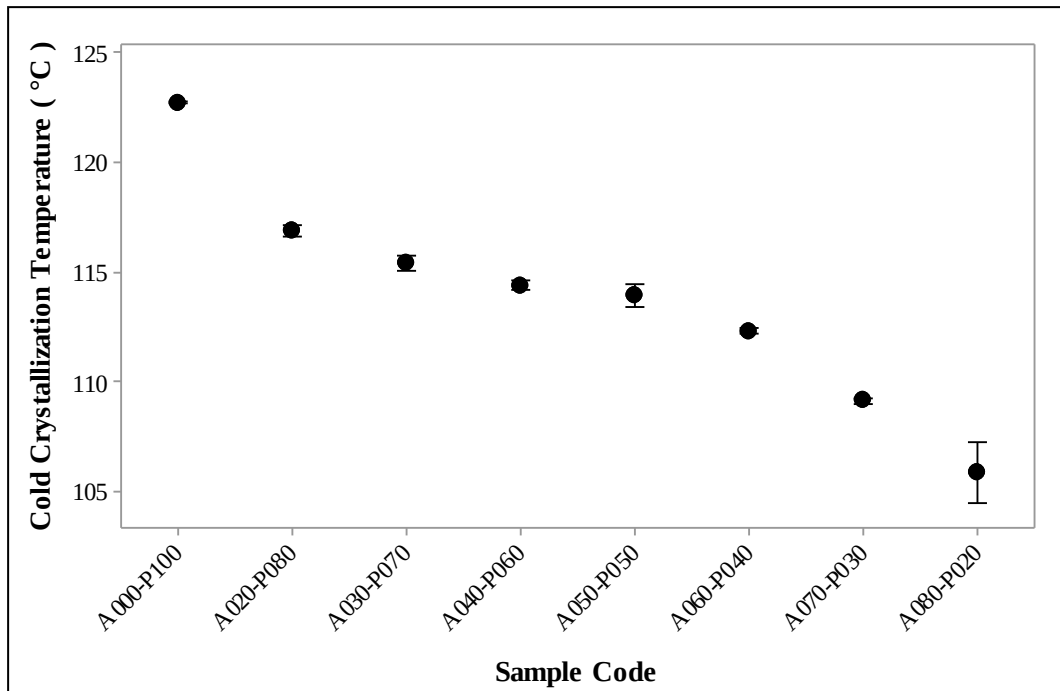


Figure 3.13 : Cold crystallization temperature of PET versus ABS concentration in ABS/PET blends.

No subration of PET melting temperature was observed which was evidence for no compatibilization interaction between ABS and PET. The glass transition temperature of PET in the blends shifted compared to the neat PET. That could be addressed to the slightly degradation of PET due to processing conditions as indicated by Cook et al [33,44].

An increase in crystallization temperature of PET from 181 °C to 198 °C indicated that ABS phases in blends acted as nucleating agents resulting in the increased PET crystallinity and hence facilitated easier injection molding for the blends. During the cooling process, ABS phases in the matrix were expected to delay the PET phase cooling after the crystallization/nucleation. This might result in an annealing effect, enhancing crystallinity and increasing the PET phase density. Such annealing effect could directly influence the crystallization kinetics as explained by Zhao et al[120]. On the other hand; observed ABS nucleation effects during the cooling process influenced the injection molding process positively resulting in reduced cycle time and facilitated easier injection molding[87,121].

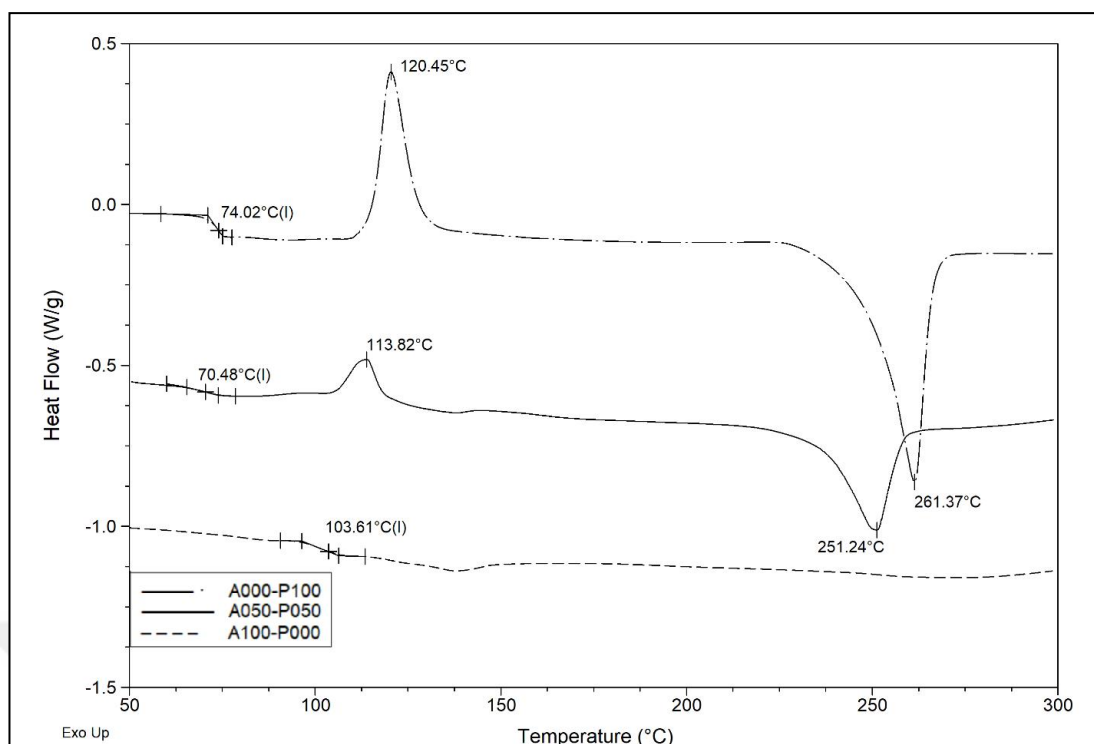


Figure 3.14 : DSC graphs of neat ABS (A100/P000), neat PET (A000/P100) and A050-P050 blend.

Table 3.1 : DSC measurement results of selected samples.

ABS/PET	T _g PET (°C)	T _{cc} (°C)	ΔH _{cc} (J/g)	T _m (°C)	ΔH _m (J/g)	T _c (°C)	ΔH _c (J/g)	χ _c %
0/100	74	120	21.39	261	43.82	181	42.08	16.5
20/80	70	117	14.91	252	42.16	198	37.85	25.1
30/70	70	115	13.24	251	38.45	200	33.87	26.5
40/60	70	114	11.49	252	33.43	201	30.72	26.9
50/50	70	114	6.40	251	27.91	194	21.65	31.7
60/40	69	112	4.04	251	20.34	195	14.17	30.0
70/30	68	109	3.93	252	15.63	194	4.70	28.7
80/20	65	106	2.36	251	10.41	110	2.07	29.6
100/0	104	-	-	-	-	-	-	-

The dimensional stability of prepared blends were measured as described in Chapter 2.3.5 and measurement results were given in Figure 3.15. Dimensional change of ABS aged at 125°C for 48 h was -9,50 % and that of PET was -0,49 %. Boldizar et al[75] reported dimensional change of ABS as 6 % for the aging conditions of 90 °C for 96 hours which is lower due to the lower aging temperature. At addition of 20 wt.% PET, the dimensional change was measured as -2,10 %. Dimensional change caused by temperature induced stress relaxation decreased to – 1,0 % for the 50 wt.% PET blend.

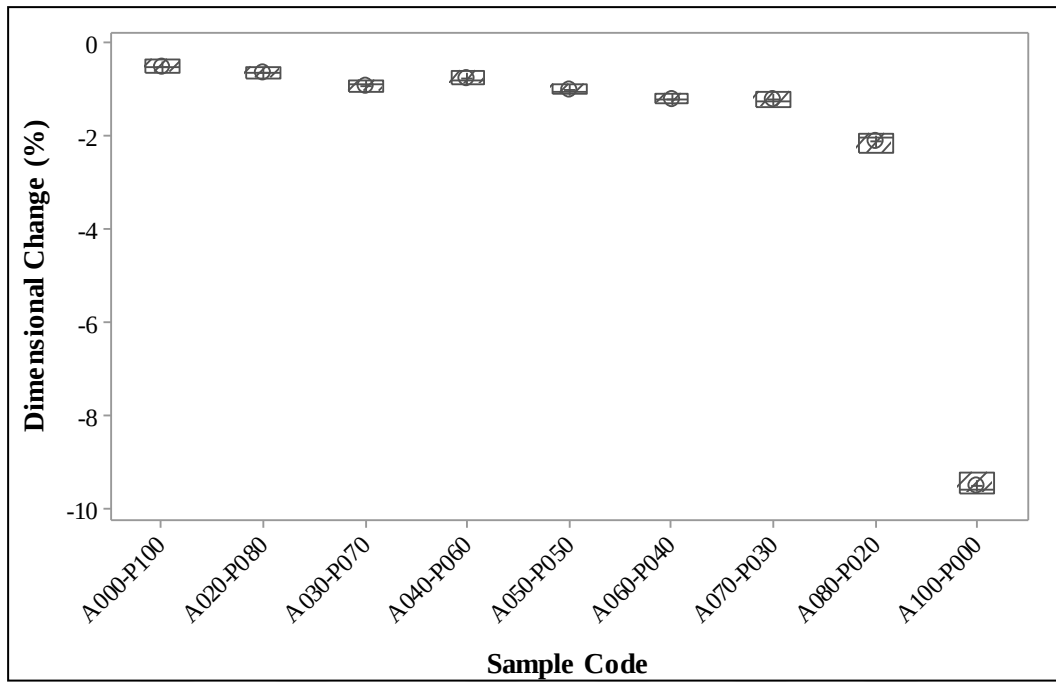


Figure 3.15 : Dimensional change versus blends after conditioning at 125 °C for 48 hours.

Increased dimensional stability under aging conditions could help to improve the paint curing process, especially for the production of visual parts that require higher process temperatures or shorter paint curing times to lower the process cost. ABS was not suitable material due to inadequate dimensional stability at elevated temperature. Weakly-Bollin et al[65] reported that stress relaxation induced by temperature rise, especially above 75-80 °C, caused dimensional instability for parts produced from ABS. This was especially crucial, when a thermal curing process was applied after a painting or coating process. The low thermal stability of ABS required a process condition of lower temperature and longer thermal curing period. That resulted in decreased productivity rate or increased investment costs [63,106,107]. Adding PET into the ABS phase with its elongated PET fibrils parallel to the flow direction might act as reinforcing agents and so compensate the ABS phase stress relaxation resulting in better dimensional stability.

Table 3.2 indicated the results of gloss measurement applied according to Chapter 2.3.6. These results revealed that blending ABS with PET did not alter the gloss. Indeed, Kale et al[42] noted that the PET could be used to improve the gloss value of ABS. As discussed in the morphology investigation section, ABS rich phase was selectively migrating towards the part surface in the solidification phase of the injection molding process, while the PET rich phase was detected below the ABS rich

skin. In addition, as indicated in the rheology investigation section, PET had much lower viscosity. When the temperature decreased below the crystallization temperature, PET suddenly solidified and behaved as a solid filler or reinforcing agent in the blend system surrounded by ABS in the molten state. Due to this fact, there was no obvious gloss difference measured for the ABS/PET blends containing 30 wt. % or more ABS, since the ABS phase was located on the surface.

Table 3.2 : Gloss measurement results of prepared samples.

	ABS	80/20	70/30	50/50	30/70	20/80	PET
Gloss (GU) 20°	78 ± 2	79 ± 2	86 ± 2	85 ± 3	84 ± 2	75 ± 2	75 ± 2
Gloss (GU) 60°	90 ± 2	85 ± 3	88 ± 3	89 ± 2	90 ± 3	85 ± 2	85 ± 3

In Figure 3.16, calculated and measured density of blends versus blend ratio was plotted. PET with its 1.33 g/cm³ amorphous phase density and its 1.39 g/cm³ crystalline phase density strongly influenced the density of blends[121,122]. Figure 3.16 showed, except for the neat polymers, all blends differed from the theoretical density calculated by equation 4 described in Chapter 2.3.8. This difference was evidence that the density of PET phase increased with increase in the crystallinity of the PET that was also revealed by DSC analysis.

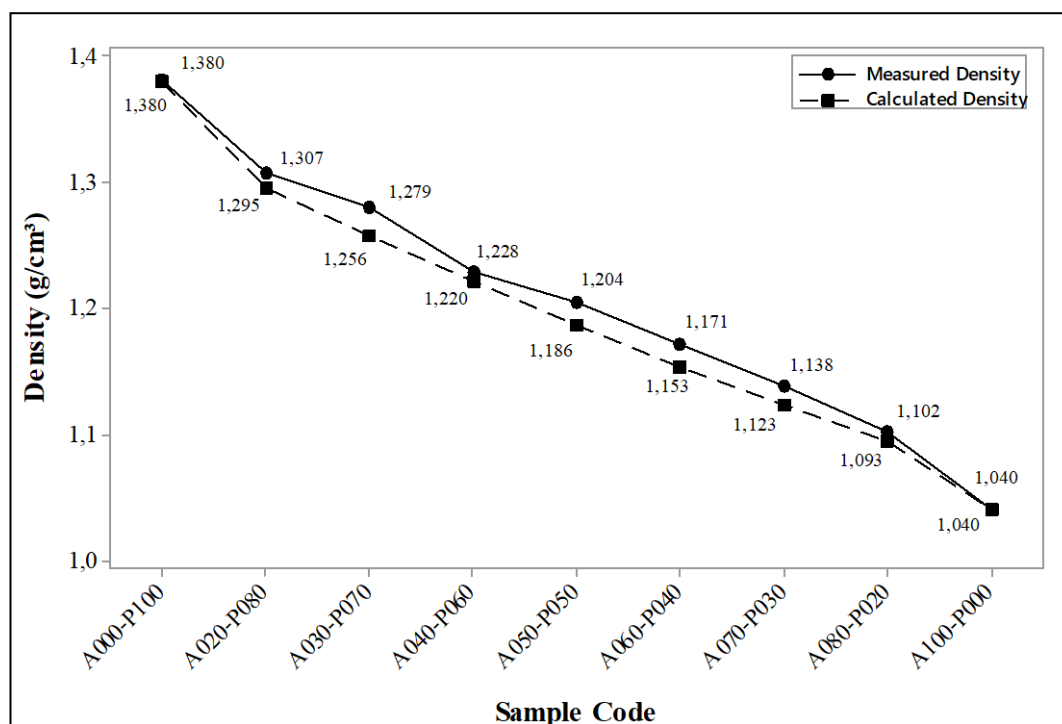


Figure 3.16 : Density versus prepared ABS/PET blends.

The mechanical properties of ABS, PET and their blends was measured according to chapter 2.3.9.1 and was shown in Figure 3.17. The neat PET had higher tensile strength and elongation value at yield. Addition of 20 wt. % PET into ABS enhanced the tensile strength by 17 %, tensile modulus by 10 % and elongation at yield by 12 %. PET within the ABS behaved like a reinforcing agent. The PET reinforcing effect became more significant beyond 30 wt. % PET loading level that led to increase in the tensile strength by 21 %. As it was discussed before in the morphology discussion, for PET loading levels higher than 30 wt. %, PET formed a continuous phase within the ABS matrix, and enhanced the ABS lower mechanical properties.

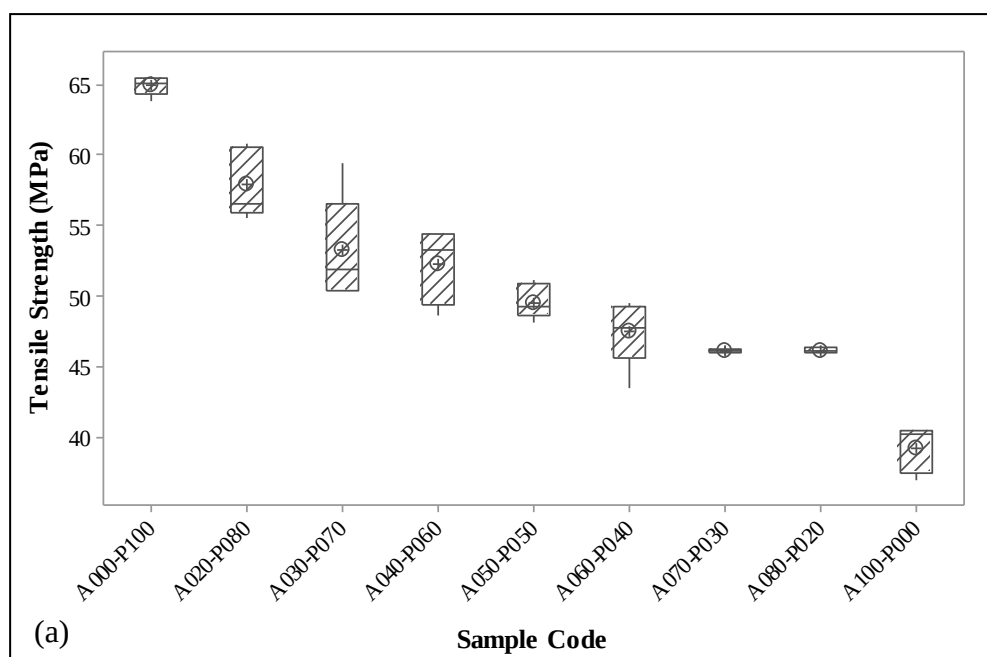


Figure 3.17 : Tensile properties of prepared ABS/PET blends; a)Tensile Strength, b) Strain at Yield and c) Tensile Modulus.

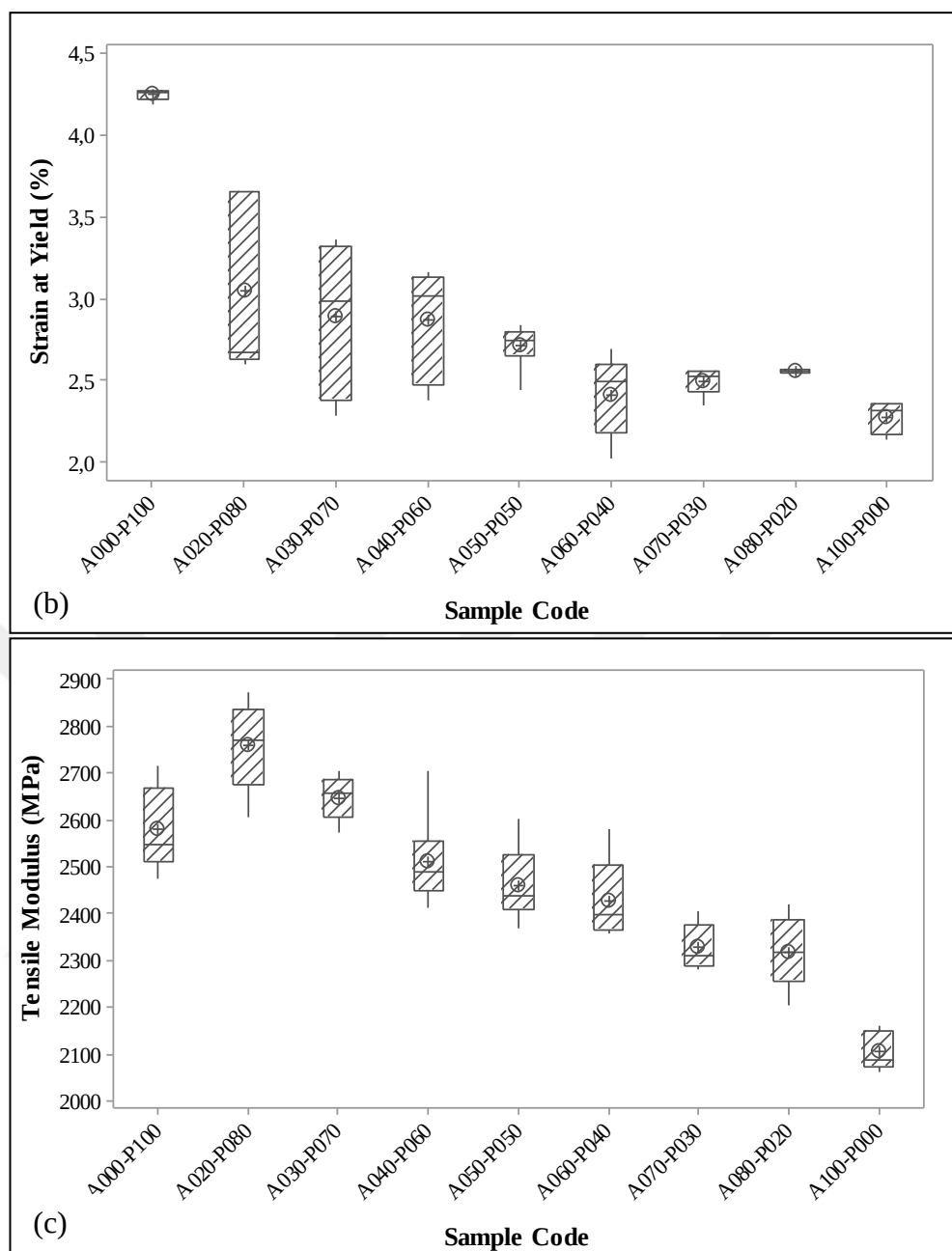


Figure 3.17 (continued): Tensile properties of prepared ABS/PET blends; a) Tensile Strength, b) Strain at Yield and c) Tensile Modulus.

Figure 3.18 indicated how the ABS concentration affected the notched Izod impact strength. Adding 20 wt.% PET into ABS (A080-P020) decreased the notched impact strength drastically. That could be addressed to immiscibility of the phases and also formation of voids due to the high deformation rates [49].

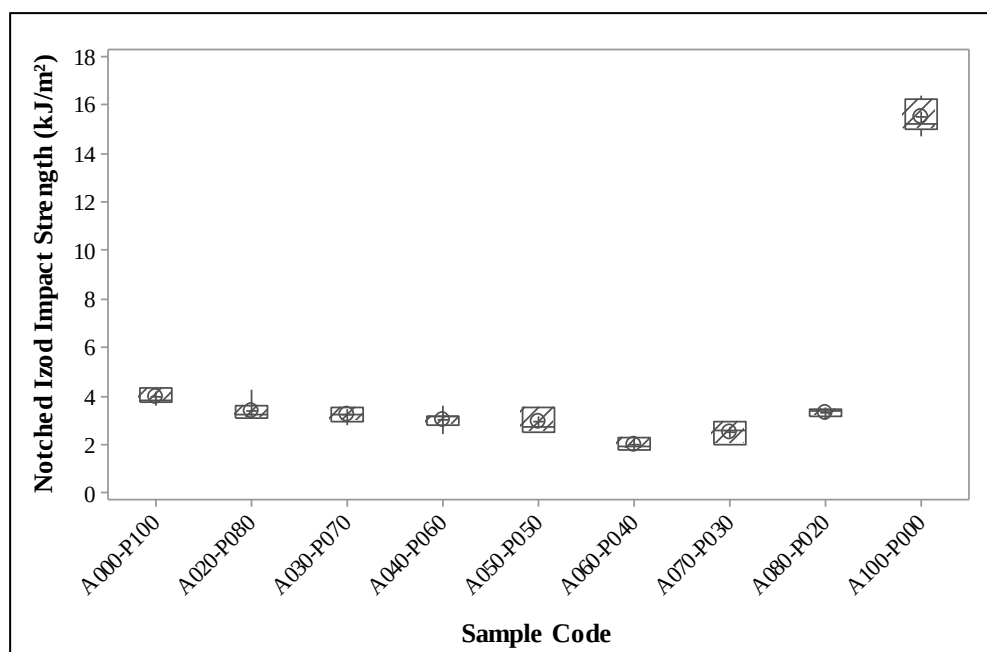


Figure 3.18 : Notched Izod impact properties of prepared ABS/PET blends

ABS had higher impact strength due to toughening effect of homogeneously dispersed fine rubber domains while PET had no such domains. During the high deformation rates, PET phase was not able to absorb this energy. Increased PET crystallinity caused by ABS phase was expected to decrease the notched impact resistance of the PET phase as observed from Figure 3.18. For higher loading levels of PET, co-continuous PET and ABS domains might have tried to withstand the deformation front and most probably, the failure occurred in the PET phase leading to similar impact strength to the neat PET[42]. In addition, immiscible morphology might have inhibited the stress transfer between the phases.

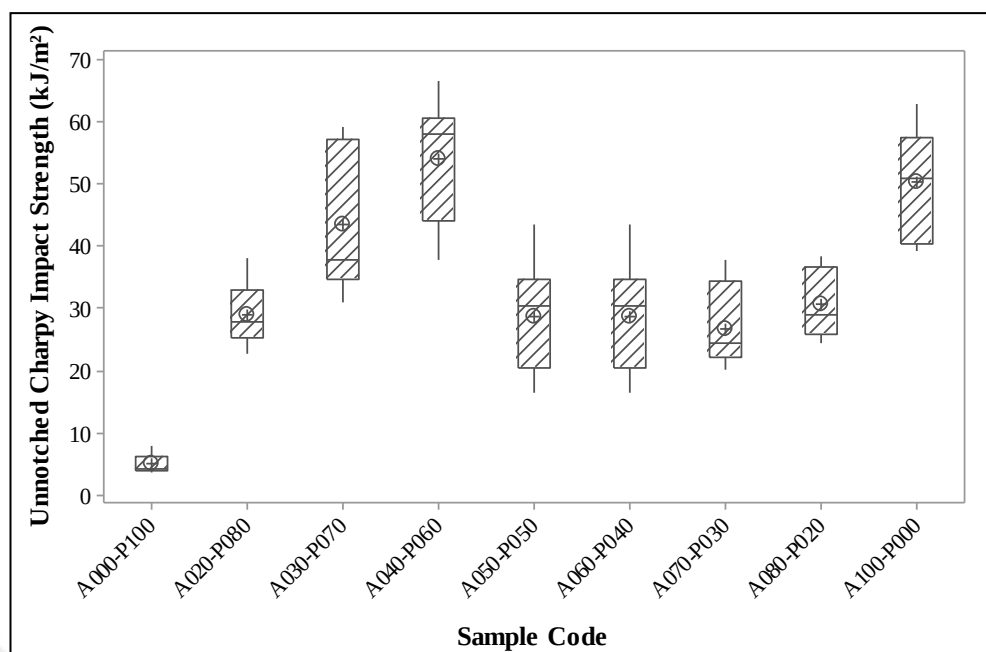


Figure 3.19 : Unnotched Charpy impact properties of prepared ABS/PET blends

The unnotched Charpy impact strength was applied as described in Chapter 2.3.9.2. Impact strength versus ABS concentration was showed Figure 3.19. The neat PET exhibited the lowest unnotched Charpy impact strength due to lack of toughening domains. When ABS was added into PET phase, the impact strength increased because the butadiene part of ABS phase acted as an impact modifier. The unnotched impact strength increased from 4,9 to 53,9 kJ/m² as the ABS level increased to 40 wt. %. At 50 wt.% ABS, a co-continuous morphology occurred as shown in the morphology studies; Figure 3.11. That reduced the toughening efficiency from the rubber phase particle agglomeration instead of fine dispersion as explained by Joseph et al[30]. As the ABS concentration increased further, the PET behaved like a reinforcing agent in an amorphous ABS matrix and improved the tensile strength while having no significant effect on the unnotched impact properties.

By blending ABS and PET, injection processability of PET was improved due to higher viscosity of PET/ABS blend. Phase morphology investigation of ABS/PET blends showed that phase morphology was dependent on blend ratio varying from sea/island to continuous structures. Gloss values did not exhibit significant differences as compared to the neat ABS due to the ABS-rich domains on the part surfaces. With the ABS-rich covered surfaces, no difference was expected for the paintability and existing ABS paint procedures could be applicable. Adding even 20 wt. % PET into ABS enhanced the dimensional stability after aging at elevated temperatures.

ABS blends with 20–30 wt. % PET could offer an appropriate solution due to better dimensional stability at elevated temperature conditions as well as reasonable mechanical properties to overcome the inadequate ABS dimensional stability. This better ABS/PET blend dimensional stability is expected to improve paintability. For the rest of the study 30 wt. % PET as selected as blend ratio.

3.3 Effects of Different Processing Conditions on Compatibilized ABS/PET Blends

In this section, the injection molding process conditions and effect of addition of compatibilizer were investigated for the 70/30 wt. % ABS/PET blends.

Compatibilizers' ratio were defined as 3 % wt. For further blend preparations. As a compatibilizer; four different type of compatibilizer were used as described in Chapter 2.1. Sample codes and details of blend formulations were given Table 2.6.

Intermeshing twin-screw extruder was used to prepare blends as described in Chapter 2.2.1 and the temperature profile was set to constant as given in Table 2.9.

In order to investigate the effect of injection molding parameters on blend properties, two different injection molding processing profile were used as given in Table 2.14.

Morphology investigation were applied as described in Chapter 2.3.3. It was observed from the Figure 3.20; higher injection molding process profile caused higher and irregularly shaped PET particulates in uncompatibilized A070-P030 blends. Even though the PET phase was still in the dispersed phase, increased injection molding temperature disclosed the viscosity differences of both phases resulting in coalescence and agglomeration of PET phases as described by Malaika et al[123].

When the compatibilizer MA-g-SEBS (Kraton FG-1901G) added the formulation in extrusion process, distribution of PET phases were improved by getting smaller particle sizes with more uniformity (Figure 3.21). Tanrattanakul et al[73] reported the effect of MA-g-SEBS on PET for toughening by decreasing the domain particle size. Due to emulsifying action of grafted copolymer, decreased the interfacial tension between ABS and PET reduced the coalescence tendency of dispersed PET phases. That improved the adhesion of phases in the blend[87].

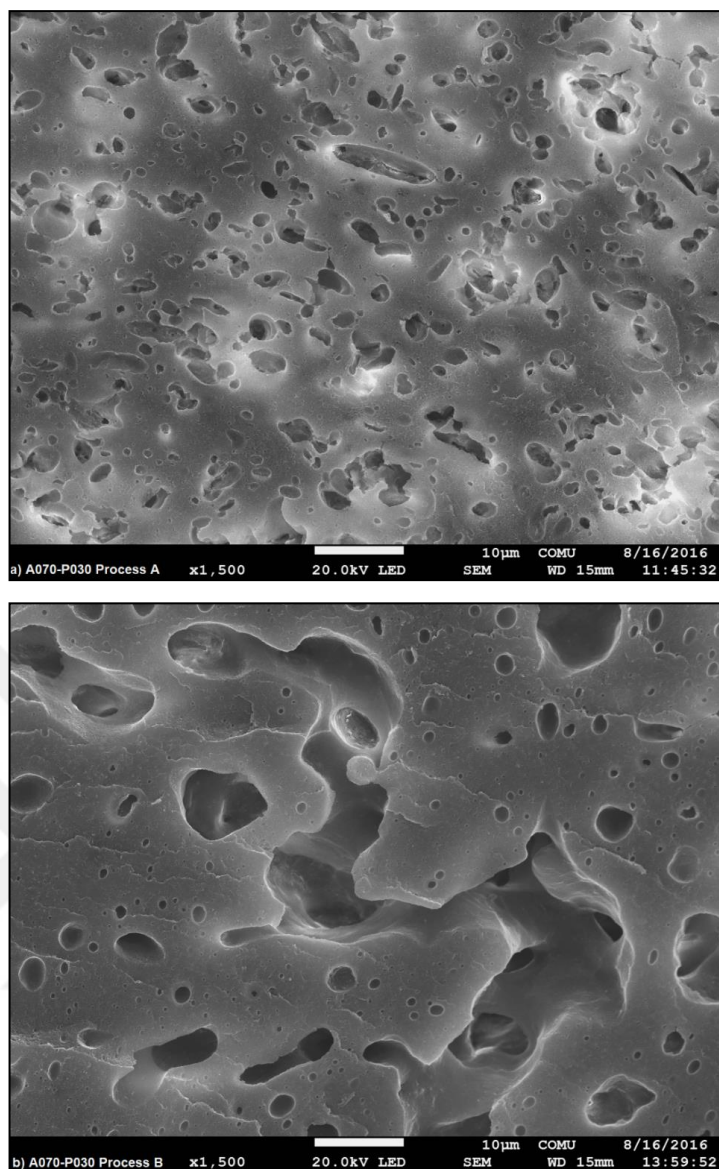


Figure 3.20 : KOH etched SEM images in the perpendicular to flow (PF) direction with regards to processing conditions: a) A070-P030 Process A, b) A070-P030 Process B

When the maleic anhydride content of SEBS decreased i.e., by changing compatibilizer to Kraton FG-1924G, particle size of PET phases in the blend increased (Figure 3.21). Less functionalized SEBS phases with less viscosity had a tendency to elongate more in molten state that resulted more irregular shaped PET particulates. This particle size was mostly related with the viscosity of PET, type and presence of compatibilizer as explained by Jayaraman et al [124] and Sengupta et al [125]. Similar behaviour was also observed for Fusabond N493 (MA-g-EP) which has 0,9 % maleic anhydride as reactive group. Reactive group of compatibilizer might react with PET. That reaction could result to formation of a copolymer which was acting as an emulsifier to reduce coalesce tendency during processing[84,87] (Figure 3.23). The

evenly dispersed PET phases in the twin-screw extruder process can be reassembled or coarsened during the high-temperature injection process (process B) as explained by Canto et al[84] for PBT/ABS blend.

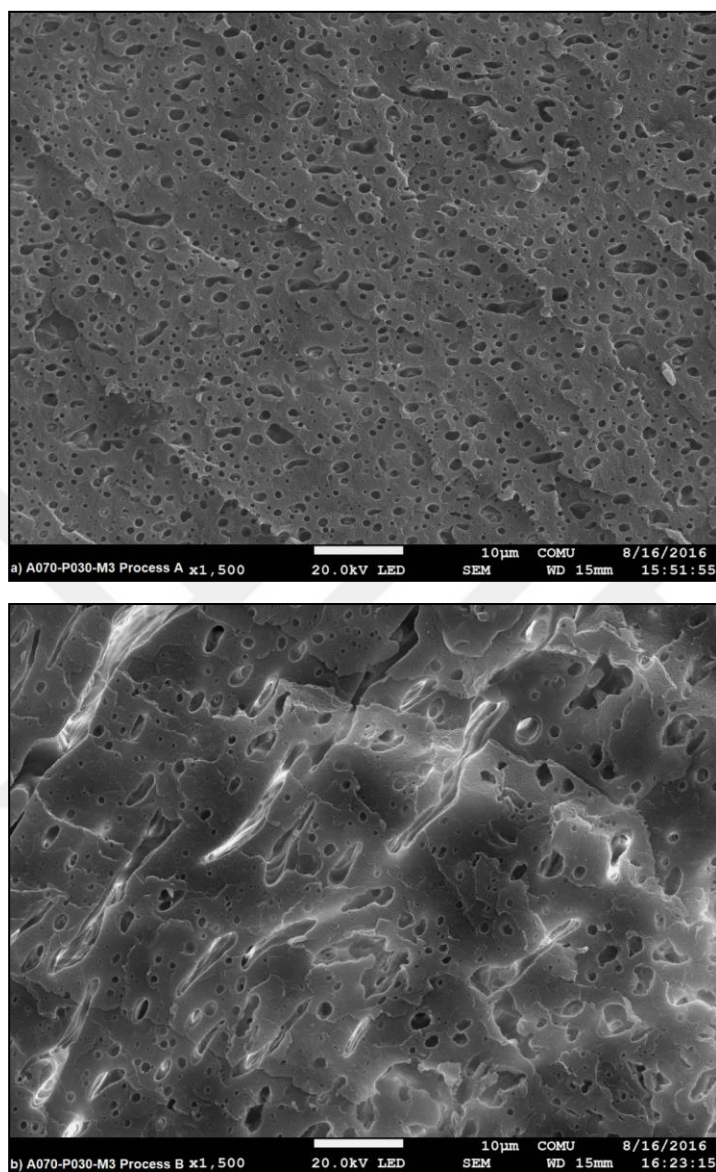


Figure 3.21 : KOH etched SEM images in the perpendicular to flow (PF) direction with regards to processing conditions: a) A070-P030-M3 Process A, b) A070-P030-M3 Process B

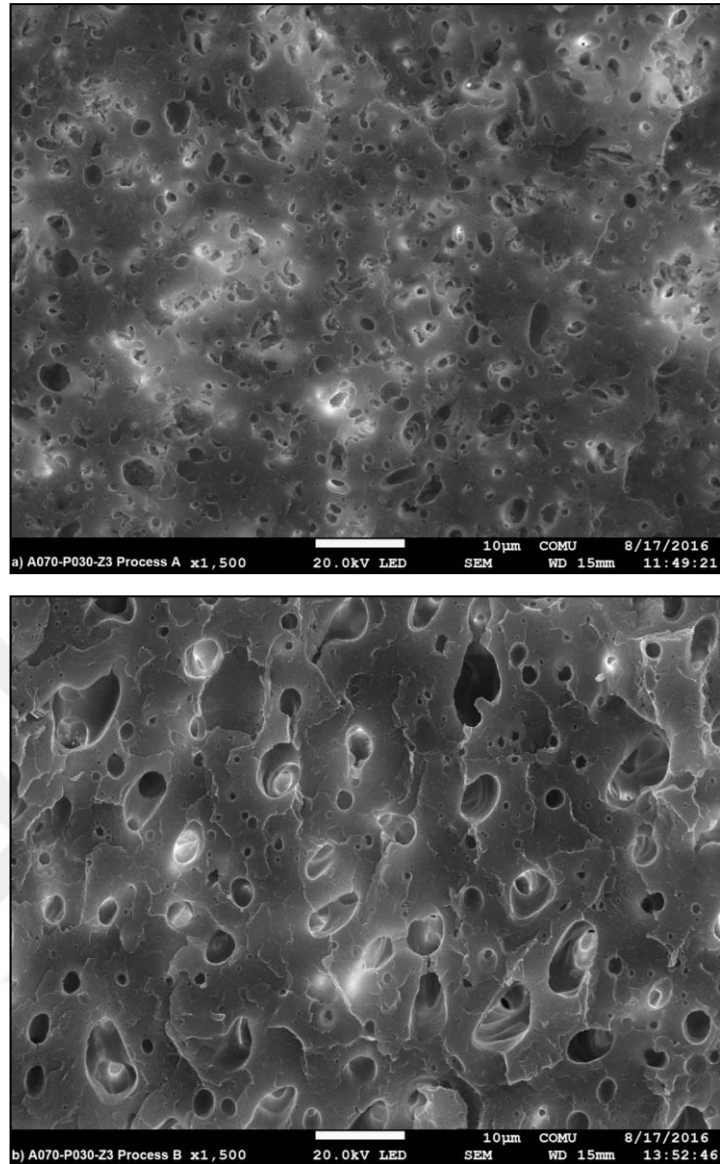


Figure 3.22 : KOH etched SEM images in the perpendicular to flow (PF) direction with regards to processing conditions: a) A070-P030-Z3 Process A, b) A070-P030-Z3 Process B

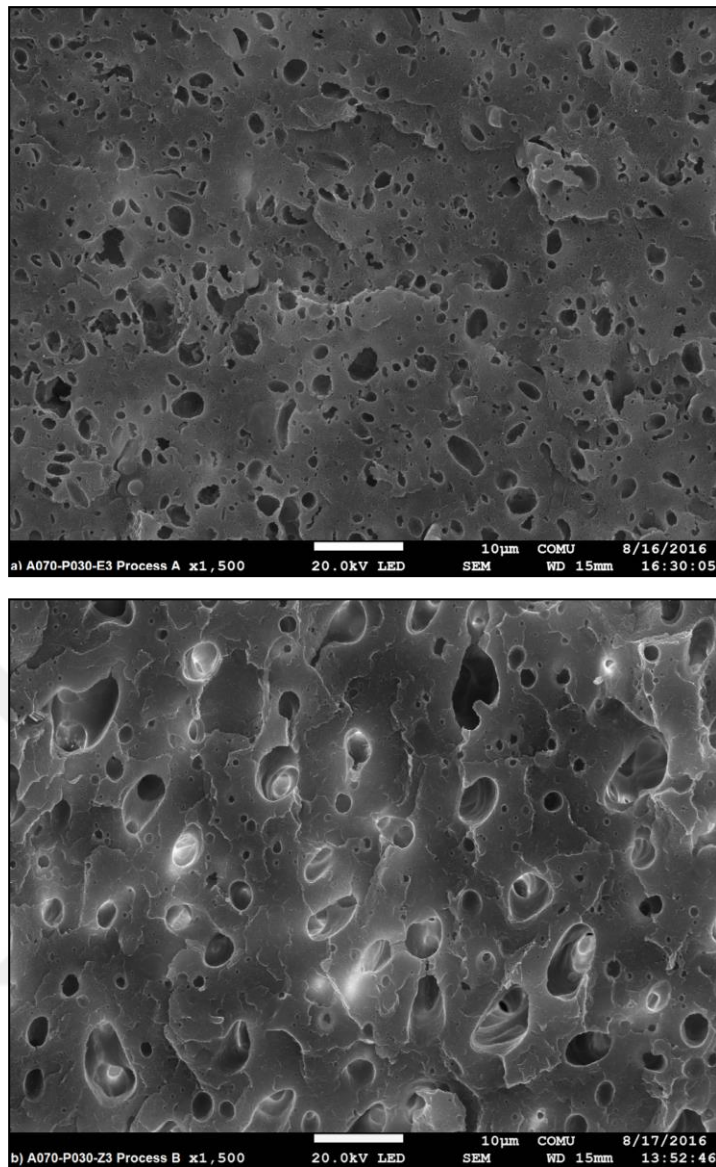


Figure 3.23 : KOH etched SEM images in the perpendicular to flow (PF) direction with regards to processing conditions: a) A070-P030-E3 Process A, b) A070-P030-E3 Process B

SEM images of PETG added ABS/PET blend as compatibilizer was showed in Figure 3.24 concerning different injection molding conditions. This image indicated that PETG did not create any significant morphology change. Similarly, Focke et al[69] indicated that ABS and PETG were mixed with different ratios and the uncompatibility in between were reported even though impact properties improved. Addition of poly(styrene-butadiene) triblock copolymer as compatibilizer in to blend as little as 1% was reported as the proper way of reduction in the domain sizes[30].

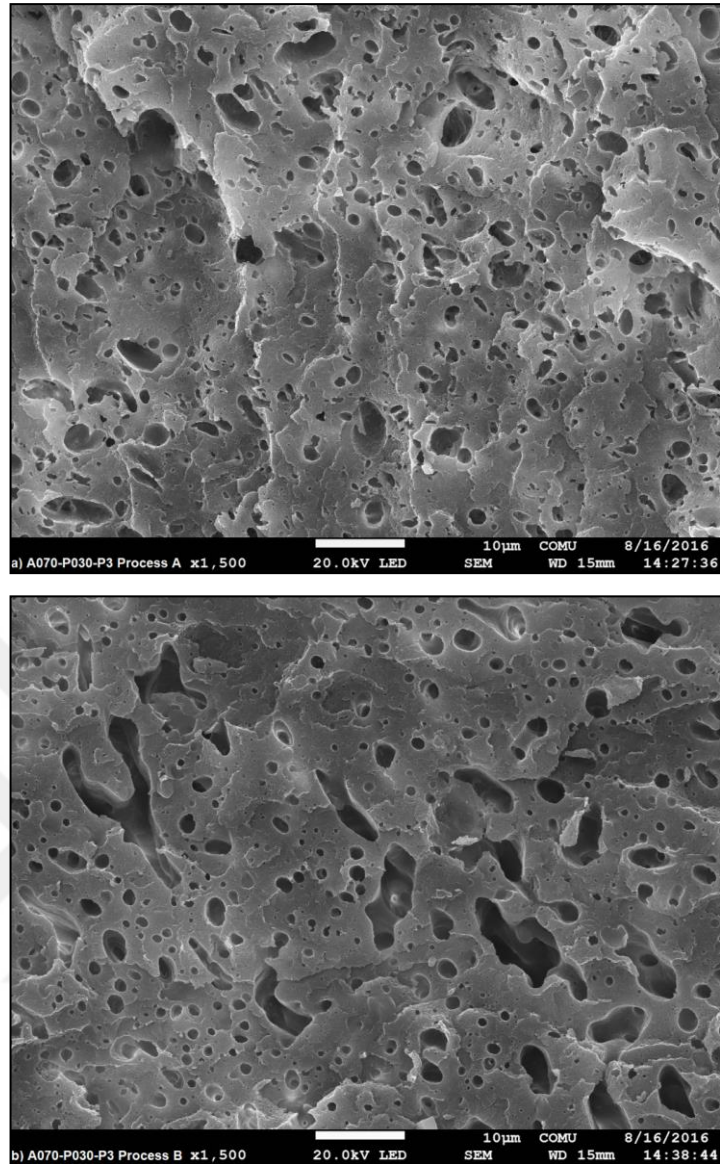


Figure 3.24 : KOH etched SEM images in the perpendicular to flow (PF) direction with regards to processing conditions: a) A070-P030-P3 Process A, b) A070-P030-P3 Process B

SEM investigations revealed that, addition of compatibilizer excluding PETG had an effect on morphology by reducing the dispersed PET phase in ABS matrix. Several researches[25,30,39,43,45,68,71] reported similar results. Although having a compatibilized ABS/PET phases, injection molding process had a huge influence in final phase dispersion[33] by coarsening the minor phase as PET under processing conditions to create bigger and instable particulates[70]. Injection molding at lower temperature profile (Profile A), did not allow PET phase to be less viscous state and to agglomerate. In that way, stability of dispersion with smaller particle size were protected.

Thermal properties of blends prepared with Profile A were investigated as described in Chapter 2.3.4 Measurement results were given in Table 3.3. As described in Chapter 3.2, the glass transition temperature (T_g) and melting point (T_m) of PET were obviously maintained in the uncompatibilized and compatibilizer added ABS/PET blends as similar to work done by Zhao et al[43] (Figure 3.25). Expected shift of PET or ABS glass transition temperature did not observed by the addition of compatibilizer. Neglectable shifts of PET glass transition temperature could be addressed by the PET degradation during the processing as indicated by Cook et al [33,44] and Xue et al [39].

Table 3.3 : DSC measurement results of selected samples.

Sample Code	T_g^{PET} (°C)	T_g^{ABS} (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	% Crystallinity
A070-P030	77	104	109	2,30	257	13,34	207	10,22	8,13
A070-P030-M3	76	105	127	4,49	255	14,39	204	8,56	7,29
A070-P030-Z3	80	106	130	1,71	255	12,79	203	8,90	8,16
A070-P030-E3	77	105	127	7,11	255	13,65	209	1,21	4,82
A070-P030-P3	77	104	127	2,51	253	14,07	202	12,09	8,51
A000-P100	82	-	-	-	257	39,4	196	40,77	29,01
A100-P000	-	104	-	-	-	-	-	-	-

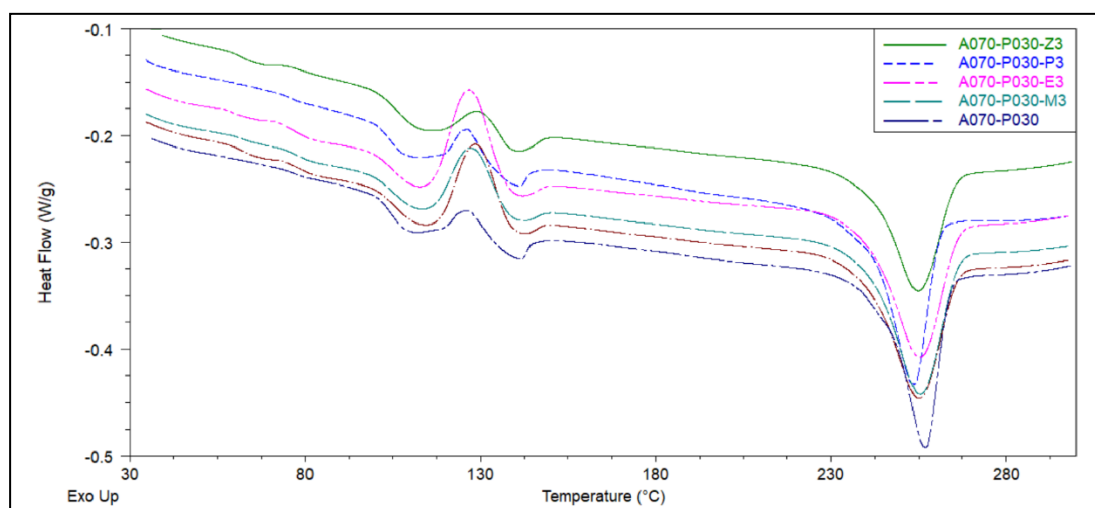


Figure 3.25 : DSC graphs of compatibilizer added ABS/PET blends.

Initiated cold crystallization behaviour by ABS phases were slightly varied from 127 °C to 130 °C which might be the result of accelerating the movement of macromolecular chains of PET in the ABS matrix. As also seen from cold crystallization peak in Figure 3.25, addition of compatibilizer increased the heat of

fusion at cold crystallization (ΔH_{cc}) from 2,30 J/g to 7,11 J/g. This attitude might be an evidence of improved annealing effect of amorphous PET domains and also increased spherulites sizes as explained by Scheirs et al[87]. Similar behaviour of MA-g-SEBS were also reported by Fung et al[126]. Most increase in heat of fusion of cold crystallization of PET phase was observed for addition of MA-g-EP due miscible structure of rubber. It was assumed that MA-g-EP accelerated the growth of spherulite more than other compatibilizers do. Another observation was that; crystallinity ratio of PET in the blends were varied between 4,82 % to 8,51 % with increased the melting enthalpy of PET as similar to the work of Zhao et al[43] related with the increased mobility of PET domains in the matrix, which also supported the findings about cold crystallization temperature.

Effect of injection processing conditions on sample A070-P030-Z3 were investigated and DSC measurement results were given in Table 3.4. Even though the injection molding process could not create high shear on the melted polymer, it was assumed from the Figure 3.26 that degradation of PET phase was more at higher processing temperature due to difference in the glass transition temperature of PET. At lower processing temperatures (Profile A), T_g for PET was measured as 80 °C but at high temperature profile (Profile B) it was noted as 77 °C. Phinyocheep et al [127] reported that screw speed of extrusion did not affect the crystallinity of PET in natural rubber/PET blends. At high temperature profile (Profile B), the cold crystallization temperature was measured 6 °C less. That might be related with the effect of processing conditions. Effect of mixing time for PTT and PC were investigated by Chiu et al[41] and reported that the cold crystallization temperature could be higher at longer mixing times.

Table 3.4 : DSC measurement results of A070-P030-Z3 samples at different injection processing profiles.

Sample Code	T_g^{PET} (°C)	T_g^{ABS} (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	% Crystallinity
A070-P030-Z3 Process A	80	106	130	1,71	255	12,79	203	8,9	8,16
A070-P030-Z3 Process B	77	105	124	2,95	255	15,08	208	9,6	8,93

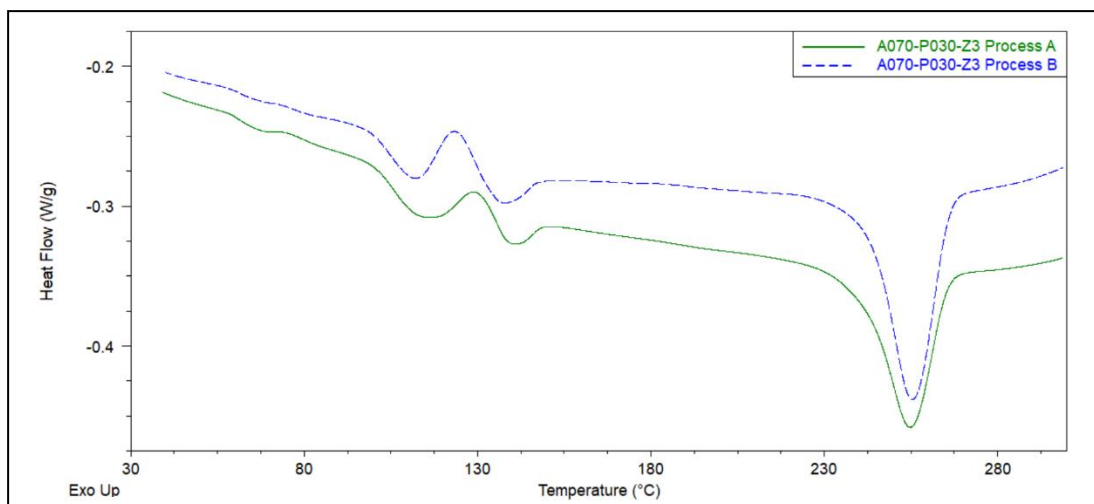


Figure 3.26 : DSC graphs of A070-P030-Z3 at different injection molding processing conditions.

Tensile test results were obtained by following the procedure described in Chapter 2.3.9.1 and shown in Figure 3.27 in accordance with the processing conditions.

The uncompatibilized ABS/PET blend (A070-P030) had higher tensile strength and tensile modulus value for the both processing conditions. This result could be related with reinforcing behaviour of PET phases[27] as discussed previously in Chapter 3.2. However, the standard deviation Process B (2,54) was wider than Process A (1,47). That might be related with the degradation of chains resulting scattering in the value of mechanical properties[128]. This wide distribution of data was also observed for the compatibilized blends as shown in the Figure 3.27.

Addition of 3 wt.% compatibilizer into ABS/PET blend decreased the modulus slightly from 2361 MPa to 2106 MPa (A070-P030-Z3) for Processing A and 2230 MPa to 2105 MPa (A070-P030-Z3) for Processing B. This could be addressed to presence of higher amount of diblok content of MA-g-SEBS compared to A070-P030-M3 which had 2260 MPa tensile modulus for Process A and 2160 MPa for Process B. As Zhao et al[43] reported, addition of SMA as compatibilizer into ABS/PET blend created a decrease in tensile and flexural strengths due to created copolymers resulting increased interfacial strengths with a reduction of the droplet coalescence rates during the force application.

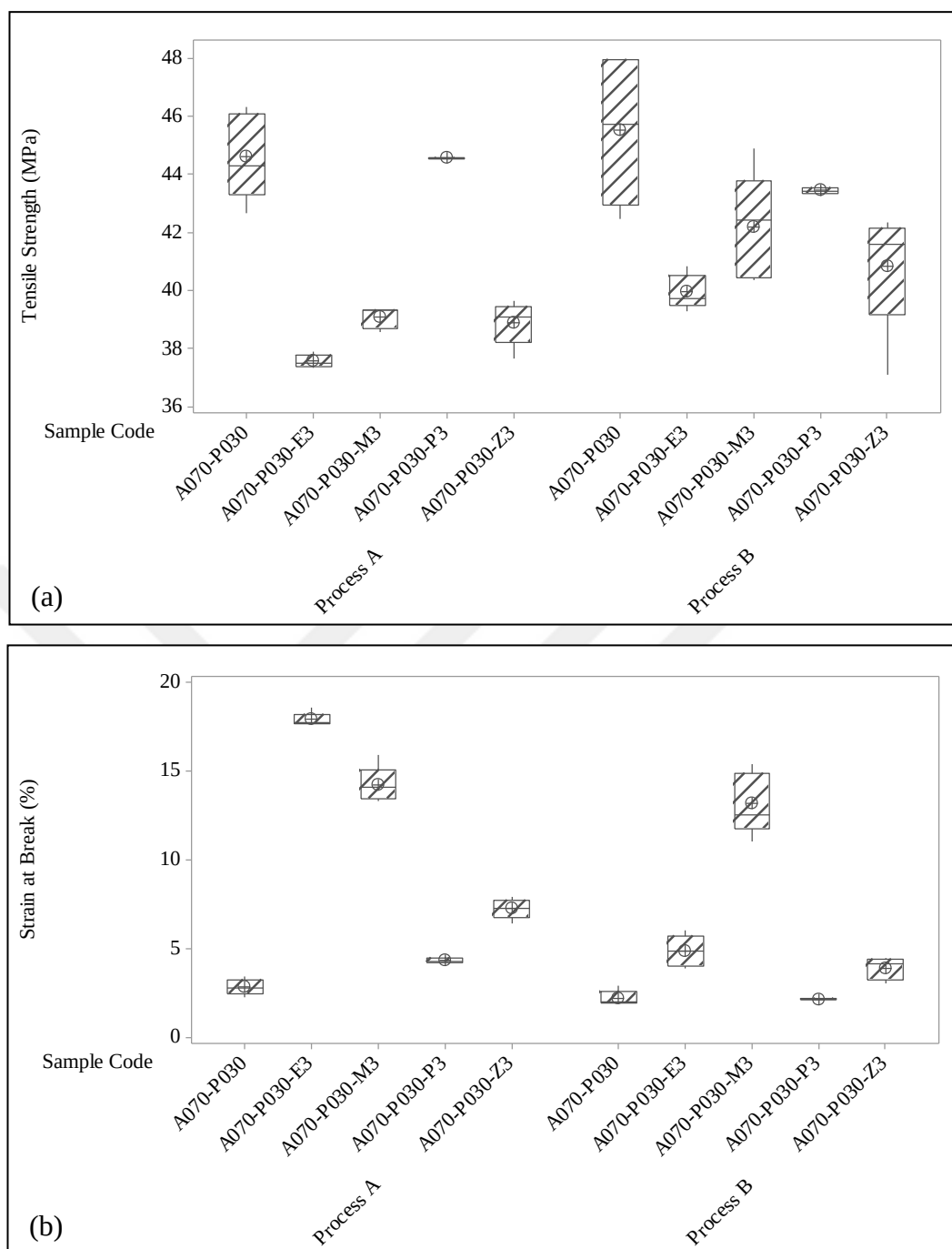


Figure 3.27 : The effect of processing conditions on tensile strength and strain at break values of A070-P030 and several compatibilizer added blends: a) Tensile Strength, b) Strain at Break and c) Tensile Modulus.

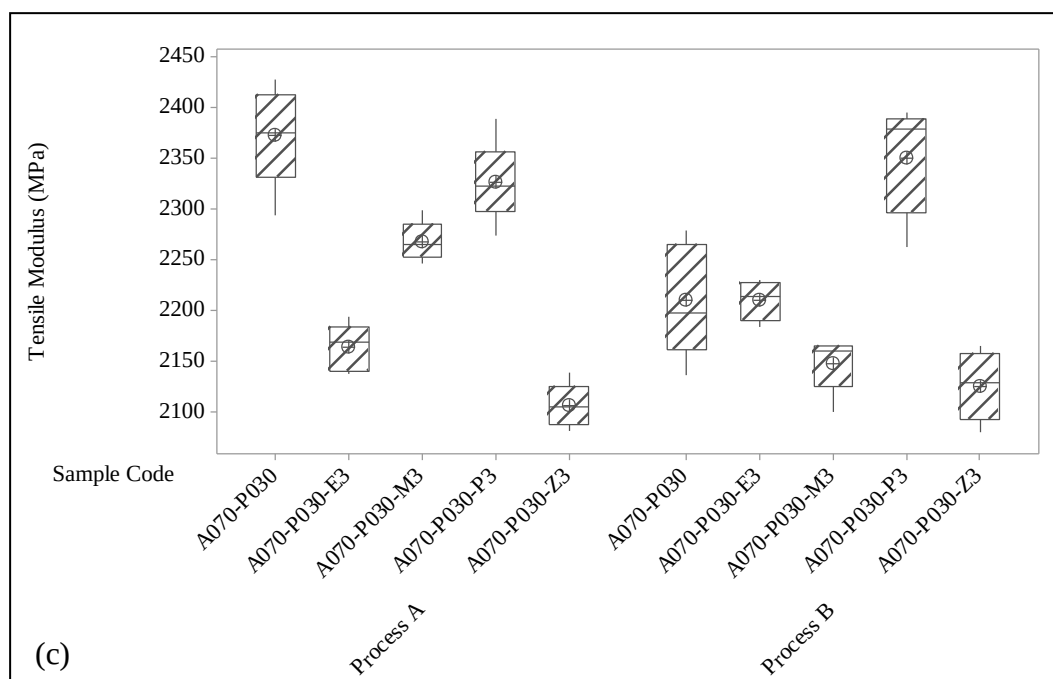


Figure 3.27 (continued): The effect of processing conditions on tensile strength and strain at break values of A070-P030 and several compatibilizer added blends: a) Tensile Strength, b) Strain at Break and c) Tensile Modulus.

Strain at break value for ABS/PET blend were increased from 2,85 % (A070-P030) to 17,89 % (A070-P030-E3) as 527 % for Process A and in Process B 2,20 % (A070-P030) to 4,87 % (A070-P030-E3) as 120 % due to improved interfacial interaction via compatibilizers as similar to Padhan et al[96]. Lower strain at break values were recorded for high processing conditions as Process B such as maximum decrease was observed for A070-P030-E3 as -72% from 17,89 % to 4,87% due to degradation of double bonds in compatibilizer resulting an decrease in stress transfer and chain mobility as explained by Cook et al[33].

Figure 3.28 showed the notched Izod impact properties obtained as described in Chapter 2.3.9.2. By the addition of compatibilizer, the impact strength increased from 1,88 kJ/m^2 to 4,37 kJ/m^2 with addition of Kraton FG1924X (A070-P030-Z3) for Process A. That observation showed similarity with to the results of several works[33,39,43,44,67,68,126]. It assumed that this improvements might be related with reaction of epoxidized group of grafted maleic anhydride with PET as described by Carté et al [93] and Scheirs et al[87]. Similarly, addition of PETG improved the notched impact strength from 1,88 kJ/m^2 to 3,46 kJ/m^2 . Similar behaviour was also observed for Process B with slightly lower than Process A.

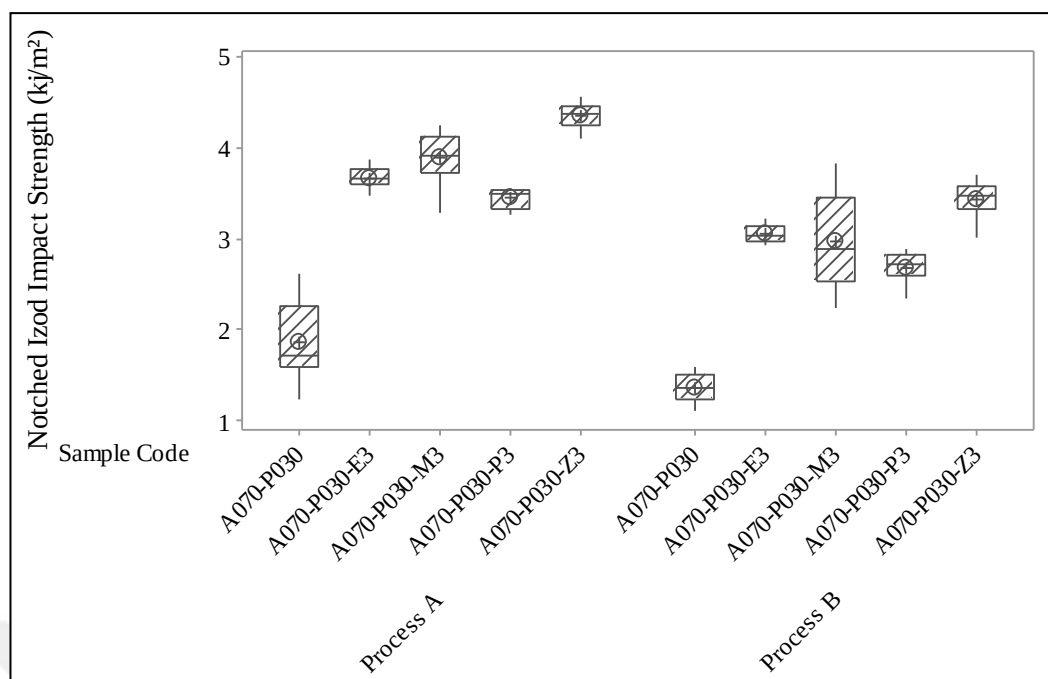


Figure 3.28 : The effect of processing conditions on impact properties of A070-P030 and several compatibilizer added blends.

For uncompatibilized ABS/PET, impact strength was measured as 1,88 kJ/m^2 for Process A and 1,43 kJ/m^2 for Process B. This differentiation in impact properties of Uncompatibilized ABS/PET blend, processed with the conditions A and B could be related with the degradation for PET phases. Cook et al[33,44] previously reported similar results.

For compatibilized blends, similar behaviour was also observed for high temperature profile (Process B) resulting in decrease in the impact properties. Similar results were reported by Larocca et al[129].

As a summary of this section; lower process temperature profile (Process A) in injection molding resulted in better morphological, mechanical and thermal properties for both compatibilized and uncompatibilized blends. Addition of MA-g-SEBS (Kraton FG 1901x) and MA-G-EPA as a compatibilizer hence morphology further while improving the impact performance. However, those compatibilizers resulted in lower tensile modulus and tensile strength while improving the strain at break values.

3.4 Effect s of ABS/PMMA Ratio on Thermal and Mechanical Properties

In this section of the thesis, in order to investigate effect of Poly(methyl methacrylate) PMMA ratio on ABS were investigated by physical, mechanical and thermal properties. Prepared formulations and sample codes were given Table 2.5.

All the ABS/PMMA blends were prepared in a corotating twin-screw extruder as explained in Chapter 2.2.1 with fixed processing conditions. Temperature profile for twin-screw extrusion was given in Table 2.9.

Test specimens were produced according to Chapter 2.2.2. Injection processing temperatures were given in Table 2.12 to inject all blends and the neat polymers.

The morphology of ABS/PMMA blends were characterized as described in Chapter 2.3.3. Unlike the general etching process, etching time was limited for 1 minute.

In Figure 3.29 showed a weak phase contrast and no clear morphology due to the biphasic morphology of ABS and low electron density differences of PMMA with ABS for the 10 and 50 % wt. PMMA. Figure 3.30 showed SEM images of blend of 10 %wt. PMMA.

In the center of the samples, PMMA fibrils were observed after the etching ABS phases. Those PMMA fibrils were observed just for 5 wt.% PMMA loading in contrary to Setiavan et al[130]. However after 5 wt.% loading level of PMMA, it was not possible to obtain reasonable SEM images after etching process due to increasing of miscibility of PMMA in SAN phases of ABS as reported by various researchers [1,131,132].

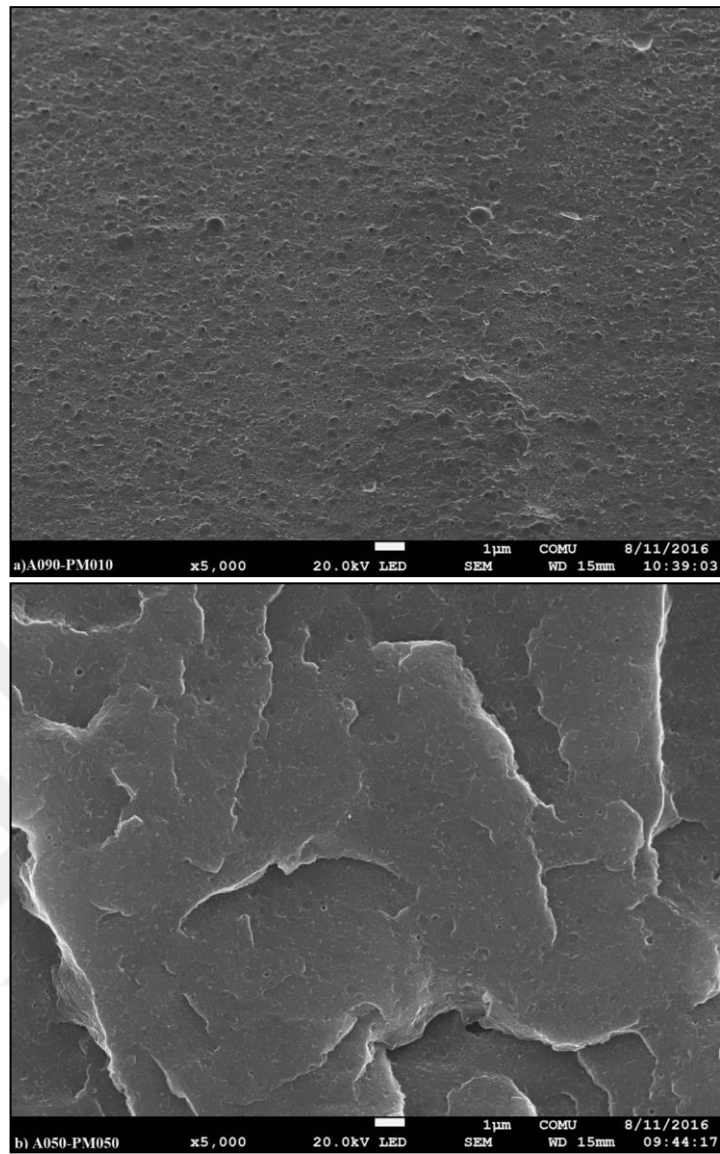


Figure 3.29 : SEM images of selected ABS/PMMA blends a) A090-PM010 and b) A050-PM050.

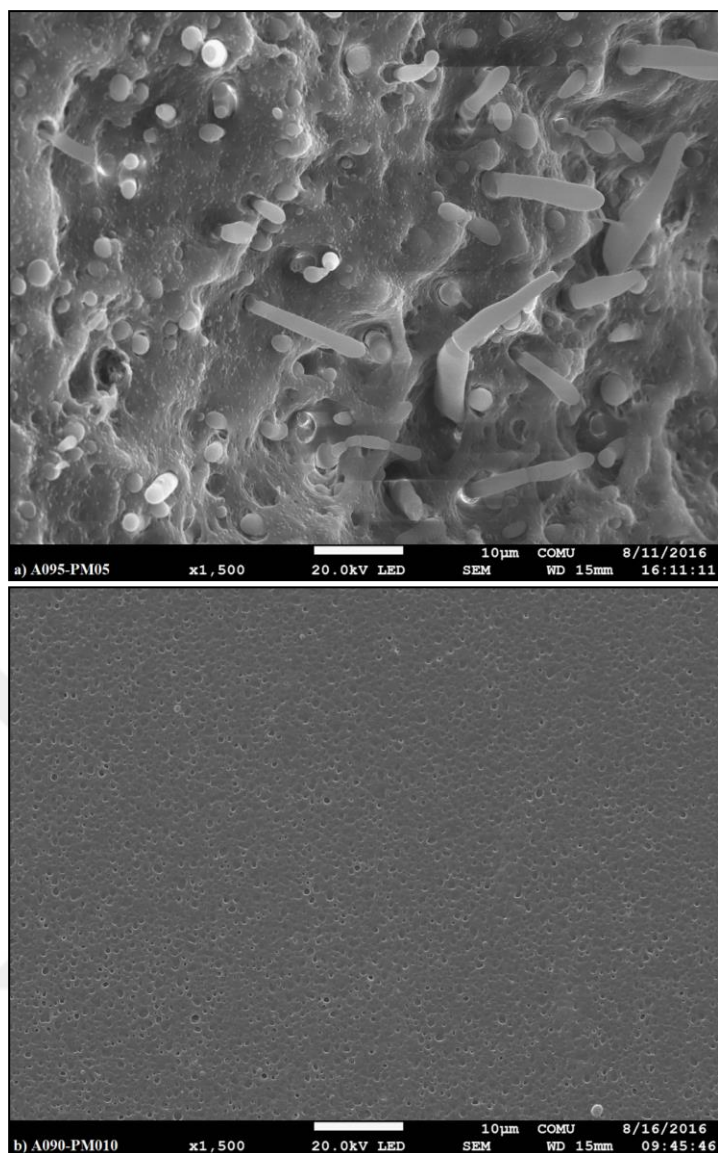


Figure 3.30 : SEM images of selected ABS/PMMA blends after acetone etching a) A095-PM05 and b) A090-PM010.

Differential scanning calorimetric experiments were applied as indicated in chapter 2.3.4 and shared in Figure 3.31 and Table 3.5 to characterize the glass transition temperatures (T_g) of pure polymers and their blends. In order to characterize miscibility of blends, measurement of T_g was widely used[133]. As reported previously [24,131,133], blends having a single glass transition was defined as miscible or single-phase structure. More than one glass transition points with variation from the neat polymer by shifting to each component could be accepted as partially miscible but for those who shows two glass transitions without variant from the neat polymer can be accepted as immiscible systems.

According the DSC measurement results, single glass transition temperature were recorded for 50 % and 75 % loading of PMMA due to miscibility of ABS in PMMA phase as reported by Kumaraswamy et al[133]. For the blend compositions (the PMMA ratio of 5, 10 and 25 %), two different Tg were observed.

Table 3.5 : DSC measurement results of ABS/PMMA blends.

Sample Code	Tg - PMMA	Tg - ABS	Tg - Combined
A100-PM000		104	
A095-PM005	117	103	
A090-PM010	123	103	
A075-PM025	125	104	
A050-PM050			112
A025-PM075			117
A000-PM100	122		

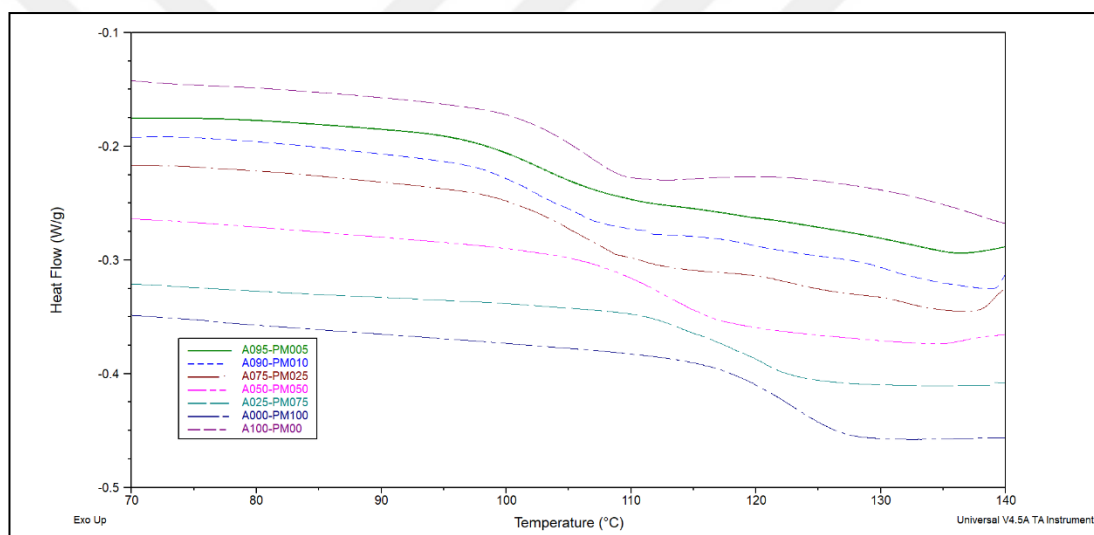


Figure 3.31 : DSC graphs of ABS/PMMA blends.

Results of gloss measurements according to Chapter 2.3.6 were showed in Figure 3.32. Addition of even 5 wt. % PMMA in to ABS phases improved the gloss from 88,54 GU to 92,9 GU. For A025-PM075 samples, gloss value reached to 99,41 GU. Those improvement in the gloss values by addition of PMMA could be explained that PMMA phases could be cover the surfaces of specimen and enhanced the gloss value compare to neat ABS as reported by Kim et al[72].

In mechanical measurements, tensile testing was applied according to chapter 2.3.9.1. The results were shown in Figure 3.33. Tensile modulus value of blend did not increase up to 25 % PMMA addition. When the PMMA ratio was 50 %, modulus value of blend

started to increase (from 2106 MPa to 2308 MPa). When major phase was PMMA as 75 % wt. in blend, modulus was measured as 2449 MPa.

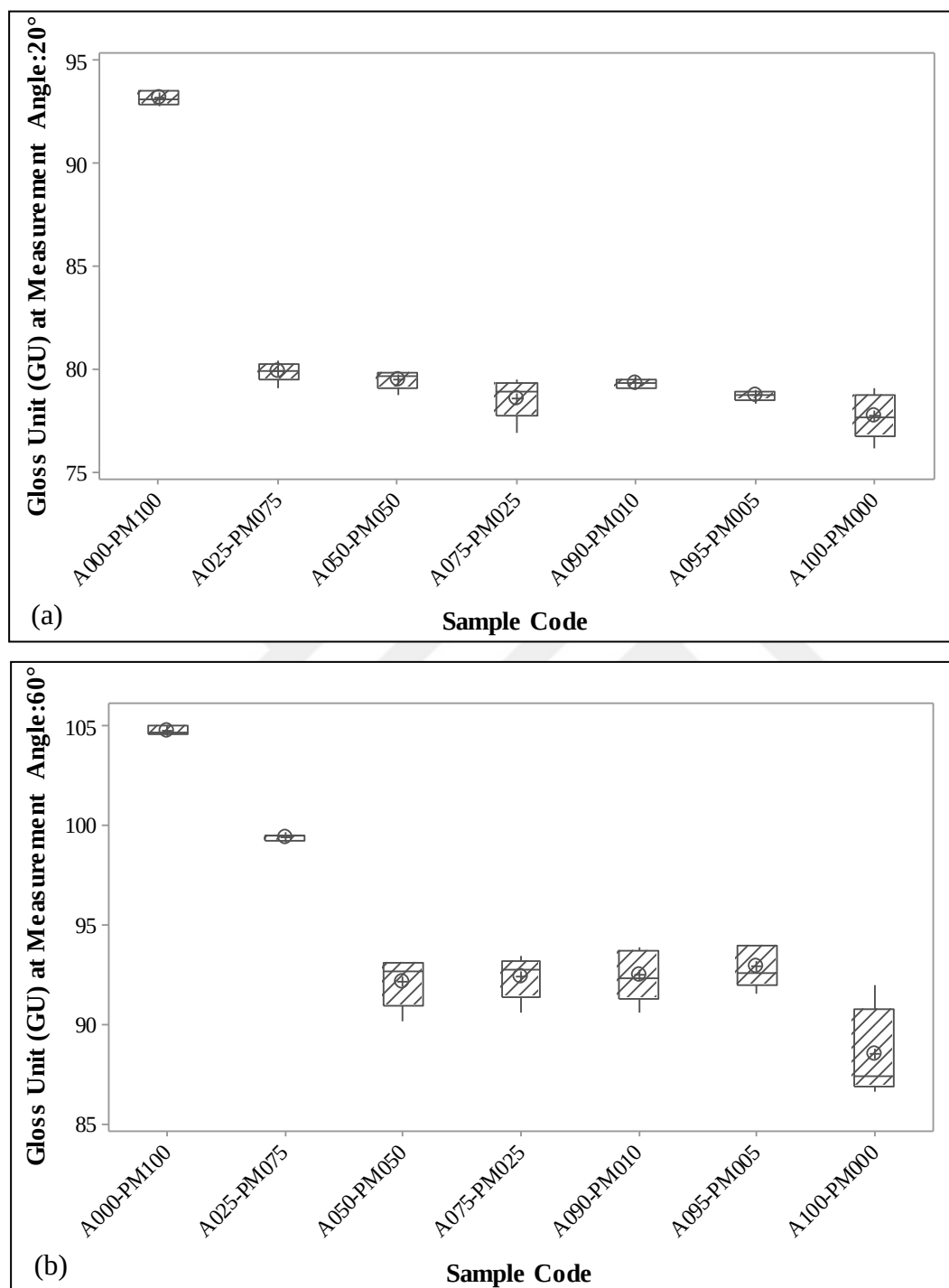


Figure 3.32 : Gloss measurements for ABS/PMMA blends: a) Measurement Angle 20° and b) Measurement Angle 60°

As indicated in morphology and DSC measurements, when composition ratio reach to 50 wt. % or 75 wt. %, both phases were miscible. That caused an interaction between ABS and PMMA resulting a reduction in the chain movement [134]. So the rigidity of

the blend increased. Similar trend in the tensile strength was observed. 27 % increase in tensile strength (from 39,2 MPa to 49,7 MPa) was observed as addition of 50 wt. % PMMA into ABS. As Kim et al[135] and Lee et al[136] reported that in ABS/PMMA blends, the tensile properties were increased similar to linear additive rule.

An interesting result were also obtained from strain at break values of the blends. As expected, with addition of 25 wt. % ABS into PMMA, strain at break value was improved from 3,67 % to 18,25 % due to contribution of elastic or rubbery phase of ABS [137,138]. In addition, strain at yield value were recorded as similar with neat ABS up to 50 wt. % loading of PMMA. When the PMMA ratio reached to 50 wt. % (A050-PM050), strain at yield value started to increase to 2,61 %. This behaviour must be the result of strain-controlled plastic deformation behaviour of ABS/PMMA blends as explained by Bubeck et al[137] for PC/ABS/PMMA. The energy needed for plastic deformation was absorbed by the rubber particle of ABS cavitation at first and after reaching a critical value, SAN ligaments started to deformation with deformation.

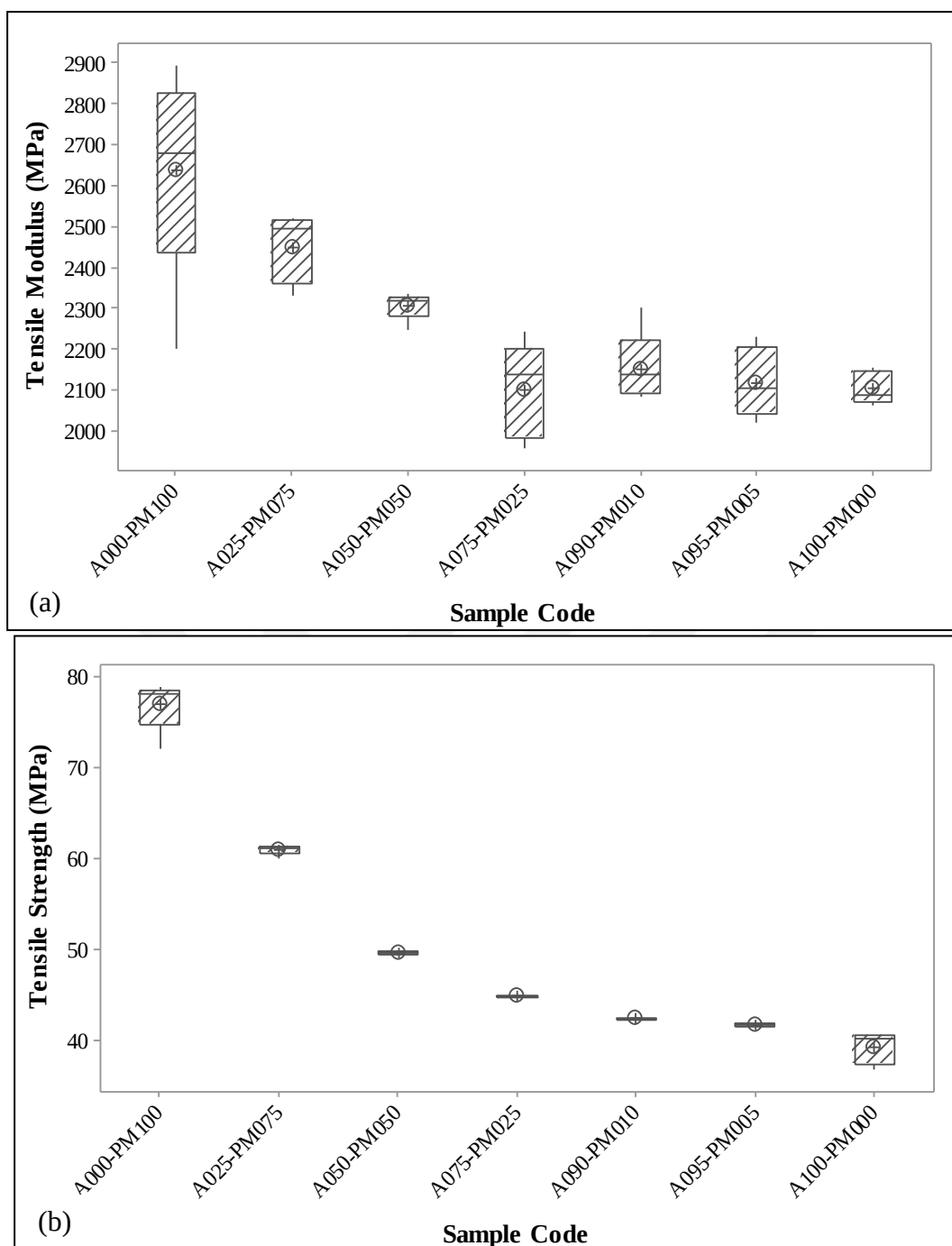


Figure 3.33 : Tensile properties of ABS/PMMA blends: a) Tensile Modulus, b) Tensile Strength, c) Strain at Yield and d) Strain at Break.

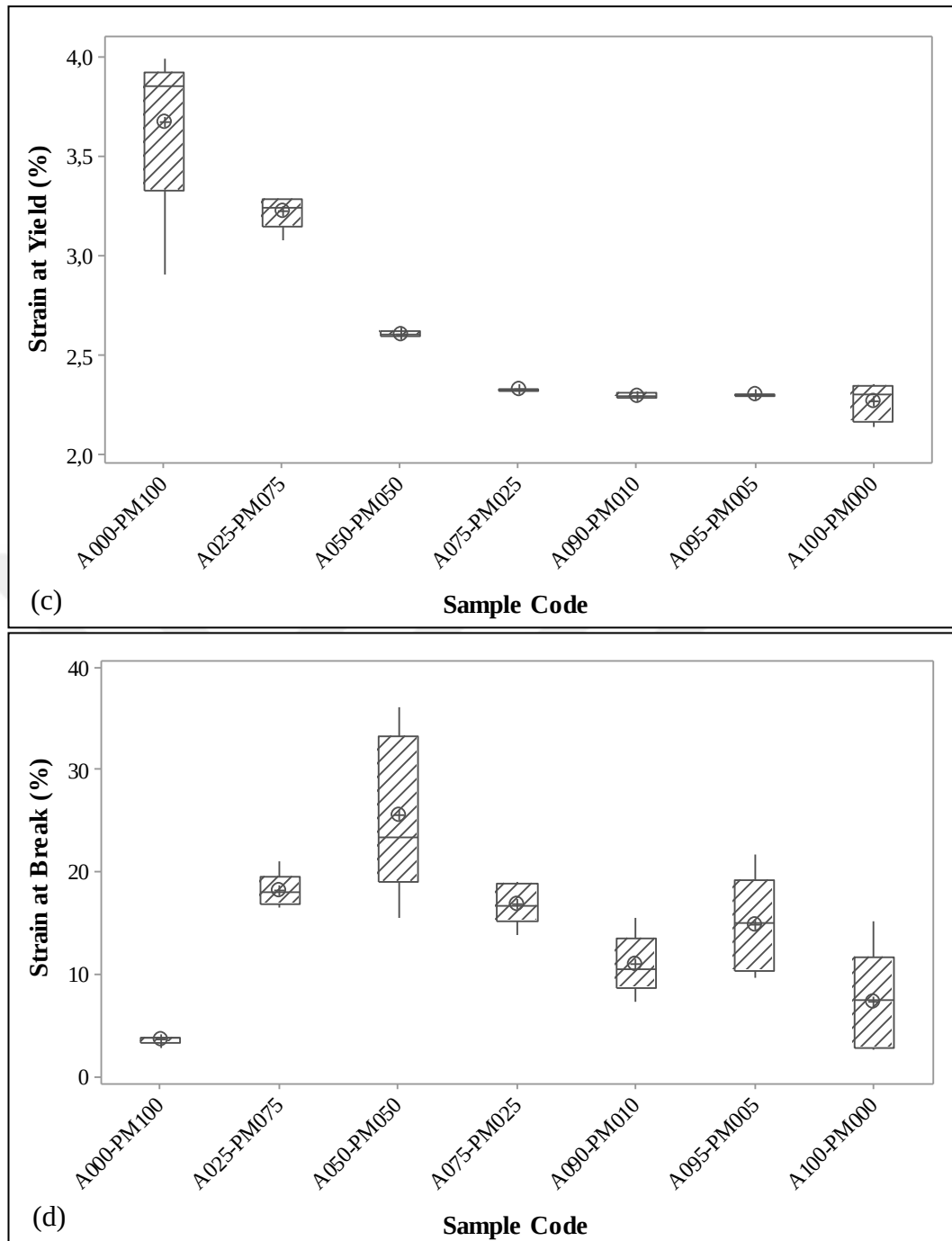


Figure 3.33 (continued): Tensile properties of ABS/PMMA blends: a) Tensile Modulus, b) Tensile Strength, c) Strain at Yield and d) Strain at Break.

As shown in Figure 3.34, It was observed that impact strenght of blend reduced by increase in PMMA content. As reported by Kim et al[132], miscibility affected the notched impact properties of blends. As it obvious from the graph, by the addition of ABS (25% wt.) phase into PMMA phase, impact property was improved from 1,62 to 3,73 kJ/m² as a results of partial miscibility. When ABS content reached up to 50 % wt. (A050-PM050) impact strength was 4,60 kJ/m² with improvement of 183 % as

results of well mixed PMMA phases with SAN matrix and grafted butadiene rubbers[135] and also homogenous force transfer between phases.

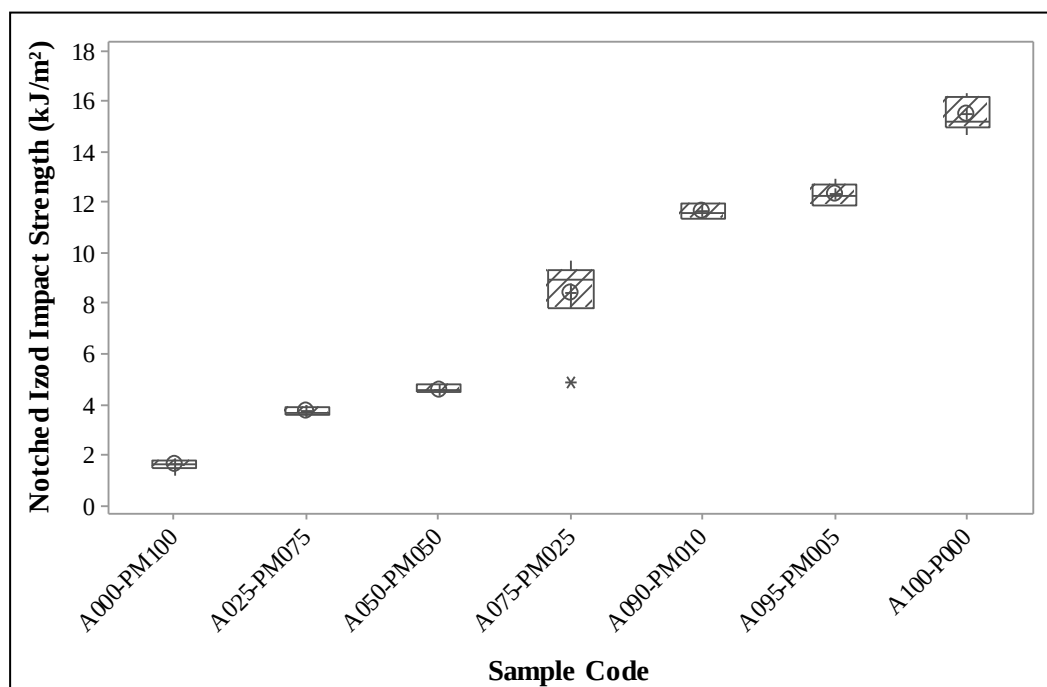


Figure 3.34 : Notched Izod impact properties of ABS/PMMA blends.

In summary, addition even small amount of PMMA into ABS enhance the gloss values. ABS blends with 5–10 wt. % PMMA could offer an appropriate solution by providing better surface appearance as well as reasonable mechanical properties.

3.5 Effects of Different Compatibilizers on ABS/PET/PMMA Terblends on Thermal and Mechanical Properties

In order to investigate the effect of different compatibilizers on properties of ABS/PET/PMMA terblends, different formulations were prepared as given in Table 2.6. All the ABS/PET/PMMA blends were prepared in a co-rotating twin-screw extruder as described in Chapter 2.2.1 with fixed processing conditions. Temperature profile for twin-screw extrusion was given in Table 2.9.

Arburg Allrounder 320 C injection molding machine was used to produce test specimens according to Chapter 2.2.2. Injection processing temperatures were given in Table 2.11 to inject all blends and the neat polymers.

The DSC curves of ABS/PET/PMMA blends with and without compatibilizers were shown in Figure 3.35. In order to dissociate the glass transition temperatures of ABS from that of PMMA, heating speed was decreased to 5 °C/minutes (Table 3.6).

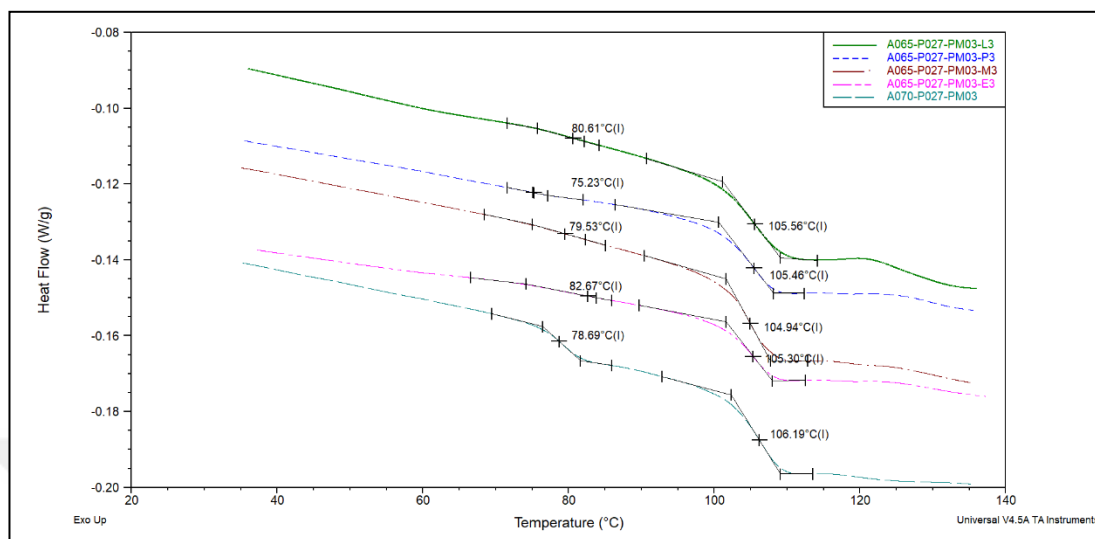


Figure 3.35 : DSC graphs of ABS/PET/PMMA terblends with and without compatibilizer.

Table 3.6 : DSC test results for 5 °C/min for ABS/PET/PMMA blends

Sample Code	T _g PET	T _g ABS	T _{cc}	ΔH _{cc} (J/g)	T _m	ΔH _m (J/g)
A070-P027-PM03	78,7	106,2	120	6,41	255,33	8,47
A065-P027-PM03-L3	80,6	105,6	123		259,81	11,2
A065-P027-PM03-P3	75,2	105,5	122		259,44	10,79
A065-P027-PM03-M3	79,5	104,9	122	4,91	259,18	12,03
A065-P027-PM03-E3	82,6	105,3	125	2,98	259,13	6,47

A slight improvement on the glass transition of the ABS was observed compared to previous results of T_g of ABS in ABS/PET blends. It was previously reported that lower heating speed should decrease the glass transition[139]. However, observed increase in T_g of ABS may be due to the compatibility of PMMA with ABS [133]. It was observed that T_g of PET decreased with addition of E-BA-GMA compare to other type of compatibilizer. This attribution might be related with degradation of butyl acrylate in E-BA-GMA since there was no stabilizer. Due to that initiated degradation might decrease in the chain length of PET[33,44] resulted in lower T_g.

Gloss values of the prepared samples were determined as described in Chapter 2.3.7. ABS was major phase in terblends and was supposed to occupy the mold surfaces described in previous Chapter 3.2.

Gloss is the measurement of reflected light beam from the surface [140] and only differences between the samples was the compatibilizing agent which was not supposed to effect surface properties, drastically [14,141]. As it shown in Figure 3.36.a, the gloss values in 20^0 were not differentiated from each other.

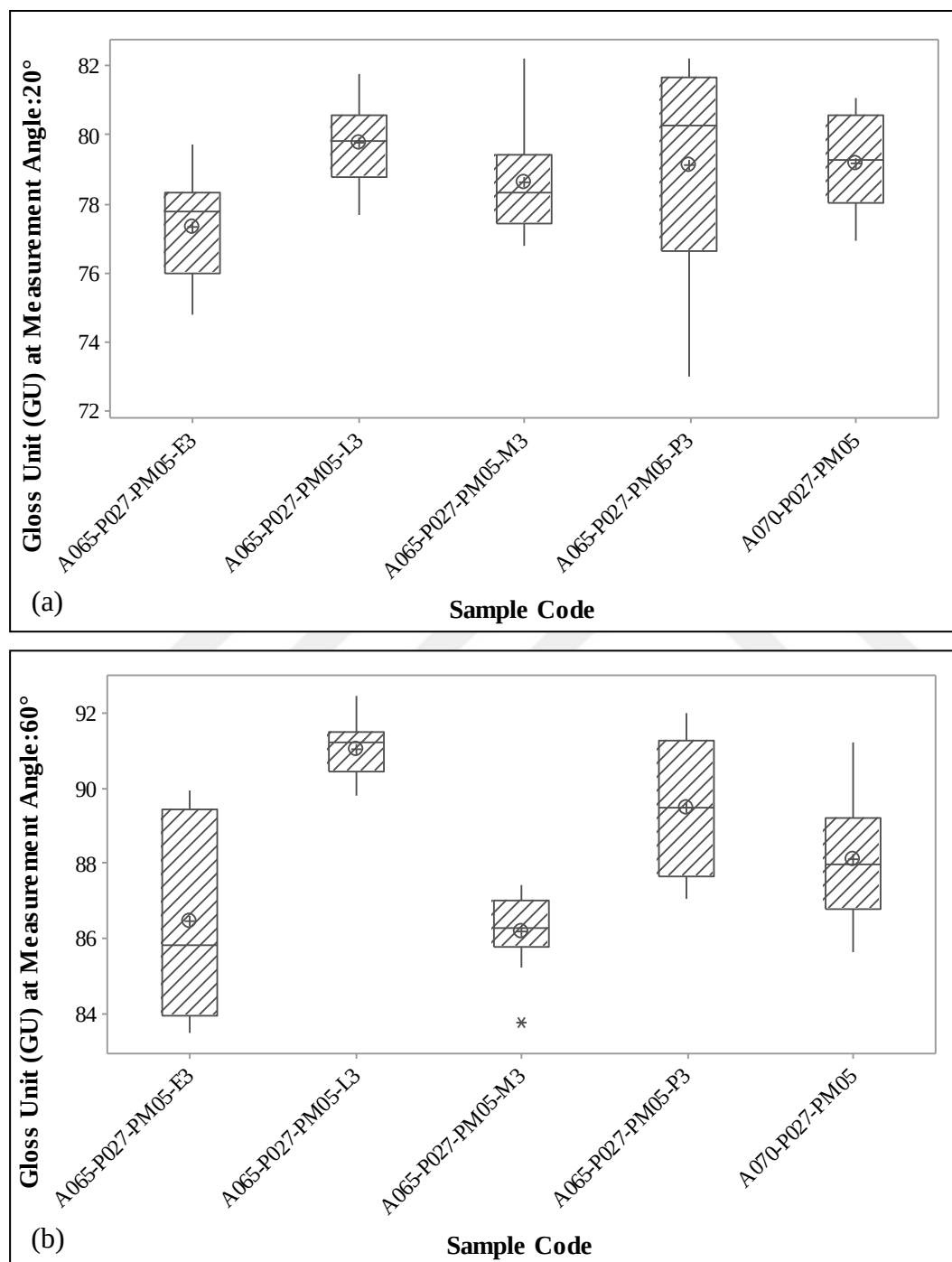


Figure 3.36 : Gloss measurements of ABS/PET/PMMA terblends with and without compatibilizer. a) Measurement Angle 20^0 and b) Measurement Angle 60^0

Different types of compatibilizer slightly effected the gloss value in 60^0 compared to uncompatibilized blend (A070-P027-PM05). Slight improvement in gloss values for

different types of compatibilizer E-EA-GMA and E-BA-GMA might be related with crystalline phase of compatibilizers. Similar observation was previously reported by Bociaga et al[142] for addition of coloring pigments into ABS. Scheirs[87] tried to explain this improvement in gloss value by side effect of compatibilizer. Compatibilizers might act as wax that migrated to the surface.

In order to check the formulation accuracy, density measurements were done according to Chapter 2.3.8. As it shown in the Figure 3.37, density values were between 1,12 to 1,13 g/cm³, which were in line with theoretically expected values according to the rule of mixture.

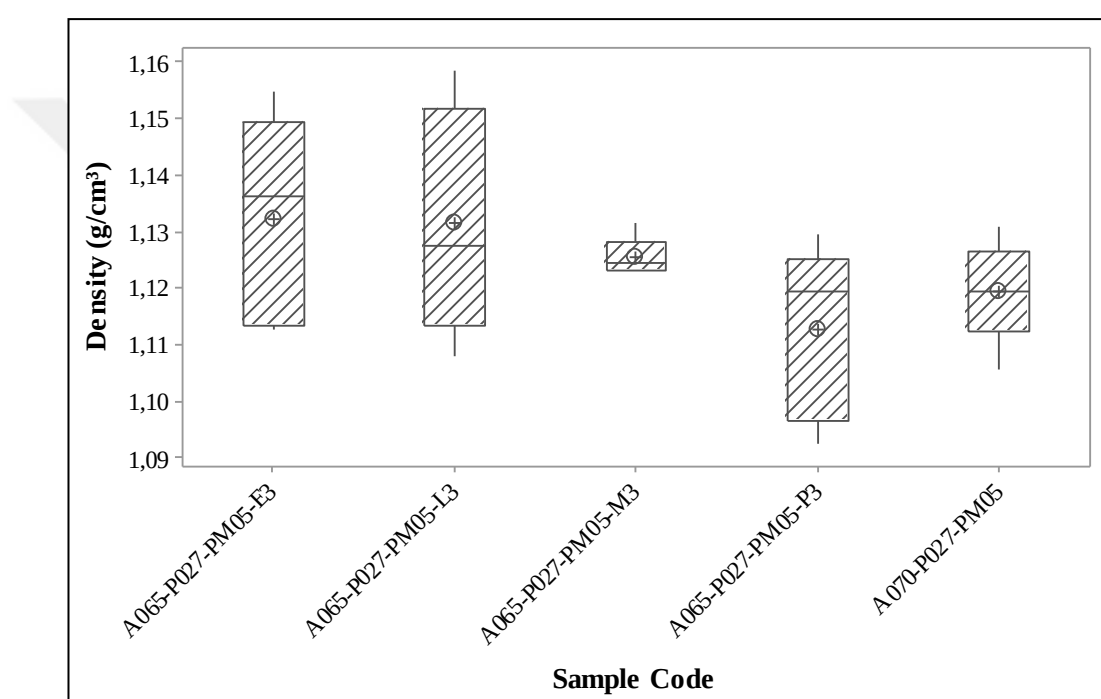


Figure 3.37 : Density measurements of ABS/PET/PMMA terblends with and without compatibilizer.

Tensile properties of terblends were measured according to Chapter 2.3.9.1 and shared in Figure 3.38. Blend without compatibilizer (A070-P027-PM05) had the highest tensile modulus value of 1911 MPa because of fiber like reinforcing effect of PET and PMMA[1,27,132,134] seen in SEM micrograph in Figure 3.10 and Figure 3.30. When compatibilizers having the rubbery structure were added into formulations, modulus values decreased down to 1689 MPa especially for the MA-g-EPDM which was miscible in PET phases [87]. For the other type of compatibilizers, tensile modulus value represented similar values as uncompatibilized blend. Although the materials (A065-P027-PM05-L3 and A065-P027-PM05-M3) has a rubbery content, it did not

cause any changes in the modulus value because rubbery content, i.e. SEBS, was not compatible with the PET.

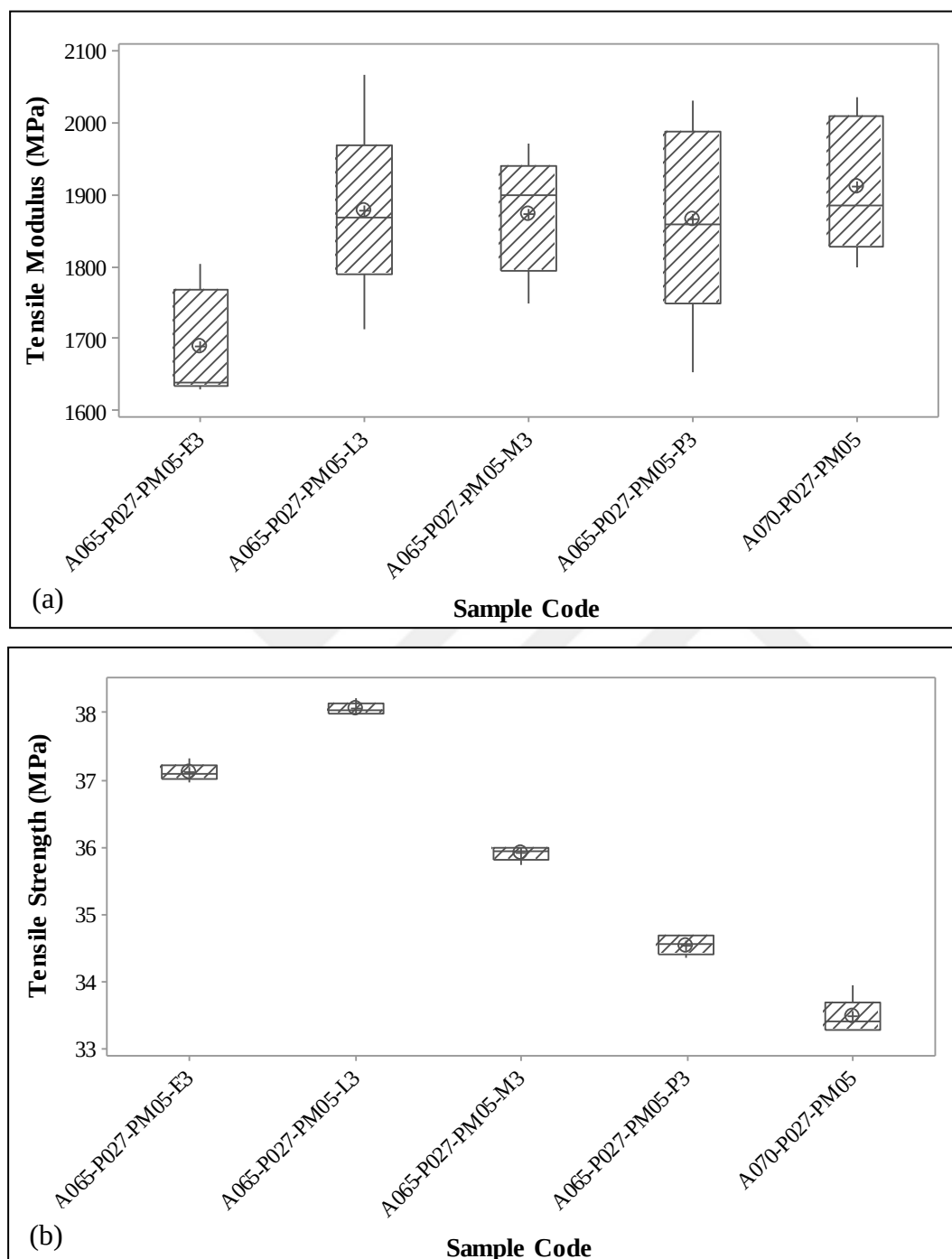


Figure 3.38 : Tensile properties of ABS/PET/PMMA terblends with and without compatibilizer: a) Tensile Modulus, b) Tensile Strength and c) Strain at Yield.

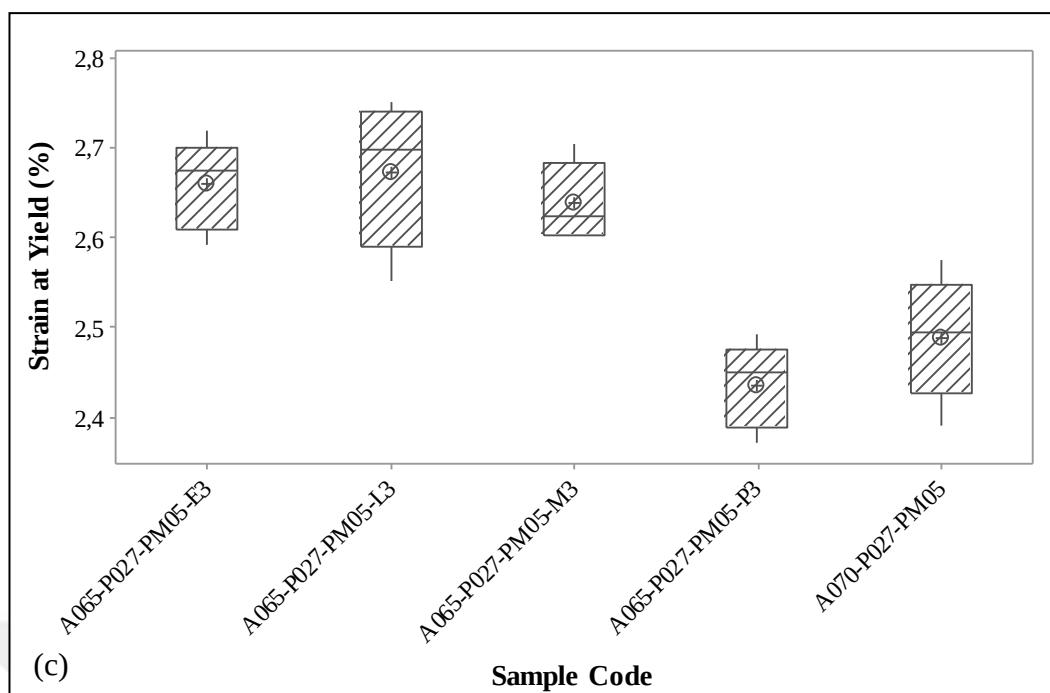


Figure 3.38 (continued): Tensile properties of ABS/PET/PMMA terblends with and without compatibilizer: a) Tensile Modulus, b) Tensile Strength and c) Strain at Yield.

Highest tensile strength as 38,1 MPa were measured for samples having E-EA-GMA compatibilizer. However, decreasing effect of rubbery-based compatibilizer (MA-g-EPDM) on modulus was not recorded. Due to improved interfacial adhesion even a slight increase from 33,9 MPa (A070-P027-PM05) to 34,5 MPa (A065-P27-PM05-P3) and 37,1 MPa (A065-P27-PM05-E3) were recorded. This behaviour could be explained by miscibility of functional group of compatibilizers with PET as explained by several researchers previously [69] [44,52].

The behaviour of tensile strength values of blends resulted slightly different from the modulus values. That could be explained as the measurement range of tensile modulus in a limited strain ranges as described in ISO 527 [114] standard which was the slope of stress-strain curve at 0,05 to 0,25 % without any plastic deformation. However, for the tensile strength, strain values could be much higher than those values. These high elongations were expected to create more deformation of the polymeric chains and also domains. This deformations were expected to be effected from the all ingredients of the formulations especially after exceeding the energy limits of void formation for each component[138].

The strain at yield value also mostly related with main phase of the blend [69,138] this value fluctuated between 2,48 % (A070-P027-PM05) and 2,67 % (A070-P027-PM05-L3).

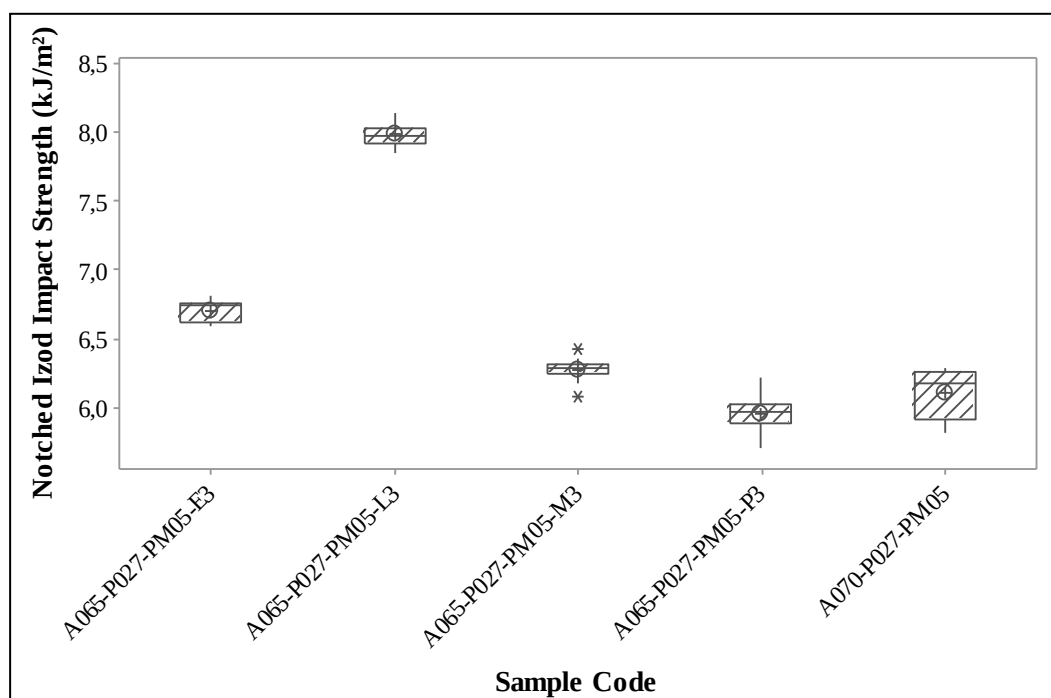


Figure 3.39 : Impact properties of ABS/PET/PMMA terblends with and without compatibilizer.

In order to investigate crack propagation under impact loading, notched Izod impact strength measurements were done as described in Chapter 2.3.9.2 and shared in Figure 3.39. By the addition of E-EA-GMA, notched Izod impact property was increased as 30 % from 6,11 to 7,99 kJ/m². This improvement was mostly related with the increased interfacial interaction between ABS and PET phases due to reaction of epoxide group of E-EA-GMA and PET as described by Hale et al[70,71,143]. The compatibilizers should create an interphase between the main phase (ABS) and PET by reacting with the end group of PET [144].

Unnotched impact strength measurement results were shared in Figure 3.40. By incorporation of PMMA into ABS/PET blend, unnotched impact strength were severely increased compared to ABS/PET blend. Also by the addition of any compatibilizer into terblend, further improvement in unnotched impact strength value was recorded. Highest strength value was obtained by the addition of E-BA-GMA (84,4 kJ/m²). Addition of E-EA-GMA also improved the strength to 78,6 kJ/m² as a results of creating a copolymer with PET by the reaction of GMA with end group of

PET as indicated by Scheirs et al [87]. Even though the compatibilizer (MA-g-EPDM) enhanced the miscibility with PET[69], having relatively high processing temperature to melt MA-g-EPDM possibly caused in degradation ABS.

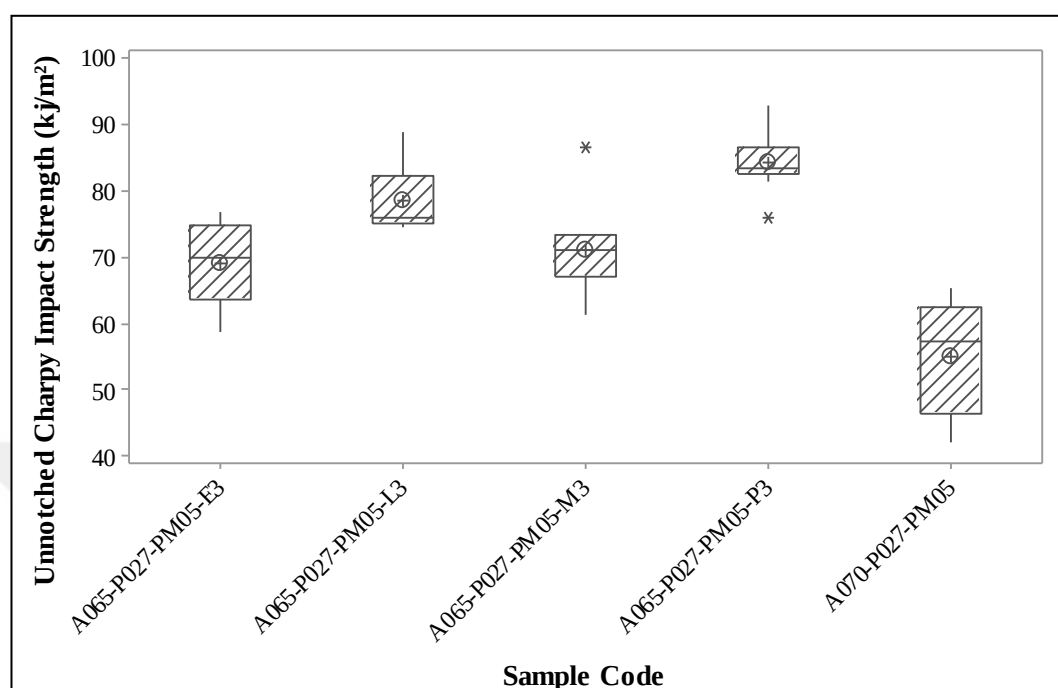


Figure 3.40 : Unnotched impact properties of ABS/PET/PMMA terblends with and without compatibilizer.

Among the different types of compatibilizers, E-EA-GMA and E-BA-GMA enhanced the mechanical properties of ABS/PET/PMMA blends without resulting any losing physical properties such as gloss values.

3.6 Effects of Nano Calcium Carbonate Reinforcements on ABS/PET/PMMA Blends

In order to investigate the combined effect of addition of different types of compatibilizers and nano CaCO_3 as filler into ABS/PET/PMMA terblends on properties, different formulations were prepared as given in Table 2.7. At first 10 wt. % nano CaCO_3 filler containing materials with ABS or PET resin carriers were produced as masterbatch and after drying them the masterbatches were introduced into the terblend in order to make sure about the concentration of the filler.

All the ABS/PET/PMMA terblend nanocomposites were prepared in a co-rotating twin-screw extruder as described in Chapter 2.2.1 with fixed processing conditions. Temperature profile for twin-screw extrusion was given in Table 2.9.

Arburg Allrounder 320 C injection molding machine was used to produce test specimens according to Chapter 2.2.2. Injection processing temperatures were given in Table 2.11.

Morphology investigation was performed as described in Chapter 2.3.3. It was observed from the Figure 3.41; two-phase morphology with PET particles being coarsely dispersed in the continuous ABS matrix was observed. Clear interfacial boundaries especially at the fractured surface which may be related with high interfacial tensions in between the phases indicating a poor adhesion, and this can be not sufficient compatibility of the polymer[123]. Due to having similar electron negativity of ingredients and also existence of the compatibilizer, it was not possible to get distinguished differences in the SEM images without etching. Only difference was that; due to better low temperature resistance of E-BA-GMA[20,71,145], some elongated regions similar to ductile fracture characteristics could be identified on the frozen fractured surfaces of samples.

It was seen from the Figure 3.42 that PET phase appeared as empty holes or “porosity” in the SEM images of blends, which were dissolved by 10 wt. % KOH in ethanol. PET formed a dispersed phase whose size depends on the composition especially in the mid region of test bars. Because of their low viscosity, they are selectively positioned at the center due to higher shear forces caused by injection pressure in the center. Similar observation was reported by Jing et al[90] for PC/PET sample. In E-EA-GMA compatibilized terblend (Terblend-L) resulted in more homogenous and spherical dispersed PET phases in ABS matrix. It was explained by Scheirs et al [87] the reaction between carboxylic acid end groups of PET and glycidyl methacrylate (GMA) end groups resulted in such morphology. Even though E-BA-GMA contained glycidyl methacrylate (GMA) end groups, the quantity of GMA in E-BA-GMA was less than that of E-EA-GMA. Therefore, performance of compatibilization of E-BA-GMA was lower. This behaviour might be also related with the viscosity differences of compatibilizers. Viscosity of E-BA-GMA reported as 12 g/10 min. at 190 °C 2,16 kg by the producer that was less than E-EA-GMA reported as 6 g/10 min. at 190 °C 2,16 kg by the producer. That difference might result in difference of dispersion level as reported by [86].

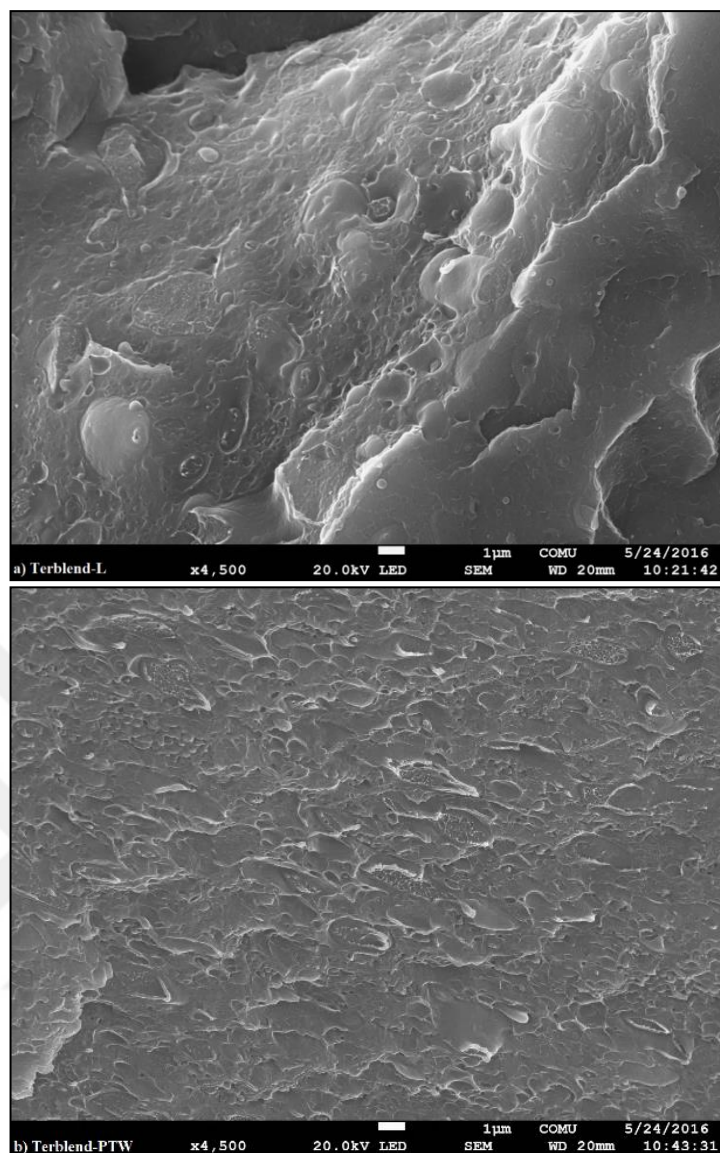


Figure 3.41 : SEM images of prepared blends without etching (a) Terblend-L and (b) Terblend-PTW.

SEM images of 2,7 wt. % nano sized calcium carbonate filled terblend prepared by using ABS carrier masterbatch (Terblend-L-A) and similar terblend prepared by using PET carrier masterbatch (Terblend-L-P) were shared in Figure 3.43 and Figure 3.44 respectively. As it was seen from the SEM images, distribution and shape of the dispersed PET phases were different from each other. Terblend-L-A exhibited smaller domain size and rounded PET particles compared to that Terblend-L-P. Smaller domain size and rounded PET particles in Terblend-L-A might be related with selective localization of nano sized CaCO_3 in ABS as similar to selective migration of organic montmorillonite into PA6 in PA6/PET blends due to interfacial effects [94].

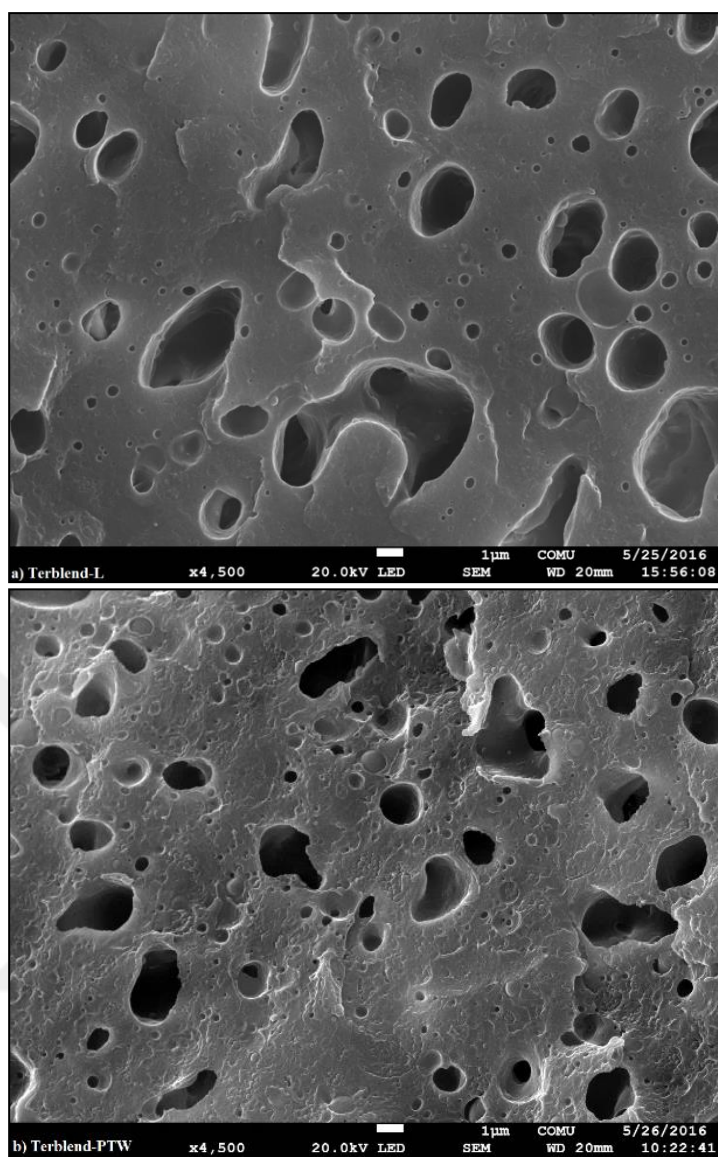


Figure 3.42 : SEM images of prepared blends with selective etching of PET phases
(a) Terblend-L and (b) Terblend-PTW.

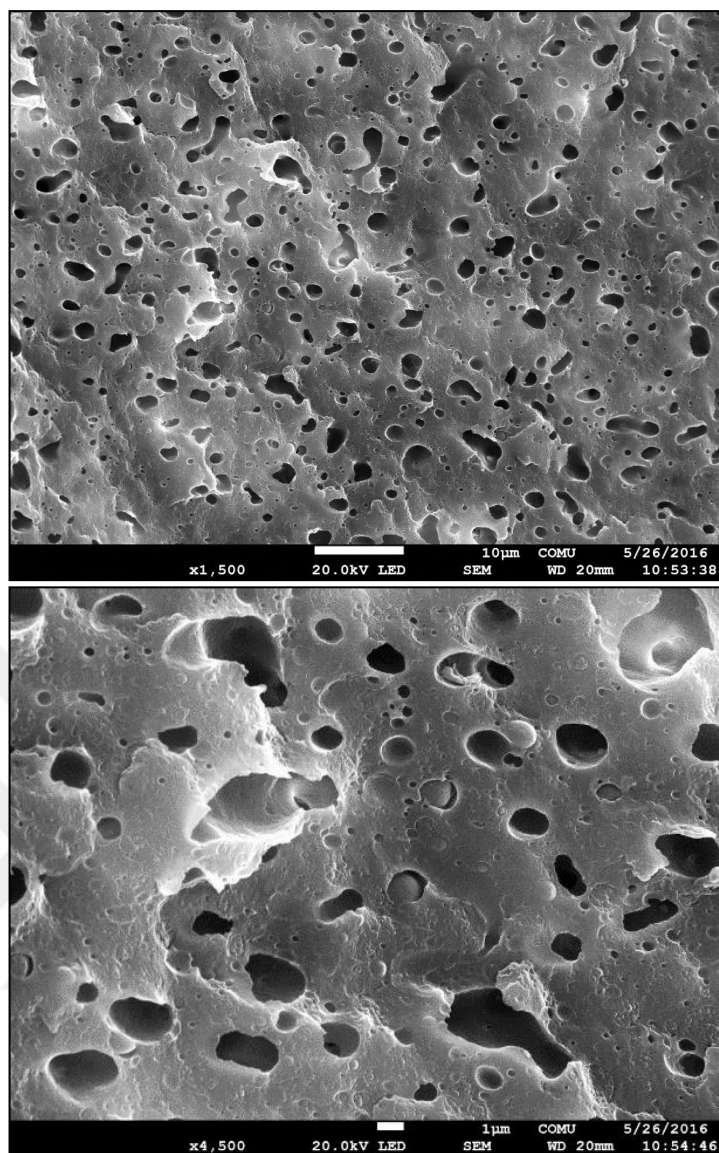


Figure 3.43 : SEM images of prepared blend (Terblend-L-A) with selective etching of PET phases.

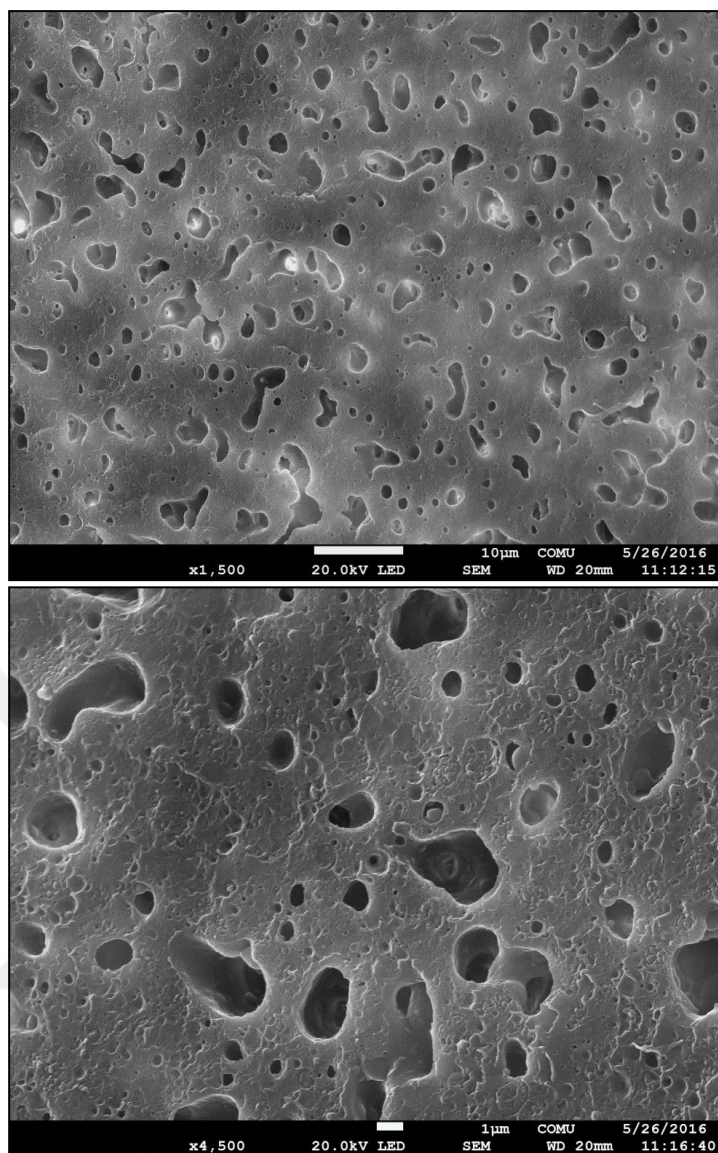


Figure 3.44 : SEM images of prepared blend (Terblend-L-P) with selective etching of PET phases.

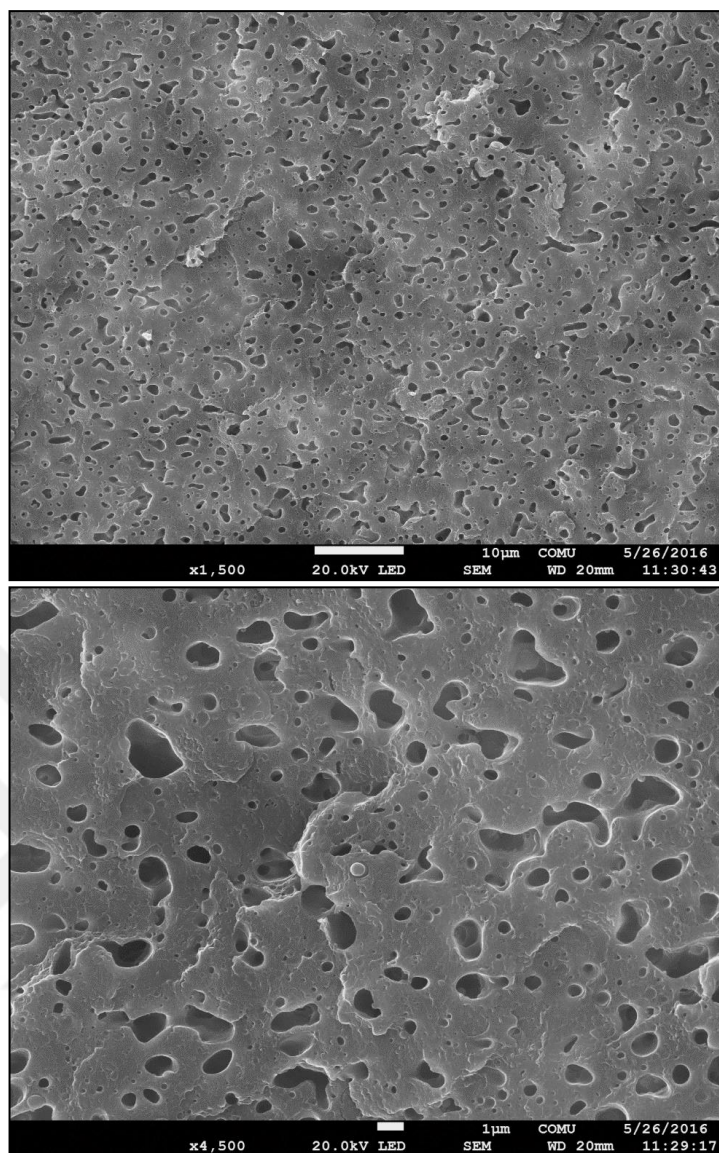


Figure 3.45 : SEM images of prepared blend (Terblend-PTW-A) with selective etching of PET phases.

Similar observation was also recorded for the terblends containing E-BA-GMA. Only difference was that much bigger and irregularly shaped PET domains were clearer. This could be a result of either degradation of E-BA-GMA or lower viscosity of E-BA-GMA at that processing temperature. Either degradation or low viscosity could improve the coalescence of PET phases or difficulty in dispersing the PET phases as indicated by Chiu and Ting[41] in their work related with PTT/PC blend.

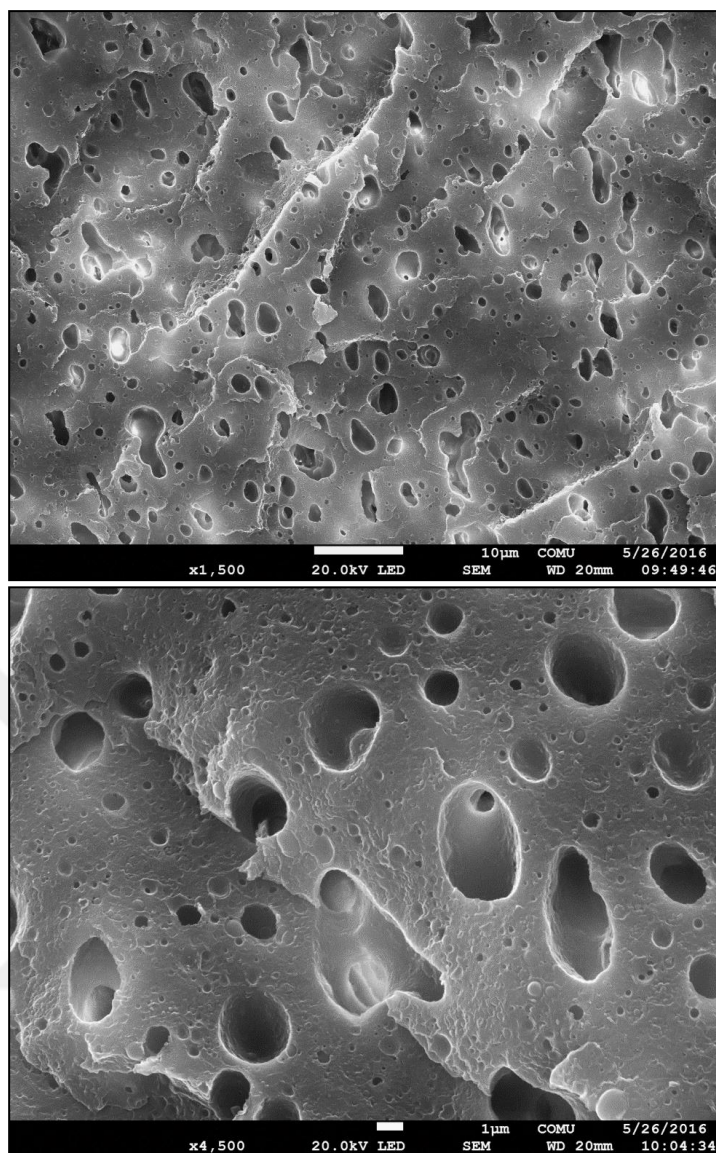


Figure 3.46 : SEM images of prepared blend (Terblend-PTW-P) with selective etching of PET phases.

Thermal investigation were applied according to Chapter 2.3.4 and the results were summarized in Table 3.7. The glass transition temperature of all types of terblends increased compared to unfilled PET.

However, the glass transition depletion of PET phase caused by processing was not detected. Similar result was reported by Di Lorenzo et al[104] and explained that, addition of surface coated nano CaCO_3 resulted an increase in the glass transition temperature of PET by improved polymer filler interaction. Another approach was indicated by Liu et al [146] in their study related with that addition of E-BA-GMA in PLA matrix, compatibilizers could act as chain extender during processing.

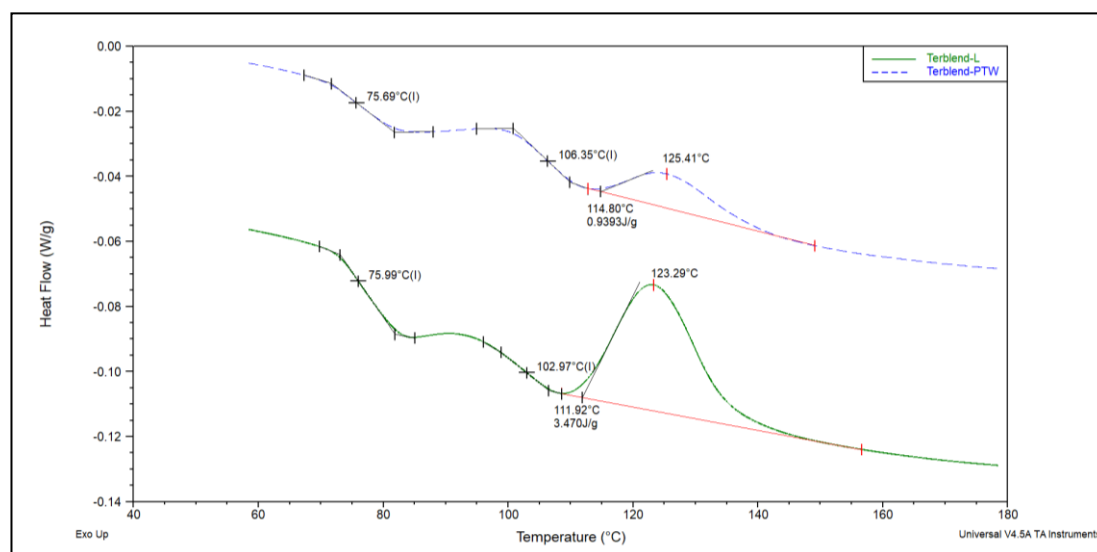
Table 3.7 : DSC measurement results of prepared terblends

Sample Code	T _g PET	T _g ABS	T _{cc}	ΔH_{cc} (J/g)	T _m	ΔH_m (J/g)	T _c	ΔH_c (J/g)	χ_c %
Terblend-L	76	103	123	3,47	258	12,72	203	10,15	25,2
Terblend-L-A	76	104	124	4,53	258	12,85	201	7,25	22,7
Terblend-L-P	75	105	124	7,05	259	17,48	200	9,41	28,4
Terblend-PTW	76	106	125	0,94	258	10,89	199	6,92	27,1
Terblend-PTW-A	77	106	125	0,70	258	10,78	200	6,76	27,4
Terblend-PTW-P	77	104	123	0,45	260	13,48	201	8,55	35,5

There was no clear variation in the glass transition temperature of ABS phases. ~1-2 °C variation in T_g might be related with the effect of partially miscible PMMA phases and compatibilizers.

The significant difference was observed in the heat of fusion at the cold crystallization values that depends on the type of compatibilizer (Figure 3.52). During the heating stage, amorphous phases of PET might start to nucleate right after the glass transition. Due to having more polymeric chain flexibility after T_g, metastable crystals nucleated and growth concluding with reordering of metastable crystals[147].

As it was indicated previously, cold crystallization temperature was suppressed from 120 °C to 109 °C by decreased frozen PET chain mobility as ABS content increased [27]. The addition of any type of compatibilizers brought the cold crystallization back to 123 °C. Improved interaction between main phase ABS and PET by the addition of compatibilizer might decrease the chain mobility of PET. Due to that, nucleation and reorganization of metastable PET crystals might be postponed to higher temperatures.

**Figure 3.47 : Partial DSC graphs of prepared blend Terblend-L and Terblend-PTW.**

Another interesting finding was that, with the addition of nano CaCO_3 masterbatches with PET carrier (Terblend-L-P and Terblend-PTW-P), heat of cold crystallization values were higher than that of the ABS based masterbatches.

Twice extrusion process; preparation of nano CaCO_3 filled PET masterbatch and then preparation of blends, improved the dispersion of nano particles. This type of well distributed nano particles could also improve the crystallinity of PET as similar to that of the neat polymer within the blend[104].

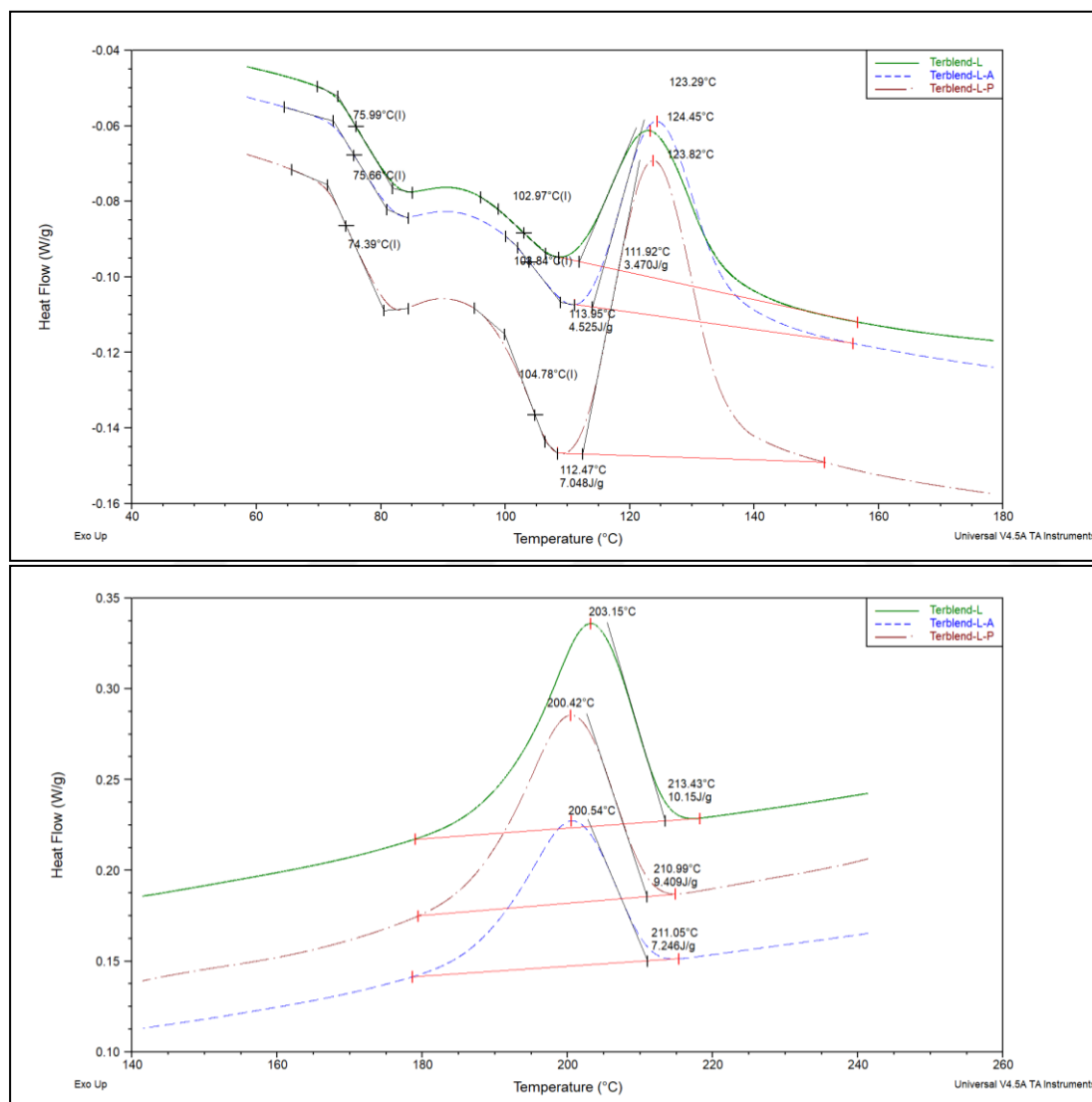


Figure 3.48 : Partial DSC graphs of prepared blend Terblend-L, Terblend-L-A and Terblend-L-P.

In the melting temperature of crystalline PET, phases were not depleting regardless of the composition. T_m of PET in the blends oscillated around 259 °C Wellen [148]. The crystallization temperature during the cooling process increased from 181 °C to 194 °C by the addition of ABS. Addition of E-BA-GMA or alternatively of E-EA-GMA

increased T_c to 199°C or 203 °C, respectively. An increase in crystallization temperature indicated that, addition of compatibilizers improved the nucleation effect of ABS resulting in the increased PET crystallinity and hence facilitated easier injection molding for the blends.

It could be explained that the addition of other phases like ABS, PMMA, compatibilizer or nano particle, initiated crystals of PET in a terblend. This improvement could definitely eased PET injection process as indicated by Scheris et al [87].

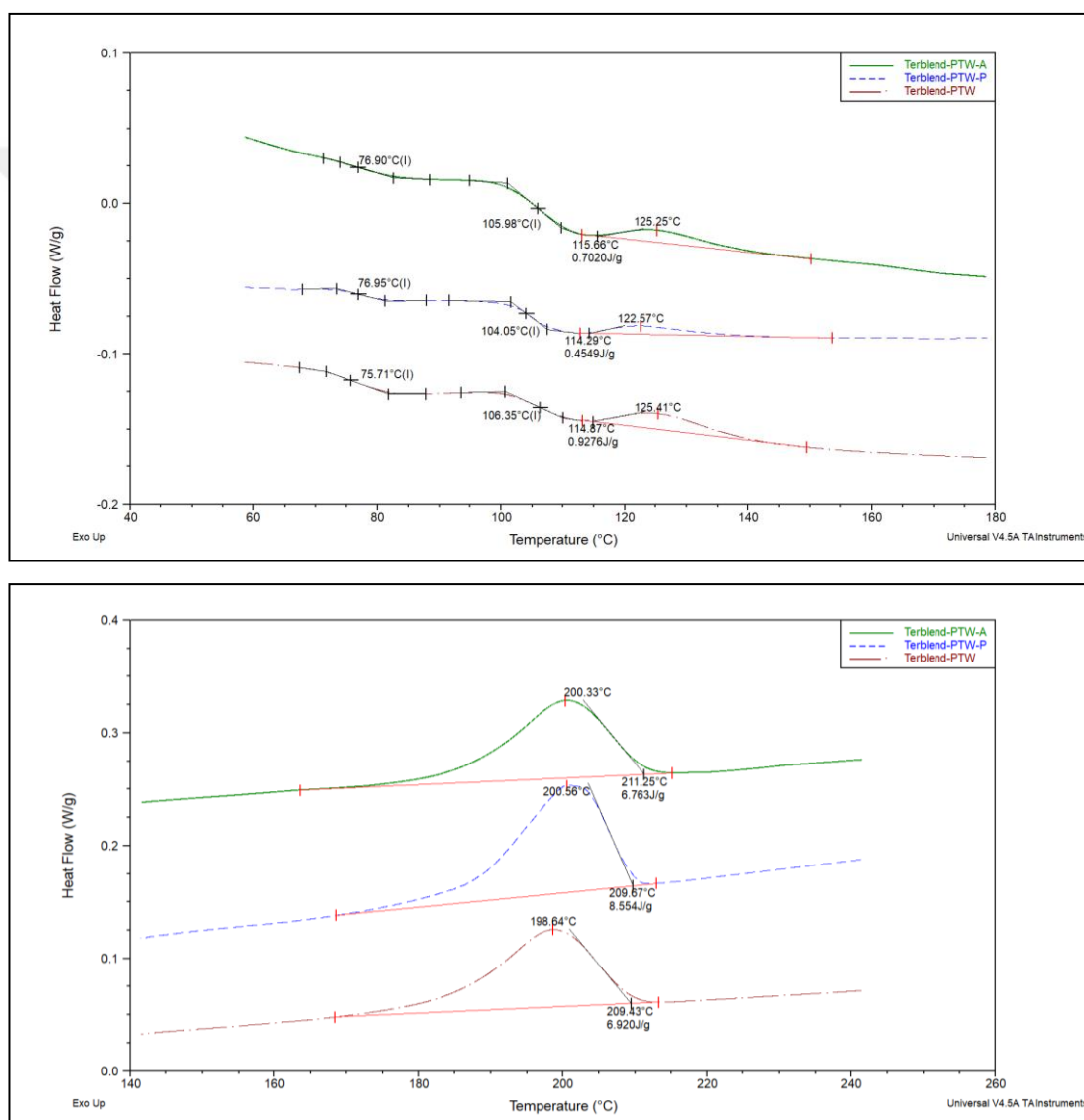


Figure 3.49 : Partial DSC graphs of prepared blend Terblend-PTW, Terblend-PTW-A and Terblend-PTW-P.

The dimensional stability of terblends and nanocomposites were measured as described in Chapter 2.3.5 and shared in Figure 3.50. For all the terblends, change in

dimensions with respect to the test temperature were increased. In the case of addition of a PET carrier masterbatch containing 2,7 wt. % CaCO_3 (Terblend-L-P and Terblend-PTW-P), the dimensional stability is slightly improved.

As it was pointed out previously in Chapter 3.2, dimensional change of neat ABS, PET, blend containing 30 wt.% PET after aging were reported as -9.50 %, -0.49 %, -1,19%, respectively (Figure 3,15).

For unfilled terblends (Terblend-L and Terblend-PTW), the dimensional change at 125 °C is measured as -1,21 % and -1,15% respectively. When PET carrier nanofiller introduced the matrix these values were shifted up to -0,96% (Terblend-L-P) and -0,99% (Terblend-PTW-P).

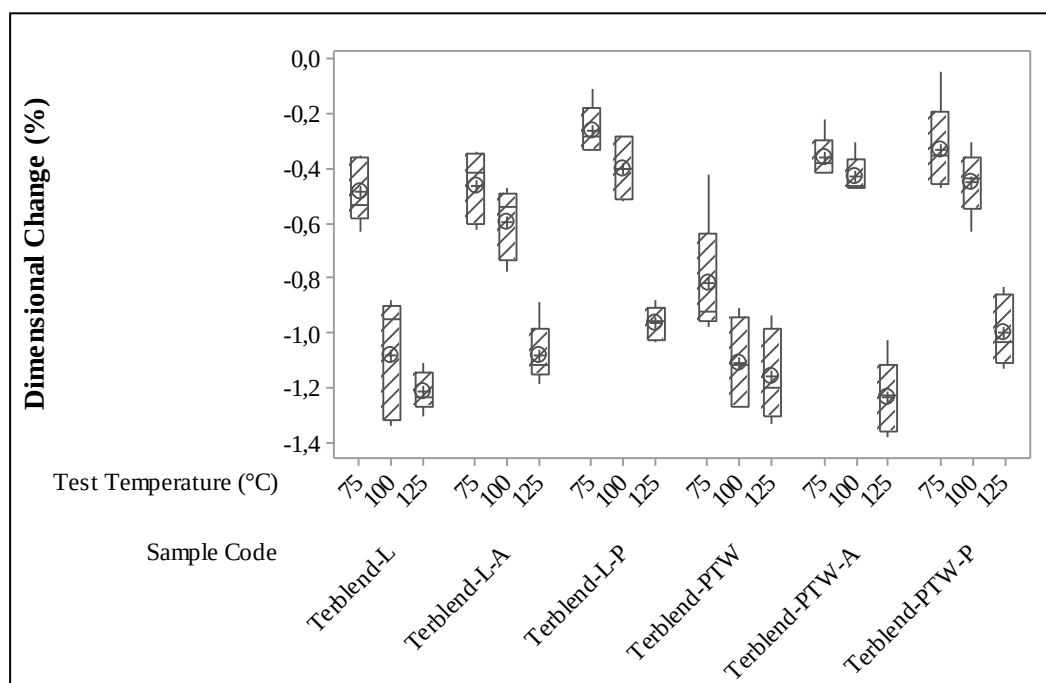


Figure 3.50 : Dimensional change versus terblend after conditioning at 75, 100 and 125 °C for 48 hours.

Cooling time differences in different areas and different layers were creating an internal stresses in the injection-moulded parts and so solidified layers especially on the surfaces were created the residual internal stresses.

In order to have less internal stress in the injected parts, higher injection temperature to decrease viscosity and less holding pressure should be preferred as discussed by the research of Postawa and Kwiatkowski[149]. As pointed out in the thermal studies (Table 3.7) initiated solidification of the PET (crystallization temperature) improved with the addition of nano CaCO_3 and ABS and so, at first the PET fibrils and droplets

are expected to occur. During the holding/packing stage of the injection molding, low viscosity ABS phases could cool down to below T_g with less internal stress because of applying less time for holding/packing pressure. This can be related with increased glass transition temperature of ABS that could help solidification at the feeding channels.

Figure 3.51 showed the gloss measurements. As reported previously in Chapter 3,2 and shown in Table 3.2, the gloss value of ABS at 60° measurement angle was 90 ± 2 GU and for the blend containing 30 wt.% PET (A070-P030) 88 ± 3 GU. When the gloss of Terblend-L and Terblend-PTW were measured as 66 ± 1 and 71 ± 2 , respectively. By the addition of PET carrier, Nano sized CaCO_3 masterbatch (Terblend-PTW-P) that value were found to decrease to 57 ± 1 .

Several factors such as; compounding conditions, phase morphology, mismatch of refractive indices[46] and micro surface roughness resulted by addition of filler [57] could affect the surface gloss[140]. As explained in the morphology investigation section of ABS/PET blends (chapter 3,2), ABS phase was selectively migrating towards the part surface in the solidification phase of the injection molding process. Nano sized CaCO_3 existence increased roughness of ABS-rich skin.

Even though Kale et al[42] noted that the PET could be used to improve the gloss value of ABS, addition of Nano sized filler into amorphous product could decrease the gloss value of the material due to increase the surface roughness. Creating a terblend could also decrease the gloss value due to mismatched refractive indices on the surface of the material[46].

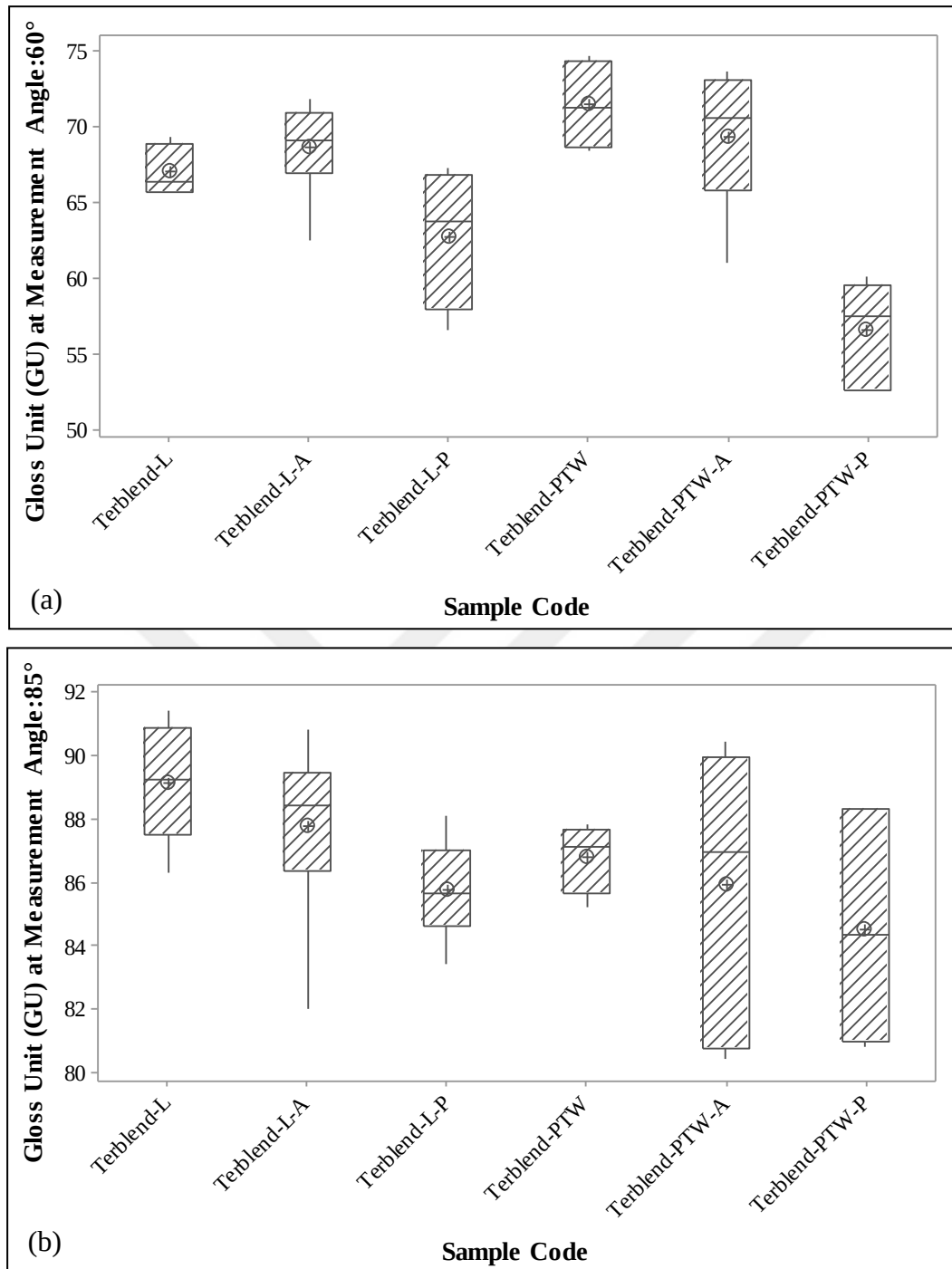


Figure 3.51 : Gloss measurements of terblends and nanocomposites: a) Measurement Angle 20° and b) Measurement Angle 60°

In Figure 3.52, tensile properties applied according to Chapter 2.3.9.1 for terblends and nanocomposites were shared. Unfilled compatibilized terblends did not show a significant difference in tensile properties. Elongation at yield value for all the samples were varying around 2,4 %. It was related with that the major phase (ABS) countered reaction against applied tensile force before cavitation and deformation[69,138]. The addition of nano filler decreased the chain movement in the major ABS phase and also

for PET as discussed in thermal properties. Due to that, elongation at yield value was found to be reduced to 2,17 %. Strain at break value drastically decreased from 54,3 % (for Terblend-PTW) to 16,5 % (for Terblend-PTW-P). Nano CaCO_3 filled terblends showed an improvement in the tensile modulus due to polymer/filler interaction. Nanocomposites did not show improvement in the tensile strength as a result of having low aspect ratio of the irregular cubic structure of filler compared to high aspect ratio nano fillers like MMT[10]. When strain values exceed strain value corresponding to the particle/polymer bonding strength, voids resulted permanent deformation. However, usage of nano size filler having a low aspect ratio resulted in tensile strength similar to unfilled matrix in contrary to behaviour of micron sized CaCO_3 filler[98].

Terblend-L-P had higher tensile modulus and tensile strength value 2105 MPa and 36,0 MPa, respectively. However, Terblend-PTW-P did not show the same trend.

Due to rubber phase of E-BA-GMA, the individual strength of compatibilizer would be lower. Insufficient PET dispersion as discussed in morphology section would also result in lower strength.

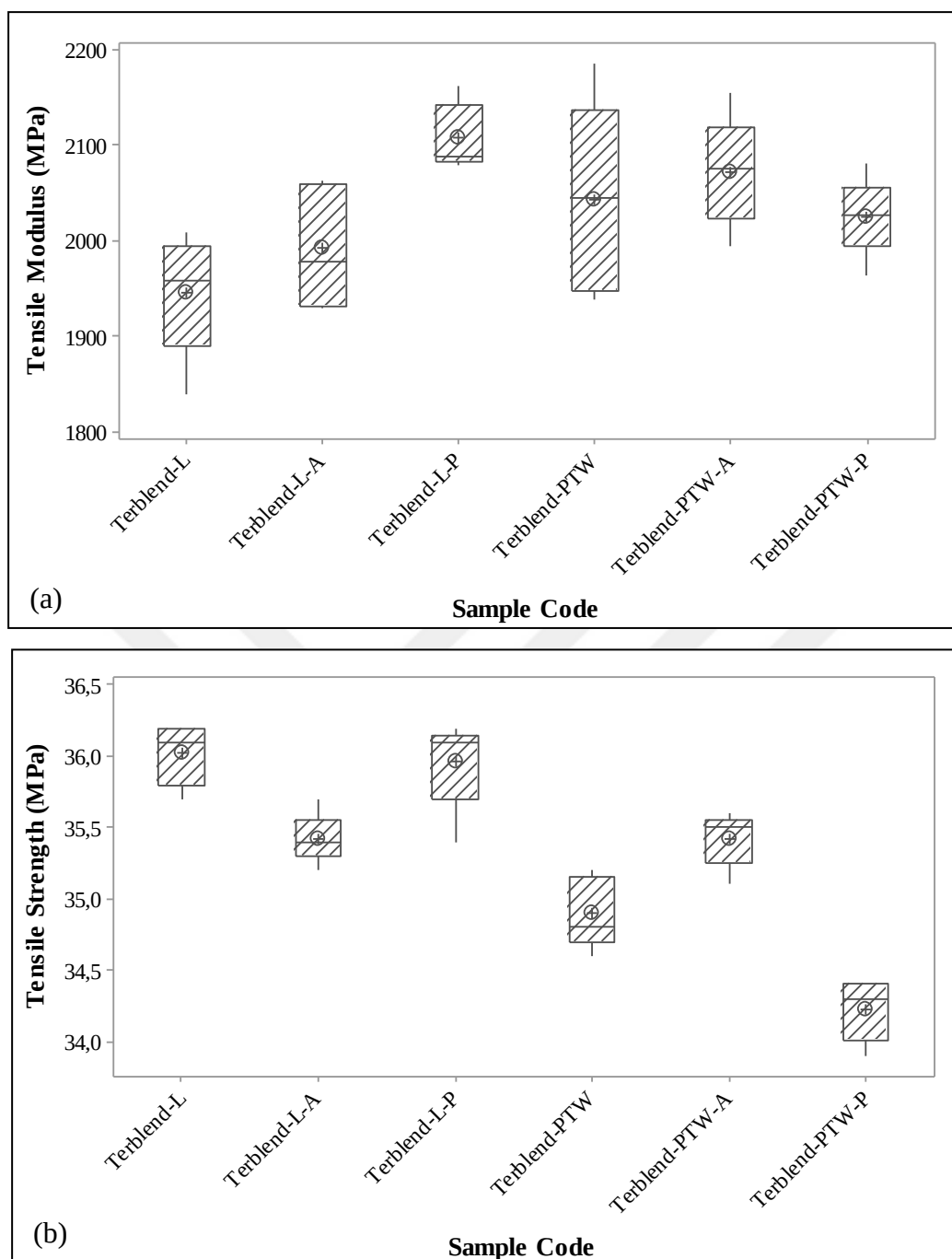


Figure 3.52 : Tensile testing measurements of terblends and nanocomposites: a) Tensile Modulus, b) Tensile Strength, c) Strain at Yield and d) Strain at Break.

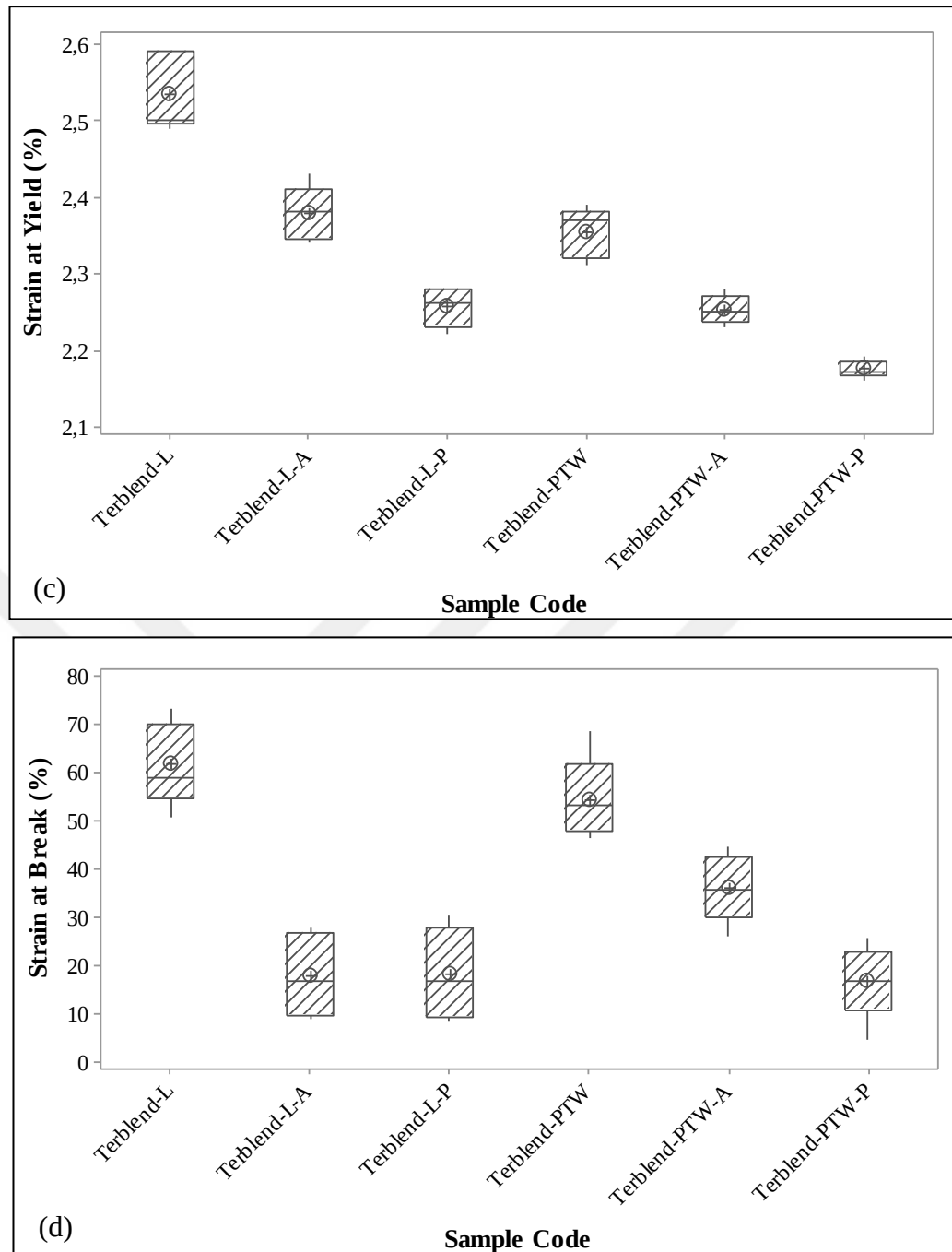


Figure 3.52 (continued): Tensile testing measurements of terblends and nanocomposites: a) Tensile Modulus, b) Tensile Strength, c) Strain at Yield and d) Strain at Break.

Notched impact properties of terblends and nanocomposites shared in Figure 3.53. Homogenously dispersed fine rubber domains of ABS had resulted in higher impact strength[43,129]. On the other hand, by the addition of PET[33,44,96] and PMMA[150] due to not having such a domains, it was expected to absorb less energy at high deformation rates like notched impact tests.

Due to effect of improved interaction of blend ingredients by addition of compatibilizers[30,49,67] impact strength were increased up to 6,23 kJ/m² (Terblend-L). By the incorporation of nano sized low aspect ratio CaCO₃, impact strengths were slightly decreased to 6,01 kJ/m² (Terblend-L-P) but this decrease is less compared to micron sized CaCO₃ filler as discussed by Jiang et al[98]. This effect could be explained by the larger interfacial area of nano sized CaCO₃ leading an improvement of bonding strength between the particle and matrix compared to micron-sized filler. In addition to this, less tendency to cavitation-induced shear yielding for toughening of particle-filled polymers could be used to explain this phenomenon. Due to having less cavitation at the boundary of the nano particle and matrix, it could not trigger of shear yielding type of failure between the two cavities in the matrix [1,98].

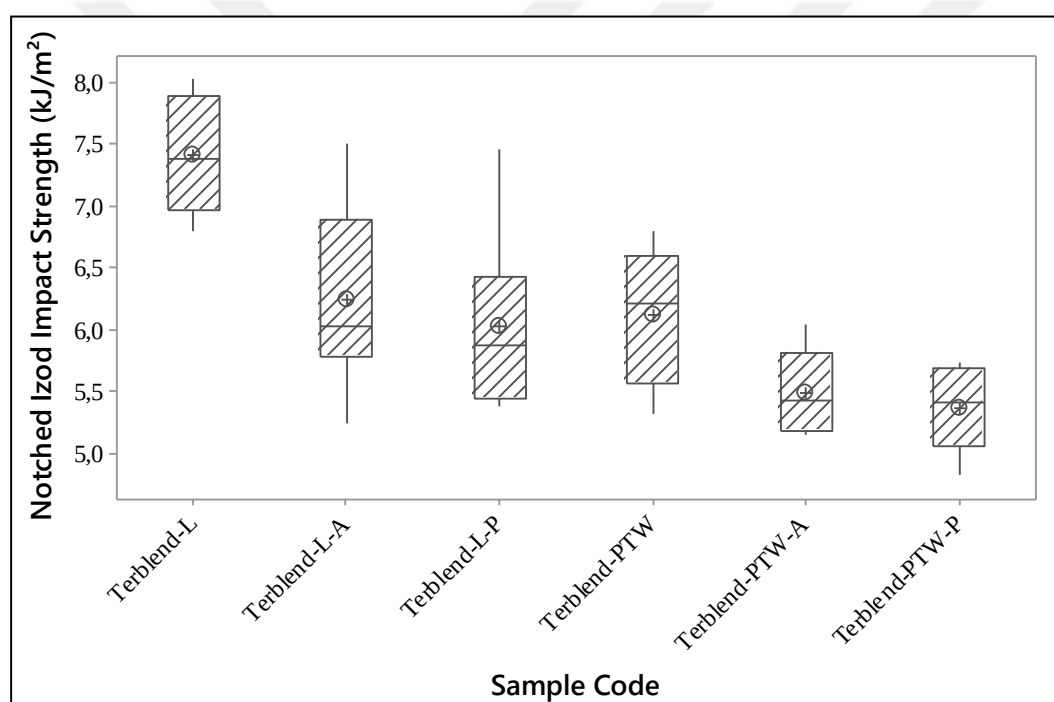


Figure 3.53 : Izod notched impact measurements of terblends and nanocomposites.

4. CONCLUSIONS AND RECOMMENDATIONS

The main objective of this study is to develop a material, which can withstand the higher process temperatures subjected during the paint curing process by improving dimensional stability while maintaining mechanical and physical properties with reasonable price to shorten the painting process cycle time by replacing the neat ABS material for the visual applications.

During this studies, possible effect of high extrusion processing temperature profile on neat ABS material were investigated. No drastic change on properties of ABS was recorded for investigated temperature profiles.

In order to investigate effect of ABS/PET ratio on rheological, morphological, thermal and mechanical properties as well as dimensional stability property after aged at elevated temperature, ABS/PET blends with varying ratios were prepared by melt blending techniques within a twin screw extruder.

It was observed that addition of ABS into PET resulted in the improvement of processability of PET.

Higher amount of ABS in blend resulted in non-Newtonian rheology and created more stable processing conditions for PET. Phase morphology of ABS/PET blends depended on blend ratio and was varying from sea/island to continuous morphology. Addition of PET did not worsen the gloss values. ABS-rich phase was selectively migrating towards the part surface in the solidification phase of the injection molding process, while the PET-rich phase was detected below the ABS-rich skin. Due to that, no difference in the process conditions was expected for the paint applications.

Due to improved stress relaxation behavior of ABS/PET blends, dimensional stability of ABS after aging conditions (aged at 125_C for 48 h) was improved with the addition of even 20 wt.% PET into ABS.

An increase in the tensile strength of blends by the increased PET content was recorded, however due to immiscible structure of ABS and PET impact strength decreased drastically.

Even though injection molding was the second and final processing step for blends, higher process profile in injection molding caused higher and irregularly shaped PET particulates in uncompatibilized blends. Also by the addition of compatibilizer, distribution and stability of PET phases were improved by getting smaller particle sizes with more uniformity. However, at high injection molding temperatures, efficiency of compatibilizers decreased due to change in viscosity. Thermal fingerprints of the ingredients of the blends were observed in uncompatibilized and compatibilized ABS/PET blends. Presence of compatibilizers in the blend increased the heat of fusion value at cold crystallization. This attitude might be an evidence of increased annealing effect of amorphous PET domains and increased spherulites sizes. Positive effect of compatibilizer was seen on the mechanical properties of blends especially on the impact properties except PETG.

5 to 10 wt. % loading of PMMA into ABS matrices improved the surface gloss slightly. For 50 wt.% and 75 wt.% loading of PMMA, single glass transition point was recorded due to miscibility of ABS in PMMA phase. Rule of mixture theory was valid for the mechanical properties of blends without effecting the strain at yield value, which is important for the snap fit applications.

Gloss values of ABS/PET/PMMA did not alter in the case of presence or unpresence of compatibilizer since the ABS covered mold surfaces due to viscosity differences of blend ingredients. Presence of E-EA-GMA compatibilizer in terblend improved tensile strength as 12 % and impact properties were increased as 30 % due to improved interfacial adhesion between phases.

Nano sized CaCO_3 was added into ABS/PET/PMMA terblend by preparing masterbatches with either ABS or PET as a carrier. Additionally, two different type of compatibilizer were introduced into the final blends. Masterbatches having different carrier were added into terblend. Masterbatch with ABS carrier resulted in smaller domain size and rounded PET phases in terblends compared to masterbatches with PET carrier. From the different types of compatibilizers, E-EA-GMA improved the

PET dispersion by the possible reaction of higher amount of epoxide group compared to E-BA-GMA.

Addition of compatibilizer and nano filler into terblends improved the thermal resistance by eliminating the decrease on glass transition temperature of PET phase, which is sensitive to the temperature. Compatibilizer type influenced the heat of fusion of PET at cold crystallization and E-EA-GMA improved the cold crystallization ratio.

In addition, the terblends containing PET carrier nano filler masterbatch, heat of cold crystallization and crystallization values were higher compared to the terblends containing ABS carrier nano filler masterbatch. That observation was valid for both types of compatibilizer.

In dimensional stability point of view, it was recorded that PMMA and nano filler did not cause a distinguished improvement. Main effect was coming from PET phase in terblends.

A slight decrease in gloss values for compatibilized and nano sized CaCO_3 filled terblends were recorded due to increase in surface roughness caused by filler.

Compatibilizer types in terblends did not show a significant difference in tensile properties. However, for nano CaCO_3 filled terblends, tensile modulus was improved. PET based nanofiller masterbatch with E-EA-GMA compatibilizer had higher tensile modulus and tensile strength value. Improved interaction of immiscible blend ingredients by addition of compatibilizers, impact strength were increased. On the other hand, incorporation of nano sized CaCO_3 , impact strengths were slightly decreased due to low aspect ratio of nanofiller.

4.1 Practical Application of This Study

Due to new trends on the markets and competition in global world creates a pressure on the shoulder of producers. The demand of visually attractiveness and introduction of fancy products into market are increasing.

Appliance, consumer electronics and automotive industries are examples of industry branches, which struggle against those market demands.

Especially for the appliance industry, front panels of home appliance, such as refrigerator, washing machines, etc..., in which customer is touch with the device are

produced from ABS. Recent trends in the market, force the producers to differentiate their products from each other's and so more colorful products has been demanded like red, blue or black colored machines.

ABS is the one of the mostly preferred product due to several properties like; low shrinkage after injection, glossy surface, proper mechanical properties and paintability. For this kind of applications, several post processes are applied like painting. However, additional such post process are relatively expansive due to high processing cost caused by due to curing at low temperature such as 75 °C for 45 minutes.

In the paint curing process, ABS is covered by paint and then curing process at 75 °C for 45 minutes, since ABS lost its dimensional stability when subjecting to at higher temperature. Due to that, lower curing temperature but longer curing time most selected. Longer curing time increases process cost because it cause to increase in storage cost, equipment cost as well as increase in electricity consumption for longer duration.

By the usage of newly developed terblend or terblend nanocomposites for replacement of ABS, higher curing temperatures like 100 to 125 °C can be used to decrease curing time. By increasing temperature and decreasing the curing time, process costs of painted products can be decreased and so more competitive product can be launched to the market.

In the production of some parts like the interior parts of automobile, or surfaces of grill, or any hot surfaces of home equipment, ABS cannot be used, although superior surface properties are required. Because ABS has lost dimensional stability at elevated temperature and those kind of parts are subjected to temperature during their service life. It will be possible to produce such parts with superior surface properties by using one of the already developed blends.

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APPENDICES

APPENDIX A: Detailed Injection Molding Process Parameters of Samples



APPENDIX A: Detailed Injection Molding Process Parameters of Samples

Table A.1 : Injection molding process parameters for ABS and its blends.

	Unit	Tensile Bar	Impact Bar	Plate
Shot Volume	cm ³	36	38,4	50
Screw Rotation Speed	rpm	10	10	20
Backpressure	bar	20	30	40

Injection Process				
	Unit	Tensile Bar	Impact Bar	Plate
1. Step				
Injection Speed	cm ³ /s	153	100	153
Injection Pressure	Bar	800	900	1200
Change Point	cm ³	18	18	25
2. Step				
Injection Speed	cm ³ /s	153	110	153
Injection Pressure	Bar	900	900	1200
Change Point	cm ³	6	8	10
3. Step				
Injection Speed	cm ³ /s	153	100	153
Injection Pressure	Bar	1000	1000	1200
Change Point	cm ³	2	3	5

Holding Process				
	Unit	Tensile Bar	Impact Bar	Plate
1. Step				
Holding Time	s	0,2	0,2	0,2
Holding Pressure	Bar	800	800	800
2. Step				
Injection Speed	s	3	6	4
Injection Pressure	Bar	600	700	400
3. Step				
Injection Speed	s	2	4	3
Injection Pressure	Bar	300	500	300

Table A.2 : Injection molding process parameters for PET.

	Unit	Tensile Bar	Impact Bar	Plate
Shot Volume	cm ³	36	40	52
Screw Rotation Speed	rpm	10	10	20
Backpressure	bar	20	30	40

Injection Process				
	Unit	Tensile Bar	Impact Bar	Plate
1. Step				
Injection Speed	cm ³ /s	153	100	153
Injection Pressure	Bar	600	600	1200
Change Point	cm ³	18	28	35
2. Step				
Injection Speed	cm ³ /s	153	110	153
Injection Pressure	Bar	800	900	1200
Change Point	cm ³	6	18	15
3. Step				
Injection Speed	cm ³ /s	153	100	153
Injection Pressure	Bar	1200	1200	1200
Change Point	cm ³	2	3	5

Holding Process				
	Unit	Tensile Bar	Impact Bar	Plate
1. Step				
Holding Time	s	0,2	0,2	0,2
Holding Pressure	Bar	800	800	800
2. Step				
Holding Time	s	3	6	4
Holding Pressure	Bar	600	700	400
3. Step				
Holding Time	s	2	4	3
Holding Pressure	Bar	300	500	300



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