SYNTHESIS AND CHARACTERIZATION OF POLY(ETHER/ESTER) BASED THERMOPLASTIC ELASTOMER NANOCOMPOSITES

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF POLY(ETHER/ESTER) BASED THERMOPLASTIC ELASTOMER NANOCOMPOSITES

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In this thesis, there are three goals; to synthesize Poly(ether/ester)s (PEEs) based on Poly(butylene terephthalate) (PBT) and Poly(ethylene glycol) (PEG) by changing the soft segment / hard segment compositions and investigate the influence of hard segment length on the structure, to synthesize PEE nanocomposites by in-situ polymerization and observe the effects of introduction of modified organoclay at different ratios to the polymer matrix, and thirdly, to prepare PEE nanocomposites by melt intercalation, and to compare in situ polymerization and melt intercalation methods in terms of mechanical, and thermal properties and morphology.

First the optimum reaction conditions were determined based on the temperature and duration of transesterification. PEEs with different PBT weight ratios varying from 37 wt% to 75 wt% were synthesized according to two different reaction procedures, namely, constant transesterification time and constant volume ratio of methanol collected. The procedure with constant volume ratio gave higher mechanical properties and molecular weight, and it was also applied for in-situ polymerization of nanocomposites. The synthesized polymers were characterized by FTIR-ATR analysis.

PEEs with 57 wt % PBT and 75 wt % PBT showed better tensile strength and elongation at fracture, thus, nanocomposites of these polymers containing 0.1%, 0.3% and 0.5% modified organoclay were prepared by both in-situ polymerization and melt intercalation methods whereas the PEE nanocomposites of 37 wt% PBT and 49 wt% PBT were obtained only by melt intercalation. The structure-properties relationships were examined by mechanical, thermal and morphological analyses. Specimens for analysis were prepared by injection molding.

For neat PEEs, the increase in weight content of PBT resulted in better mechanical properties. Melting point of PBT increased with increasing PBT as observed in DSC curves, while the glass transition temperature of PEG was not significantly affected.

For PEE nanocomposites with 37 wt % PBT, mechanical properties were not improved considering tensile strength and elongation at fracture.

In the case of 49 wt % PBT nanocomposites, addition of modified organoclay resulted in lower mechanical properties.

Considering PEE nanocomposites with 57 wt % PBT in both two methods, the addition of modified organoclay improved the mechanical properties such as tensile strength and elongation at fracture with the increase of organoclay wt%, and the best results were obtained with 0.5 wt % organoclay loading.

75 wt % PBT PEE nanocomposites with 0.1 wt % modified organoclay loading which were synthesized by in-situ polymerization gave better result than the neat polymer in terms of tensile strength. Among the nanocomposites which were prepared by melt intercalation, the highest tensile strength was obtained in PEE with 0.3 wt % organoclay loading.

DSC analysis of PEE nanocomposites with 37, 49 and 57 wt % PBT showed that with the addition of organoclay, melting point of PBT decreases due to restricted crystallinity of PBT. However, it was observed that for PEE nanocomposites of 75 wt % PBT, addition of organoclay does not have a significant effect on the melting point of PBT.

In order to discuss the dispersion of clay particles in the polymers, X-Ray Diffraction, Scanning Electron Microscopy and Transmission Electron Microscopy were used. The results of these analysis indicated that in-situ polymerization method is better than melt intercalation method in terms of dispersion of silicate layers in PEEs with both 57 wt % PBT and 75 wt % PBT.

Keywords: Poly(ether/ester) based thermoplastic elastomer, nanocomposite, in-situ polymerization

ÖZ

POLİ(ETER/ESTER) BAZLI TERMOPLASTİK ELASTOMERLER NANOKOMPOZİTLERİN SENTEZİ VE KARAKTERİZASYONU

Ezeroğlu, Fadile
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Bu çalışmanın üç amacı, yumuşak segment ve sert segment kompozisyonlarını değiştirerek Polibutilenterefitalat (PBT) ve Polietilenglikol (PEG) bazlı Poli(eter/ester) (PEE) sentezlemek ve sert segment uzunluğunun yapı üzerindeki etkisini doğrulamak; eş zamanlı polimerizasyon yöntemiyle PEE nanokompozitleri sentezlemek ve polimer matrisine farklı oranlarda modifiye edilmiş kilin katılmasının etkilerini incelemek; üçüncü olarak eriyik karıştırma yöntemi ile PEE nanokompozitleri hazırlamak ve eş zamanlı polimerizasyon yöntemi ile eriyik karıştırma yöntemini mekanik ve ısıl özellikler ile morfoloji açısından incelemektir.

Bu açıdan, önce sıcaklık ve tranesterifikasyon sürelerine göre optimum reaksiyon koşulları belirlenmiştir. Ağırlıkça %37 ile % 75 arasında değişen oranlarda PBT içeren PEE'ler iki farklı reaksiyon prosedürüne: sabit transesterifikasyon süresine ve sabit hacim oranına göre sentezlenmiştir. Sabit hacim oranı prosedürü mekanik özellikler ve moleküler ağırlık açısından daha iyi sonuç verdiğinden bu prosedür, nanokompozitlerin eş zamanlı hazırlanması için de kullanılmıştır. Sentezlenen polimerler FTIR-ATR analizi ile karakterize edilmiştir.

Ağılıkça %57 ve %75 PBT içeren PEE'ler gerilme direnci ve uzama değerlerine göre daha iyi mekanik özellikler gösterdiğinden, %0.1, %0.3 ve %0.5 oranında modifiye kil içeren nanokompozitler hem eş zamanlı polimerizasyon hem de eriyik karıştırma yöntemine göre hazırlanmıştır. %37 ve % 49 oranında PBT içeren PEE nanokompozitler ise sadece eriyik karıştıma yöntemine göre hazırlanmıştır. Yapı ve özellikleri arasındaki ilişki mekanik, ısıl ve morfolojik analizler ile araştırılmıştır. Analizlerde kullanılmak üzere numuneler enjeksiyonlu kalıplama yöntemi ile hazırlanmıştır.

Katkısız PEE'lerde, PBT ağırlık oranı arttıkça mekanik özellikler artmıştır. PBT ağırlık oranının artmasıyla PBT'nin erime sıcaklığının arttığı, PEG'in ise camsı geçiş sıcaklığının çok fazla etkilenmediği DSC analizinde gözlemlenmiştir.

% 37 PBT içeren PEE nanokompozitlerde, çekme direnci ve uzama (%) açısından mekanik özelliklerde bir iyileşme sağlanmamıştır.

%49 PBT içeren PBT nanokompozitler açısından, kilin eklenmesi mekanik özelliklerin düşmesine sebep olmuştur.

%57 PBT içeren PEE nanokompozitler dikkate alındığında, kil katma, gerilme direnci ve uzama (%) gibi mekanik özellikleri modifiye kil oranı arttıkça her iki metotta da iyileştirmiştir ve en iyi sonuçlar % 0.5 kil oranı ile elde edilmiştir.

%75 PBT içeren PEE nanokompozitleri söz konusu olduğunda, % 0.1 modifiye organik kil yüklenmiş ve eş zamanlı polimerizasyon metodu ile hazırlanmış nanokompozit en iyi gerilme direncini vermiştir. Eriyik karışım metodu ile hazırlanmış nanokompozitler arasında, en yüksek gerilme direnci %0.3 kil içeren PEE nanokompozitin mekanik analizi sonucu elde edilmiştir.

% 37, 49 ve 57 oranlarına sahip PEE nanokompozitlerinin DSC analiz sonuçlarına göre, kil eklenmesi PBT'nin kristallenmesini sınırlandırdığı için PBT'nin erime noktasını düşürmüştür. Bununla birlikte, %75 PBT içeren PEE nanokompozitleri için, kil eklemenin PBT'nin erime sıcaklığında önemli bir etkiye sahip olmadığı gözlemlenmiştir.

Polimer içinde kil parçacıklarının dağılımını tartışmak için X Işını kırınımı, SEM ve TEM analizleri kullanılmıştır. Bu analiz sonuçları, silikat katmanlarının dağılımı açısından hem %57 hem de %75 PBT içeren PEE'lerde, eş zamanlı polimerizasyon yönteminin eriyik karıştırma yönteminden daha iyi olduğuna işaret etmiştir.

Anahtar kelimeler: Poli(eter/ester) bazlı termoplastik elastomerler, nanokompozit, eş zamanlı polimerizasyon.

To My Husband, Gökhan

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NOMENCLATURE

A_0 Original, undeformed cross-sectional area, mm^2

b Width of beam tested, mm

d Depth of beam tested, mm

d Plane spacing, Å

E Young's Modulus, MPa

F Tensile Load, N

L Support span, mm

L_0 Initial gauge length, mm

ΔL Change in sample length, mm

m Slope of the tangent to the initial straight-line portion of the load deflection curve, N/mm

n Order of diffraction

T Thickness, mm

T_c Crystallization temperature, °C

T_g Glass transition temperature, °C

T_m Melting temperature, °C

GREEK LETTERS

ϵ Tensile strain, mm/mm
σ Phase angle, °
σ Tensile stress (nominal), MPa
Θ Scattering angle, °

ABBREVIATIONS

30B Cloisite® 30B
ASTM American Society for Testing and Materials
ATR Attenuated Total Reflectance
CEC Cation Exchange Capacity
CNT…….Carbon Nanotube
C_{12}PPh….Dodecyltriphenylphosphonium-monmorillonite
DMT……Dimethyl terephthalate
DR……...Draw Ratio
DMTA….Dynamic Mechanical Thermal Analysis
DSC Differential Scanning Calorimetry
GPC Gel Permeation Chromatography
MeOH…..Methanol
MMT Montmorillonite
PBT Polybutylene terephthalate
PDO…….1,3-Propanediol
PEE Polyetherester
PEG…….Polyethylene glycol
PEO…….Polyethyleneoxide
PLSN…...Polymer Layered Silicate Nanocomposites
PTT……..Poly(trimethylene terephthalate)
PTMO…..Poly(tetramethyleneoxide)
PTMT…..Poly(tetramethylene terephthalate)
SAXS… Small Angle X-Ray Scattering
SEM Scanning Electron Microscopy
SWCNT...Single Walled Carbon Nanotube
TBHDP Tributylhexadecylphosphonium bromide
TEM Transmission Electron Microscopy
TPE Thermoplastic Elastomer
XRD X-Ray Diffraction

CHAPTER 1

INTRODUCTION

A nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material [1]. Since well dispersion of the nanosized particles provides major improvements in functional and structural properties to the nanocomposites when compared with neat polymer or composites, it has a great role in industry and academic area in order to respond to the demand for new materials [2].

One of the most commonly used smectite clay, montmorillonite, is a very soft phyllosilicate group of minerals that typically form in microscopic crystals [3]. There are mainly two reasons why they are the materials of choice for polymer nanocomposites. The first one is having rich intercalation chemistry. This property allows them to be chemically modified and be compatible with organic polymers, so that they can be dispersed on a nanometer scale. Also, it is great convenient to get and use them [4]. In the structure of the montmorillonite, there is an octahedral alumina sheet between two tetrahedral silica sheets. The crystal structure's layer thickness is nearly 1 nm while the lateral dimensions of the layers are between 30 nm to several microns or larger [5]. When the behaviour of the montmorillonite to water is concerned, it is observed that montmorillonite has a quite hydrophilic character which means it is incompatible with many hydrophobic polymers and the layered silicates are not easily dispersed in most polymers. This problem can be solved by cation exchange process, a process which is used to get organophilic clay.

Organically modified layered silicates are a fast growing area of research in polymer science as they enhance the polymer's properties. Through the potential nanocomposite precursors, the ones with clay and layered silicates have been more widely studied and researched, since the starting clay materials are easily accessible and their intercalation chemistry has been researched for a long time [6]. Due to the nanometer-size particles achieved by dispersion, these nanocomposites show significantly improved thermal, mechanical, optical and physico-chemical properties compared to the pure polymer or conventional (microscale) composites [7]. In addition to these, it is also possible to get increased strength, moduli and heat resistance, decreased gas permeability and flammability.

Thermoplastic elastomers are important types of block copolymers having unusual combination of elasticity, reprocessability, low temperature flexibility, toughness and strength at relatively high temperatures [8]. The reason why they have unique properties is mainly due to the existence of physical cross-links binding the polymer chains into an

infinite network. In the case of natural rubber and synthetic elastomers, the crosslinks are covalent chemical bonds, but when the thermoplastic elastomers are concerned, these crosslinks are replaced by thermally labile tie points which are held together by physical forces [9]. In other words, thermoplastic elastomers combine two important and useful properties, namely an elasticity comparable to that of covalently crosslinked rubbers and meltability allowing for processing from the melt quite analogous to normal engineering plastics [10].

The definition of condensation polymerization can be given as a process by which two molecules join together, resulting in loss of small molecules which is often water or methanol, to form a connecting bond. The type of end product resulting from a condensation polymerization is dependent on the number of functional end groups, functionality of the monomers, i.e. the average number of reactive functional group per monomer molecule [11]. Monofunctional monomers result in low molecular weight products while bifunctional monomers give linear polymers. Polyesters, polycarbonates, polyamides, polyurethanes are the types of polymers which can be synthesized by condensation polymerization [12].

Fakirov et al. in 1990 studied the synthesis of poly(ether/ester)s based on poly(butylene terephthalate) (PBT) and poly(ethyleneglycol) (PEG) [13]. In the study, the aim was to get information about the influence of the hard segment length on the structure and to examine the properties of these copolymers at a constant length of the soft segment (PEG 1000). They used ^{1}H and ^{13}C nuclear magnetic resonance, infrared, and differential scanning calorimetry measurements in order to prove the block structure of the prepared samples. They pointed out that with the increase of the hard segment weight fraction in the copolymers, significant differences in the stress-strain dependences are observed, namely from that of rubbery materials to typical neck formation. So, it was concluded that different mechanical properties can be obtained by changing the copolymer composition. The copolymers having higher weight fraction of PBT show distinctly higher elastic modulus, yield stress and tensile strength, and lower elongation at yield and break.

In the light of that research, in this study, it was aimed to synthesize poly(ether/ester) based thermoplastic elastomer nanocomposites by changing the soft segment / hard segment / organoclay ratios and compositions and to investigate and compare the effects of introduction of organoclay to polymer matrix at different ratios. For this purpose, firstly, the optimum reaction conditions were determined by changing the temperature and duration of the reaction. After synthesis of PEEs with different PBT weight ratios varying from 37 wt % to 75 wt % at the same reaction conditions, nanocomposites of 57 wt% PBT and 75 wt % PBT polymers having 0.1 wt %, 0.3 wt % and 0.5 wt % modified organoclay were synthesized by using same in situ polymerization procedure. In addition, nanocomposites of these polymers containing 0.1%, 0.3% and 0.5% organoclay were also prepared by a co-rotating 16 mm twin screw extruder. Specimens for characterization tests were prepared by injection molding.

The synthesized polymers were characterized by using FTIR-ATR. In order to observe the dispersion of clay particles in the polymers, X-Ray Diffraction, Scanning Electron

Microscopy and Transmission Electron Microscopy were used. The thermal properties were determined by using Differential Scanning Calorimetry. In addition, the mechanical behaviour of the synthesized nanocomposites was investigated based on tensile tests, while Gel Permeation Chromatography was used to determine the molecular weight distribution of the synthesized polymers.

CHAPTER 2

BACKGROUND INFORMATION

2.1 Nanocomposites

Nanotechnology is a science which deals with the manipulation of matter on an atomic and molecular scale. There are wide application areas of nanotechnology such as, medicine, electronics, food, fuel cells, chemical sensors and sporting goods.

The definition of the nanocomposites can be given as a new class of composites that are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range. In today's technology, many manufacturers prefer to fill polymers with particles in order to get improved toughness and stiffness of the materials, to enhance their barrier properties and their resistance to fire and ignition. In some cases, this technology is used to reduce the cost of the material produced [14].

There are three types of nanocomposites, namely:

1) Isodimensional nanoparticles, where three dimensions are in the order of nanometers like spherical silica nanoparticles and semiconductor nanoclusters [15]

2) Nanotubes or whiskers, where two dimensions are in the nanometer scale and the third is larger, forming an elongated structure such as carbon nanotubes [16] or cellulose whiskers [17, 18]

3) Nanocomposites which are characterized by only one dimension in the nanometer range like polymer-layered crystal nanocomposites where the filler is present in the form of sheets of one to a few nanometer thick, to hundreds to thousands nanometers long.

2.1.1 Montmorillonite

In nanocomposites, montmorillonite is the mostly used smectite clay which is a class of 2:1 phyllosilicates. There are two-dimensional layers in its crystal lattice where a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedran by the tip. The thickness of the layer is around 1 nm, while the lateral dimensions of these layers vary from 300 Å to several microns depending on the particular silicate [19].
The structure of 2:1 phyllosilicates is shown in Figure 2.1.

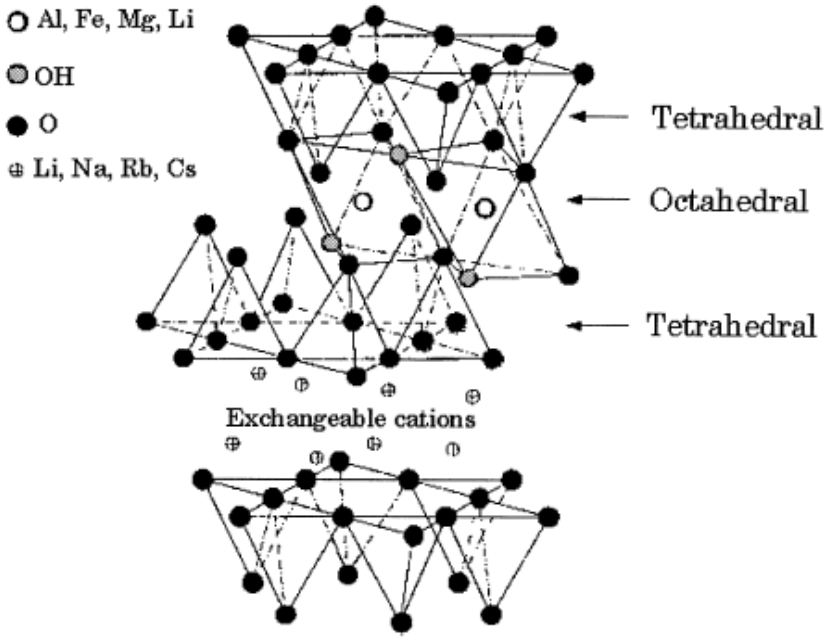


Figure 2.1 Structure of 2:1 phyllosilicates [20].

The most widely used layered silicate, montmorillonite, has gotten this attention due to its ability to show extensive interlayer expansion or swelling which is related with its peculiar structure. The efficiency of the MMT in improving the properties of the polymeric materials is primarily determined by the degree of its dispersion in the polymer matrix. However, the hydrophilic nature of the MMT surface prevents homogeneous dispersion in the organic polymer phase. To overcome this problem, it is often necessary to make the surface organophilic by ion-exchange reactions involving the exchange of organic cationic surfactants with the interlayer cations. This necessarily results in an increase in the interlayer separations. The number of surfactant molecules that reside in the galleries is determined by the cation exchange capacity of the silicate, and is measured in meq/g. The role of organic cation is to reduce the surface energy of the MMT surface, improving the wetting characteristics with the organic polymer [21].

2.1.2 Nanocomposite Structures

According to the form of the components used (layered silicate, organic cation and polymer matrix) and the method of preparation, there are three main types of composites when a layered clay is associated with a polymer. These are namely,

a) **Phase separated:** If the polymer does not intercalate between the silicate sheets, a phase separated composite is obtained. In this case, the composites' properties stay in the same range as those of traditional microcomposites.

b) Intercalated: If a single or more than one extended polymer chain is intercalated between the silicate layers which results in a well ordered multilayer morphology, intercalated structure is obtained.

c) Exfoliated: If the silicate layers are uniformly and completely dispersed in a continuous polymer matrix, then an exfoliated or delaminated structure is obtained.

These structures are shown in Figure 2.2

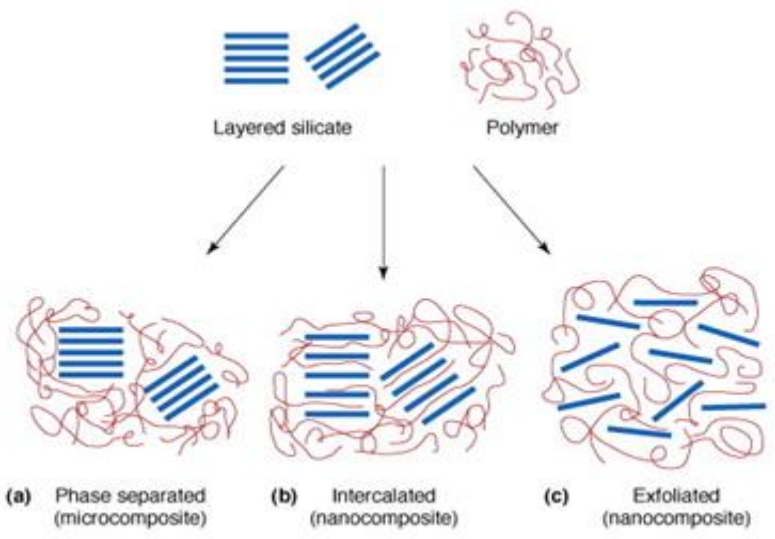


Figure 2.2 Scheme of different types of composite (a) phaseseparated microcomposite; (b) intercalated nanocomposite and (c) exfoliated nanocomposite [22].

2.1.3 Polymer Preparing Methods to Produce Nanocomposites

It is well known that polymer-clay nanocomposites usually have improved properties when compared to the neat polymers, such as higher thermal stability, better mechanical properties, reduced gas permeability and thermal expansion coefficients [23].

In the light of these informations, several methods have been studied to prepare polymer-layered silicate nanocomposites. There are mainly four methods [24] which can be named as:

1) Exfoliation - adsorption: In this process, the exfoliation of the layered silicate into single layers is carried out by using a solvent in which the polymer is soluble. Due to the weak forces which bring the layers together, layered silicates are dispersed in a proper solvent. Following this step, the polymer is adsorbed onto the sheets. As the mixture

precipitates or the solvent is evaporated, the sheets come together again in order to form an ordered multilayer structure.

2) In situ intercalative polymerization: The swelling of the layered silicate is achieved within the liquid monomer so that between the intercalated sheets, polymer formation can occur. The initiation of the polymerization is mostly done by heat, radiation or by using a catalyst. With the progress of polymerization, the d-spacing between clay layers increases gradually and the dispersion state of the clay changes from intercalation into exfoliation [25].

3) Melt intercalation: In this type of preparation, the polymer matrix and the layered silicate are mixed in the molten state. Different from the other techniques, there is no need for the solvent. When the layer surfaces are compatible with the polymer used, the polymer can crawl into the interlayer space forming either an exfoliated or an intercalated nanocomposite.

4) Template synthesis: This type of process is generally used for the synthesis of double-layer hydroxide-based nanocomposites [26]. In this case, the silicates are formed in situ in an aqueous solution containing silicate building blocks and the polymer. The polymer helps the nucleation and growth of the inorganic host crystals and gets trapped within the layers as they grow.

2.2 Thermoplastic Elastomers

The $-(A_xB_y)_n-$ type multiblock copolymers which have heterophase structure are named as thermoplastic elastomers (TPE). These materials, having hard and soft segments, form a processable melt at higher temperatures and transform into a solid rubber – like polymer upon cooling [27]. The schematic termoplastic elastomer phase structure is given in Figure 2.3

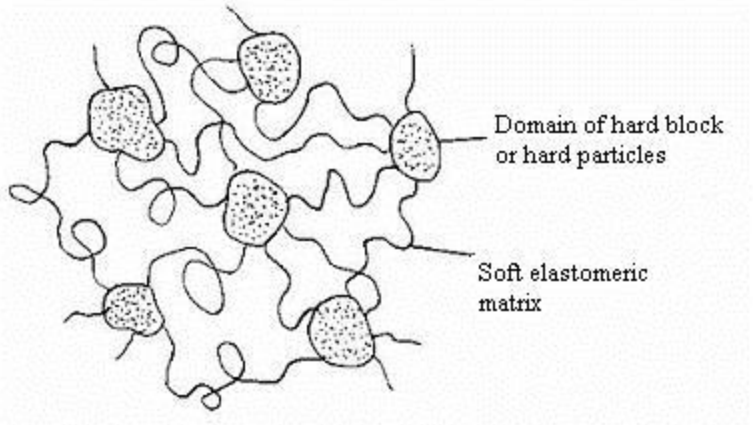


Figure 2.3 The schematic termoplastic elastomers phase structure [28].

Thermoplastic elastomers have two service temperatures. The lower service temperature regards the Tg of the elastomer phase when the upper service temperature regards the Tg or Tm, of the hard phase [29]. At low temperatures, the hard segments segregate and form a three dimensional network with physical crosslinks. If the temperature is increased above the Tm of the hard segments, then these crosslinks soften and a melt of the polymer is obtained. In the light of this information, it can be said that thermoplastic elastomer's service temperature range is between a temperature slightly above Tg of the soft rubbery phase and a temperature slightly below the Tg or Tm of the hard segment.

Thermoplastic elastomers were launched in the 1960s [30]. Since they have shown fast growth, TPEs have been the subject of many studies, symposia and conferences [31] and have found wide applications in many industrial branches like engineering materials, as they have excellent mechanical and physical properties [32]. They are encountered in commercial and industrial fields, as well as in applied and academic research [33].

In order to label the block elastomers as TPE, their internal structure must have two following conditions [34]:

1) The soft phase which is responsible for the elastic properties must have a relatively small elasticity modulus and a relatively low glass transition temperature and low density. For that reason, this phase must have weak intermolecular interactions, and a large capability for motion and rotation of the short sequences of the chains (small cohesion energy) ;

2) The hard phase which is responsible for the mechanical and processing properties must have a relatively large modulus of elasticity, a high glass transition temperature and also a relatively higher density. The blocks should have a tendency towards aggregation with the same kind of segments so that strong intermolecular interactions can occur. The intermolecular interactions of the hard blocks influence the stabilisation of the phase structure of the entire polymeric system. The hard blocks have to be characterised by a considerably larger cohesive energy density of matter than the flexible blocks, thereby a higher thermodynamic potential. The potential difference involves the driving force for the formation of a heterophase structure [35].

In the case of thermoplastic elastomers, the melt to solid transition is reversible, so, some properties of thermoplastic elastomers like, solvent resistance, compression set and resistance to deformation at elevated temperatures, are generally not as good as the ones of the vulcanized rubbers. In this view, thermoplastic elastomers are used in the areas where these properties are not so important like adhesives and footwear [36].
In terms of property-structure relationships, there are four important effects, namely [37];

1) Molecular weight: When homopolymers of similar molecular weight are compared with TPE block copolymers, block copolymers have very high melt viscosities which increase with increasing molecular weight. The reason is due to the persistence of the two-phase domain structure in the melt and the extra energy required to disturb this structure during flow.

2) Proportion of hard segment: As the proportion of hard segment of thermoplastic elastomer increases, the modulus increases. For example in this study, as the PBT content increases, the final product changes from a very weak, soft, rubberlike material to a strong material.

3) Elastomer segment: The choice of elastomer segment has a great effect on the properties of TPEs.

4) Hard segment: The choice of hard segment determines the upper service temperature and also influences the solvent resistance.

2.2.1 Poly(ether-ester) Based Thermoplastic Elastomers

Poly(ether-ester)s (PEE) are segmented block copolymers which have a thermoplastic elastomer behaviour since they consist of alternating sequences of mobile polyether and rigid polyester segments [38].

The phase separation of the polyester and polyether segments provides elastomeric properties for these block copolymers. When the rigid to soft segment ratio changes, the materials changing from soft elastomers to relatively hard plastics can be obtained. In some studies, these kinds of thermoplastic elastomers are mentioned as nanocomposites by themselves as they have an amorphous phase and crystalline lamellae [39].

2.2.2 Main Methods of Thermoplastic Elastomer Preparation

There are seven methods for preparing TPEs, namely [40];

1) Living anionic polymerization
2) Living cationic poymerization
3) Controlled radical polymerization
4) Polycondensation and polyaddition
5) Chemical modification and grafting
6) Preparation by blending
7) Preparation by dynamic vulcanization

Among these methods, the mostly used ones are condensation and addition polymerization.

2.2.2.1 Condensation (Step Reaction) Polymerization

Condensation polymerization occurs between two polyfunctional molecules to produce one larger polyfunctional molecule. The chain growth occurs in a slow and stepwise manner. For that reason, it is possible to say that the average molecular weight of the polymer increases slowly and a period of time is needed in order to have a high molecular

weight polymer [41]. In this process, each molecule has a reactive functional group, so that polymerization occurs by the reaction between these functional groups [42] and during the polymerization, there is an elimination of a small molecule such as water or methanol which means condensation polymers generally have fewer atoms in the polymer than in the reactants. Some important condensation type polymers are, polyamides, polyurethanes, polyureas, polyesters, polyethers, polycarbonates, polyanhydrides, polysulfides, polysiloxanes, phenol-formaldehyde resins and polyphosphate and polyphosphonate esters [43].

2.2.2.2 Addition (Chain Reaction) Polymerization

Addition polymerization is performed by a rapid addition of olefin molecules to a growing chain end, in other words, the monomer polymerizes in the presence of compounds which are named as the initiator. The growth centers, generated by the initiator, can either be ionic (anionic or cationic), free radical or coordinational which depends on the type of initiator system used in the reaction [44]. During this process, the concentration of the monomer decreases steadily and it is possible to observe both monomer and high molecular weight polymer at any stage of the reaction mixture. As a difference from condensation polymerization, in this process, a high molecular weight polymer can be obtained rapidly.

2.3 Previous Studies

2.3.1 Studies on Synthesis of Poly(ether-ester) Based Thermoplastic Elastomers

In a study of Szymczyk [45] in 2008, novel poly(trimethylene terephthalate)-block-poly(tetramethylene oxide) (PTT-PTMO) segmented block copolymers were synthesized by transesterification. The process was carried out in the melt of dimethyl terephthalate, poly(tetramethylene oxide) glycol (PTMO, 1000 g/mole) and 1,3 propanediol in order to get multiblock copolymers with flexible PTMO blocks varying from 20 to 80 wt% and investigate the influence of flexible segment content on the resulting mechanical and thermal properties. In terms of mechanical properties, the study showed that the tensile strength and yield strength are decreased with the increase of the flexible segment content since the degree of crystallinity decreases. On the other hand, in terms of thermal properties, it was proved that the heat capacity values at Tg increases with increasing rigid segment content, meaning that the degree of phase separation increases as PTMO segments content increases.

In another study (2009) made by Szymczyk [46], which was aimed to observe the influence of the PEO flexible segment content on PTT-block-PEO copolymers properties, like phase structure, thermal and mechanical properties, a series of PTT-b-PEO copolymers with varying composition of rigid PTT and flexible PEO segments were synthesized by using poly(ethylene glycol) (PEG, Mn = 1000 g/mol), dimethyl terephthalate (DMT) and 1,3-propanediol (PDO). The reaction was carried out by a two

stage process involving transesterification and polycondensation in the melt. The weight fraction of flexible segments was varied between 20 and 70 wt %. In the paper, it was mentioned that according to the analysis by X-ray, DSC and DMTA, there are four different phases that exist in PTT-b-PEO copolymers: crystalline PTT, amorphous PTT, amorphous PEO, and amorphous PEO/ PTT miscible blend. In addition, it was claimed that crystalline PEO was observed only at temperature below $0^{\circ}C$ for the sample containing the highest concentration of PEO segment. Lastly, it was concluded that the melting and crystallization temperatures and the degree of crystallinity decrease as the flexible PEO segment content increases.

In 2011, Szymkczyk et al [47] published another study concerning two series of multiblock poly(ether-ester)s namely; poly(trimethylene terephthalate) (PTT) as the rigid segment and poly(tetramethylene oxide) (PTMO) as the flexible/soft segments in which soft segment ratio in the polymer chain change from 20 to 80 wt %. In that study, the mainly focused topic is the effect of soft segment length with starting PTMO molecular weight at 1000 and 2000 g/mol in terms of phase structure, and thermal and mechanical properties of the synthesized copolymers. It was concluded that the copolymers containing longer soft segment have enhanced phase separation and the ones having 50-80 wt % of soft segment show elastic behavior, while the copolymers having 30 and 40 wt % of long PTMO soft segment have the best elastic properties.

2.3.2 Studies on Synthesis of Poly(ether-ester)s Based on Poly(buthyleneterephthalate) and Poly(ethylene glycol) Elastomers

Fakirov et al. [48], in 1990, studied the structure-properties relationships of poly(ether/ester)s based on poly(buthyleneterephthalate) and poly(ethylene glycol). Two series of PEEs were prepared by changing the length of the soft segments using monomers with molecular weights of 600, 1000 and 2000. The first set of samples was produced with constant mole ratio of PBT:PEG (the PBT block length being approximately the same) and the second set of samples was synthesized with constant weight ratio PBT:PEG (different PBT segment length). In order to prove the block structure, ^{1}H nuclear magnetic resonance and differential scanning calorimetry measurements were performed. The stress-strain curves for the first set resulted in a gradual change in the mechanical properties from those of engineering plastics to those of rubbery materials with the increase of the polyether segment length, at constant length of the PBT blocks. The stress-strain curves for the second set showed negligible differences. The differences were observed mainly in the modulus, tensile strength and elongation at break. In other words, the length of the soft segment influences these characteristics.

In the same year, Fakirov et al. [49] researched the annealed drawn and undrawn bristles of poly(ether/ester)s based on poly(tetramethylene terephthalate) (PTMT) and poly(ethylene glycol) PEG 1000 (in various ratios) by means of differential scanning calorimetry and small-angle X-ray scattering. In the end of the experiments, it was observed that the samples having the lowest PTMT content show on abrupt increase of the scattering intensity and the long spacing with increasing annealing temperature, this

increase becoming less pronounced with increasing fraction of the hard segment. In addition to these, DSC data suggested a dependence of the thermal behaviour on the chemical composition, orientation and annealing temperature. They also showed that the characteristics of the undrawn samples are similar to those of the homopolymer PTMT and the copolymers based on PTMT and poly(tetramethylene oxide).

In paralel with these studies, Fakirov et al [50] studied the scattering behaviour of PEE samples with or without external stress by using the SAXS tecnique. Samples with destroyed structure were prepared by additional drawing and those with regenerated structure were prepared by means of three approaches, namely; crystallization, solid state condensation and exchange reactions as well as chemical crosslinking to investigate different deformation conditions by SAXS measurements.

Another study made by Fakirov et al. [51] in 1992 deals with thermoplastic elastomers with different PBT to PEG wt% ratios and different lengths of the soft (glycol) segments (PEG 600, 1000, 2000) compared to the ones used in the previous studies (PEG 1000). SAXS measurements of the samples with or without application of external stress were performed in order to investigate the effect of the chemical composition and block length on the deformation behaviour.

2.3.3 Studies on Synthesis of Nanocomposites by In-Situ Polymerization

In a study by Chang et al. [52], synthesis of poly(butylene terephthalate) (PBT) incorporated between the montmorillonite layers was performed from dimethyl terephthalate and 1,4-butane diol by the method of in situ interlayer polymerization in order to get intercalated nanocomposites. In the study, firstly, the modified clay and 1,4-butane diol were stirred for 30 minutes at room temperature. Dimethyl terephthalate and isopropyl titanate that had been mixed in a separate tube was added to the butanediol-organoclay mixture. The temperature of the reaction mixture was raised to 190 ^{o}C and kept at this temperature for an hour. Then, the temperature was increased to 230 ^{o}C and was maintained there for 2 h. In this step, the side product of the reaction, methanol was obtained. In order to finalize the reaction, the mixture was heated to 260 ^{o}C and stirring was continued for additional 3 hours at a pressure of 1 Torr. The synthesized polymer nanocomposite was obtained after cooling to room temperature, washing with water and drying under vacuum at 70 ^{o}C for 1 day.

In a paralel study performed by Chang et al. [53], by using the same procedure discussed in reference [52], a series of poly (trimethylene terephthalate) (PTT) nanocomposites which contain an organically modified montmorillonite (C_{12}PPh-MMT) were synthesized by in situ intercalation polymerization from dimethyl terephthalate (DMT) and 1,3-propanediol (PDO). It was the goal of the study to investigate the thermal and mechanical properties of PTT nanocomposites which were melt-spun at different organoclay contents and different draw ratios (DRs) to produce monofilaments.

2.3.4 Studies on Synthesis of Thermoplastic Elastomer Nanocomposites by In-Situ Polymerization

In 2012, Szymczyk [54] published a new study dealing with nanocomposites which are based on poly(trimethylene terephthalate)-block- poly(tetramethylene oxide) (PTT-PTMO) segmented copolymer and COOH-functionalized single-walled carbon nanotubes (SWCNTs) by using in situ polymerization method. In the study, it was observed that the nanocomposites having low SWCNTs (<0.5 wt %) show uniform dispersion of CNT in the matrix. In addition, it was mentioned that according to tensile tests, the tensile strength of the nanocomposites with 0.05–0.3 wt % loading of SWCNTs are better than that of neat PTT-PTMO copolymer without reduction in elongation at break.

In the same year, a new study by Szymczyk [55] et al was performed in order to investigate poly(trimethylene terephthalate-block-tetramethylene oxide) (PTT–PTMO) copolymer/organoclay nanocomposites which are prepared by in situ polymerization. It was observed that silicate layers do not affect the glass transition temperature of the PTMO-rich soft phase, melting temperature of PTT hard phase, and degree of crystallinity of the nanocomposites. Also, it was mentioned that tensile modulus and yield stress increases without decreasing elasticity as the organoclay ratio in the polymer matrix increases.

CHAPTER 3

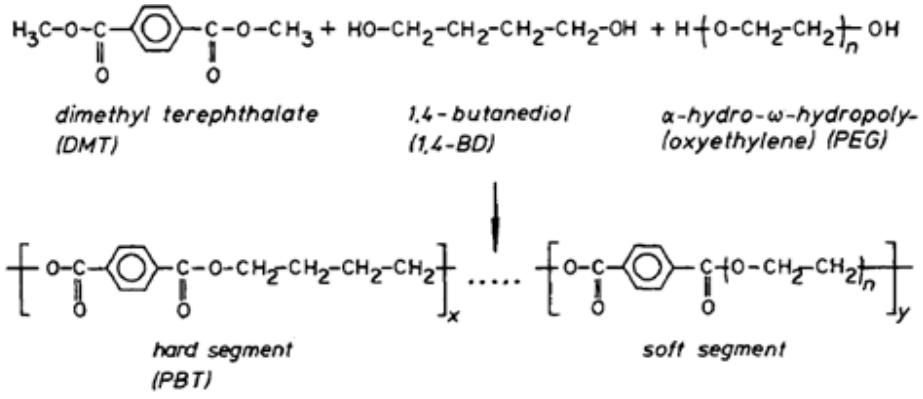
EXPERIMENTAL SECTION

3.1 Materials

The PEE based polymers and nanocomposites were synthesized by using commercial grade materials. In the experiment, dimethyl terephthalate (Fluka, USA), 1,4-Butane diol (Sigma-Aldrich, USA) and poly(ethylene glycol) with different number average molecular weights (600, 1000, 2000) (Sigma-Aldrich, USA) were used as received. The catalyst was isopropyl titanate (Sigma-Aldrich, USA), while the antioxidant was the tetrakis(methylene(3,5-dit-butyl-4-hydroxyphenylhydro-cinnamate))methane (Irganox 1010, Ciba-Geigy, Switzerland). For the preparation and synthesis of nanocomposites, two different clays were used, namely, Cloisite 30 B and Modified Clay. Cloisite 30 B was obtained from Southern Clay Products while modified clay was obtained from Kocaeli University which was synthesized by using the procedure in the study of Ozkoc et. al. [56].

3.2 Synthesis of PEEs and PEE Nanocomposites Based on Poly(butylene terephthalate) and Poly(ethylene glycol)

The syntheses of PEEs and PEE nanocomposites were performed according to the reaction given in Figure 3.1.



where n= 12-45 (mol. wt. 600, 1000, 2000)
x= 1-20 (mol.wt. 220-4400)
y= 1 (mol.wt. 720, 1120, 2120)

Figure 3.1 Reaction Procedure of the Synthesis of PEE and PEE Nanocomposites

During the reaction process, MeOH is obtained as a side product.

Experimental set up is given in Figure 3.2

Figure 3.2 Experimental Set Up

3.2.1 Synthesis of PEEs Which are Obtained at Different Reaction Conditions with the Same PBT wt%

All of the synthesized PEEs throughout the thesis are given in this part. Most of these syntheses were performed in order to determine the optimum reaction conditions. In the discussion part, only the ones which were synthesized at the same reaction conditions are dealt with and the results are compared.

In Tables 3.1-3.9, for the calculation of duration of transesterification (TE), the time at which methanol release was observed was accepted as the starting point. In other words, it is the period between the time at which methanol was started to be collected in the graduated tube and the time at which the temperature was set to 260 ^{o}C. For the duration of polycondensation (PC), the calculations were made according to time passed at which

the temperature of the reaction mixture was at and above 260 ^{o}C. In some cases, the temperature was further raised to 280 ^{o}C.

Through the thesis, PEE refers to poly(ether/ester) based thermoplastic elastomer in the labels. The numbers after abbreviation show the molecular weight of PEG and weight ratio of PBT in PEE, respectively. Lastly, order of the experiment as outlined in Appendix A is given in parantheses. In the case of nanocomposites, in order to show melt intercalation method (+) is used, while (-) is used for in-situ polymerization method.

Table 3.1 Reaction Conditions of PEEs with 37 wt % PBT

Sample Name	***Temp. of TE(^{o}C)***	***Duration of TE (min.)***	***Temp. of PC(^{o}C)***	***Duration of PC (min.)***	***Duration at 280 ^{o}C (min.)***
PEE/1000/37 wt%PBT(1)	175	29	260-275	240	-
PEE/1000/37 wt%PBT(2)	175	25	260	255	-
PEE/1000/37 wt%PBT(3)	175	45	260-280	195	121
PEE/1000/37 wt%PBT(4)	175	69	260-280	189	121
PEE/1000/37 wt%PBT(5)	175-220	173	260-280	195	49

Table 3.2 Reaction Conditions of PEEs with 49 wt % PBT

Sample Name	***Temp. of TE(^{o}C)***	***Duration of TE (min.)***	***Temp.of PC(^{o}C)***	***Duration of PC (min.)***	***Duration at 280 ^{o}C (min.)***
PEE/1000/49 wt%PBT(1)	175	16	255-275	240	-
PEE/1000/49 wt%PBT(2)	175	21	260-275	240	-
PEE/1000/49 wt%PBT(3)	175	17	260-275	165	-
PEE/1000/49 wt%PBT(4)	175	27	260 -275	240	-
PEE/1000/49 wt%PBT(5)	175	16	260-275	240	-
PEE/1000/49 wt%PBT(6)	175	45	260 -280	195	115
PEE/1000/49 wt%PBT(7)	175	45	260 -280	195	121
PEE/1000/49 wt% PBT(8)	175-220	165	260-280	195	52

Table 3.3 Reaction Conditions of PEEs with 57 wt % PBT

Sample Name	***Temp. of TE(^{o}C)***	***Duration of TE (min.)***	***Temp. of PC(^{o}C)***	***Duration of PC (min.)***	***Duration at 280 ^{o}C (min.)***
PEE/1000/57 wt%PBT(1)	175	26	260-275	240	-
PEE/1000/57 wt%PBT(2)	175	45	260 -280	195	116
PEE/1000/57 wt%PBT(3)	175-220	118	260-280	195	52

Table 3.4 Reaction Conditions of PEEs with 75 wt % PBT

Sample Name	***Temp. of TE (^{o}C)***	***Duration of TE (min.)***	***Temp. of PC (^{o}C)***	***Duration of PC (min.)***	***Duration at 280 ^{o}C (min.)***
PEE/1000/75 wt%PBT(1)	175	159	260-280	258	60
PEE/1000/75 wt%PBT(2)	175	54	260-280	191	30
PEE/1000/75 wt%PBT(3)	175	45	260-280	195	116
PEE/1000/75 wt%PBT(4)	175	85	260-280	184	102
PEE/1000/75 wt%PBT(5)	175-220	135	260-280	195	46

Table 3.5 Reaction Conditions of PEEs with 57 wt % PBT

Sample Name	***Temp. of TE(^{o}C)***	***Duration of TE (min.)***	***Temp. of PC(^{o}C)***	***Duration of PC (min.)***	***Duration at 280 ^{o}C (min.)***
PEE/600/57 wt%PBT(1)	175	45	260-280	180	106
PEE/600/57 wt%PBT(2)	175	45	260-280	195	122

Table 3.6 Reaction Conditions of PEEs with 67 wt % PBT

Sample Name	*Temp. of TE(°C)*	*Duration of TE (min.)*	*Temp. of PC(°C)*	*Duration of PC (min.)*	*Duration at 280 °C (min.)*
PEE/600/67 wt%PBT(1)	170	37	255	165	-
PEE/600/67 wt%PBT(2)	175	45	260-280	173	103
PEE/600/67 wt%PBT(3)	175	45	260-280	195	113

Table 3.7 Reaction Conditions of PEEs with 41 wt % PBT

Sample Name	*Temp. of TE(°C)*	*Duration of TE (min.)*	*Temp. of PC(°C)*	*Duration of PC (min.)*	*Duration at 280 °C (min.)*
PEE/2000/41 wt%PBT(1)	175	74	260-280	171	100
PEE/2000/41 wt%PBT(2)	175	45	260-280	180	108

Table 3.8 Reaction Conditions of PEE with 57 wt % PBT

Sample Name	*Temp. of TE(°C)*	*Duration of TE (min.)*	*Temp. of PC(°C)*	*Duration of PC (min.)*	*Duration at 280 °C (min.)*
PEE/2000/57 wt%PBT(1)	175	45	260-280	195	120

Table 3.9 Reaction Conditions of PEE with 75 wt % PBT

Sample Name	*Temp. of TE (°C)*	*Duration of TE (min.)*	*Temp. of PC(°C)*	*Duration of PC (min.)*	*Duration at 280 °C (min.)*
PEE/2000/75 wt%PBT(1)	175	45	260-280	195	121

3.2.1.1 Synthesis of PEEs Based on Poly(butylene terephthalate) and Poly(ethylene glycol) at Constant Transesterification Time

The reactants, 1,4-butane diol, polyethylene glycol, dimethyl terephthalate, catalyst and stabilizing agent were mixed in a 150 ml reaction vessel and heated to 175 °C. Transesterification time was held constant as 45 minutes (after starting to collect methanol) for the synthesis and then the temperature was increased to 260 °C for the polycondensation step. The reaction mixture was stirred at this temperature for one hour,

and then the temperature was increased to 280 ^{o}C. When the temperature reached 280 ^{o}C, vacuum was applied and the pressure was decreased to 2-2.5 mbar in 60-70 minutes. Since the weight ratios of PBT/PEG and molecular weight of PEG were different in the synthesized PEEs, in order to compare PEEs, the polycondensation time was held constant as 195 minutes instead of achieving a constant torque. During the reaction, the stirring rate was kept constant at 50 rpm.

Experimental details for the synthesis are given in Appendix A.

Table 3.10 PEEs with Different wt % PBT Ratios Which are Synthesized at Constant Transesterification Time Reaction Conditions

Sample Name	Duration of TE Step (min.)	Duration of PC Step (min.)
PEE/1000/37 wt%PBT(3)	45	195
PEE/1000/49 wt%PBT(7)	45	195
PEE/1000/57 wt%PBT(2)	45	195
PEE/1000/75 wt%PBT(3)	45	195
PEE/600/57 wt%PBT(2)	45	195
PEE/600/67 wt%PBT(3)	45	195
PEE/2000/41 wt%PBT(2)	45	195
PEE/2000/57 wt%PBT(1)	45	195
PEE/2000/75 wt% PBT(1)	45	195

3.2.1.2 Synthesis of PEEs Based on Poly(butylene terephthalate) and Poly(ethylene glycol) at Constant Collected Methanol Volume Ratio

Firstly, 1,4-butane diol, polyethylene glycol, dimethyl terephthalate, catalyst and stabilizing agent were added into a 150 ml reaction vessel. The temperature was set to 175 ^{o}C in order to start the transesterification step. When 75% of the methanol (calculated according to theoretical volume of MeOH by using DMT amount) was collected in the graduated tube, the temperature was gradually increased to 220 ^{o}C. The reaction mixture stayed at this temperature until the volume ratio reached 88-92 %, and then the reaction mixture was heated to 260 ^{o}C. It stayed at this temperature for one hour, later vacuum was applied. In 60-70 minutes, the pressure was decreased to 2-2.5 mbar and when full vacuum was reached, the temperature was increased once more to 280 ^{o}C. As in the previous procedure, the polycondensation time was kept constant as 195 minutes. During the reaction, the stirring rate was kept constant at 50 rpm.

Experimental details for the synthesis are given in Appendix A.

Table 3.11 PEEs with Different wt % PBT Ratios Which are Synthesized in Constant Volume Ratio Reaction Conditions

Sample Name	MeOH Volume Ratio (%)	Duration of TE Step (min.)	Duration of PC Step (min.)
PEE/1000/37 wt%PBT(5)	87.7	173	195
PEE/1000/49 wt%PBT(8)	88.6	165	195
PEE/1000/57 wt%PBT(3)	91.6	118	195
PEE/1000/75 wt%PBT(5)	88.3	135	195

3.2.2 Preparation of PEE Nanocomposites

In the study, two methods were performed to get PEE nanocomposites, namely, in-situ polymerization and melt intercalation.

3.2.2.1 Synthesis of PEE Nanocomposites by in-situ Polymerization

Nanocomposites of PEE synthesized in the study are shown in Table 3.12. As in the case of synthesis of PEEs, most of the nanocomposite syntheses were performed for the purpose of determination of optimum reaction conditions. The calculation of duration of transesterification and duration of polycondensation was done in the same manner as mentioned in the previous part.

Table 3.12 PEE Nanocomposites with 49 wt % PBT Containing 0.5% and 1% Cloisite 30B

Sample Name	***Temp. of TE(^oC)***	***Duration of TE (min.)***	***Temp. of PC(^oC)***	***Duration of PC (min.)***	***Duration at 280^oC (min.)***
PEE/1000/49 wt%PBT-0.5%(1)	175	45	260-280	195	114
PEE/1000/49 wt%PBT-1%(1)	175	22	260-275	171	-
PEE/1000/49 wt%PBT-1%(2)	175	20	260-275	240	-
PEE/1000/49 wt%PBT-1%-(3)	175	23	260-275	240	-
PEE/1000/49 wt%PBT-1%(4)	175	45	260 -280	195	114
PEE/1000/49 wt%PBT-1%(5)	175	45	260 -280	195	117

Table 3.13 PEE Nanocomposites with 57 wt % PBT Containing 0.1%, 0.3% and 0.5% TBHDP-MMT

Sample Name	***Temp. of TE(^{o}C)***	***Duration of TE (min.)***	***Temp. of PC(^{o}C)***	***Duration of PC (min.)***	***Duration at 280^{o}C (min.)***
PEE/1000/57 wt%PBT-0.1%(1)	175	108	260-280	195	46
PEE/1000/57 wt%PBT-0.3%(1)	175	98	260-280	195	47
PEE/1000/57 wt%PBT-0.5%(1)	175	162	260-280	195	47

Table 3.14 PEE Nanocomposites with 75 wt % PBT Containing 0.1%, 0.3% and 0.5% TBHDP-MMT

Sample Name	***Temp. of TE(^{o}C)***	***Duration of TE (min.)***	***Temp. of PC(^{o}C)***	***Duration of PC (min.)***	***Duration at 280^{o}C (min.)***
PEE/1000/75 wt%PBT-0.1%(1)	175	123	260-280	195	47
PEE/1000/75 wt%PBT-0.3%(1)	175	143	260-280	195	62
PEE/1000/75 wt%PBT-0.5%(1)	175	126	260-280	195	48

3.2.2.1.1 Synthesis of PEE Nanocomposites Based on Poly(butylene terephthalate) and Poly(ethylene glycol) at Constant Transesterification Time

For the synthesis, firstly PEG (as melt) and organoclay were put into the reaction vessel and mixed in the ultrasonic bath for 3 hours at 60 ^{o}C. The other reactants, 1,4-butane diol, dimethyl terephthalate, catalyst and stabilizing agent were added and heated to 175 ^{o}C. Transesterification time was held constant as 45 minutes for all the nanocomposite synthesis, and then the temperature was increased to 260 ^{o}C for the polycondensation step. The reaction mixture was stirred at this temperature for one hour, and then the temperature was set to 280 ^{o}C. When the temperature reached 280 ^{o}C, vacuum was applied and the pressure was decreased to 2-2.5 mbar in 60-70 minutes. The polycondensation time was held constant as 195 minutes. The stirring rate was kept constant at 50 rpm during reaction.

Experimental details for the preparation of nanocomposites are given in Appendix A.

Table 3.15 PEE Nanocomposites with 49 wt % PBT Ratios Which are Synthesized at Constant Transesterification Time Reaction Conditions

Sample Name	***Duration of TE Step (min.)***	***Duration of PC Step (min.)***
PEE/1000/49 wt% PBT-0.5%(1)	45	195
PEE/1000/49 wt% PBT-1%(4)	45	195
PEE/1000/49 wt% PBT-1%(5)	45	195

3.2.2.1.2 Synthesis of PEE Nanocomposites Based on Poly(butylene terephthalate) and Poly(ethylene glycol) at Constant Collected Methanol Volume Ratio

1,4-butane diol was put into reaction vessel, and then the organoclay (TBHDP-MMT) was added. At room temperature, the mixture was mixed in the ultrasonic bath for half an hour in order to disperse the organoclay. Next, the other reactants were added into the vessel in addition to catalyst and antioxidant and the constant volume ratio procedure was carried out in order to produce the nanocomposites.

Detailed information about the synthesis of nanocomposites are given in Appendix A.

Table 3.16 PEE Nanocomposites with 57 wt % PBT Ratios Which are Synthesized at Constant Volume Ratio Reaction Conditions

Sample Name	***MeOH Volume Ratio (%)***	***Duration of TE Step (min.)***	***Duration of PC Step (min.)***
PEE/1000/57 wt%PBT-0.1%(1)	91.7	108	195
PEE/1000/57 wt%PBT-0.3%(1)	90.7	98	195
PEE/1000/57 wt%PBT-0.5%(1)	90.7	162	195

Table 3.17 PEE Nanocomposites with 75 wt % PBT Ratios Which are Synthesized at Constant Volume Ratio Reaction Conditions

Sample Name	***MeOH Volume Ratio (%)***	***Duration of TE Step (min.)***	***Duration of PC Step (min.)***
PEE/1000/75 wt%PBT-0.1%(1)	85	123	195
PEE/1000/75 wt%PBT-0.3%(1)	85	143	195
PEE/1000/75 wt%PBT-0.5%(1)	87	126	195

3.2.2.2 Preparation of PEE Nanocomposites by Melt Intercalation

Polyether-ester based nanocomposites were prepared by melt intercalation in a twin screw compounder (15 cc Microcompounder, DSM Xplore). For compounding, the process temperature was set 15 ^{o}C higher than Tm values which were determined by DSC analysis and mixing time was constant at 1.5 minutes. The screw speed was kept constant at 200 rpm. The molten product obtained from the barrel was injected using the injection molding instrument.

3.3 Characterization Experiments

The mechanical behaviour of the synthesized nanocomposites was evaluated by tensile properties (tensile strength, Young's modulus, elongation at break) while Gel Permeation Chromatography was used to determine the molecular weight distribution of the synthesized polymers. The synthesized polymers were characterized by using FTIR-ATR analysis. DSC analyses were carried out to study the thermal properties. In addition, for the purpose of investigating the dispersion of clay particles in the polymers, X-Ray Diffraction, Scanning Electron Microscopy and Transmission Electron Microscopy were used.

3.3.1 Mechanical Analysis

3.3.1.1 Tensile Tests

One of the most informative mechanical experiments in order to observe property enhancement of the polymer is the determination of its stress-strain curve in tension. This is usually done by measuring continuously the force developed as the sample is elongated at constant rate of extension.

Tensile tests were performed at room temperature according to ASTM D5591 with Instron 5567 universal testing machine which is shown in Figure 3.3 at Kocaeli University, Chemical Engineering Department. Gauge length, crosshead speed and strain rate were 25 mm, 5 mm/min, and 5 min.$^{-1}$ respectively.

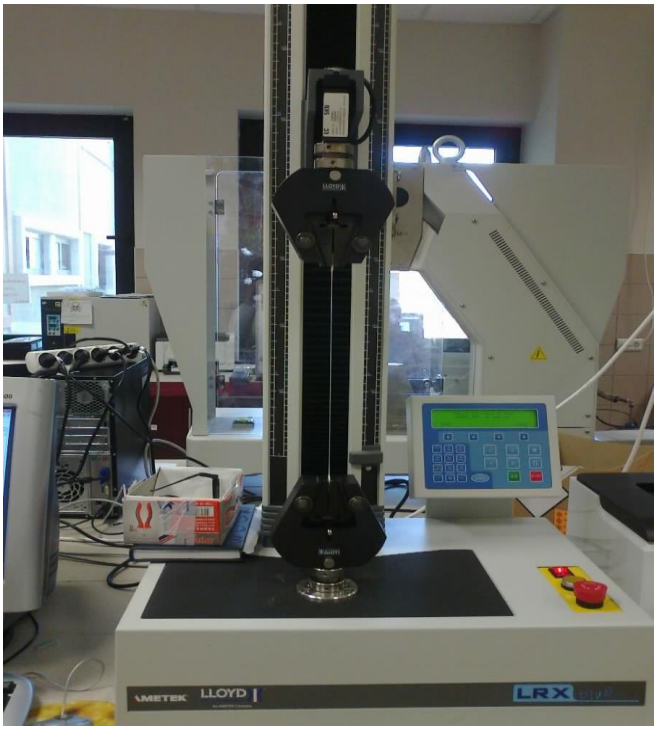


Figure 3.3 Instron 5567 Tensile Test Machine

3.3.2 Molecular Weight Determination

3.3.2.1 Gel Permeation Chromatography (GPC) Analysis

GPC is a type of size exclusion chromatography which is used for separation of analytes on the basis of size. Polymers can be characterized by a variety of definitions for molecular weight including the number average molecular weight (M_n) the weight average molecular weight (M_w), the size average molecular weight (M_z) or the viscosity molecular weight (M_v).

GPC Analyses were performed at Kordsa Global R&D Center and the weight average molecular weight (M_w) are given through the thesis.

3.3.3 Spectroscopic Analysis

3.3.3.1 Fourier Transform Infrared Spectroscopy – Attenuated Total Reflectance (FTIR-ATR) Analysis

FTIR-ATR is a chemical analytical technique which measures the infrared intensity versus wavelength (wavenumber) of light. The method relies on the detection of the

vibration characteristics of chemical functional groups in a sample, so that it provides sufficient information about the characterization of the polymer.

FTIR-ATR at Chemical Engineering Department in METU was used in order to characterize the polymer samples.

3.3.4 Thermal Analysis

3.3.4.1 Differential Scanning Calorimeter (DSC) Analysis

Differential scanning calorimetry, DSC, is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. The sample and reference are held at nearly the same temperature during the experiment. When the sample undergoes a thermal transition, the power to the two heaters is adjusted to keep their temperatures the same and a signal proportional to the power difference is plotted.

This technique enables one to measure the heat of transition and also to calculate Tm and Tg values of the polymer sample. By this way, it is possible to determine the different phases of the polymer samples.

In this thesis study, differential scanning calorimetry analysis was performed at the METU Central Laboratory. Measurements were carried out in the temperature range of -100 °C to 260 °C with a heating rate of 10 °C/min under nitrogen atmosphere. In order to compare the thermal properties of PEEs and PEE nanocomposites, double run was done and glass transition temperature and melting temperature of the samples were determined according to second heating of these samples in these analyses.

3.3.5 Morphological Characterization

3.3.5.1 X-Ray Diffraction (XRD) Analysis

X-Ray Diffraction (XRD) is a technique used in order to characterize intercalated structures. In the case of XRD analysis, since the multilayer structure is preserved in the intercalated structures, the interlayer spacing is determined, but when the composite has an exfoliated structure, no more diffraction peaks are visible in the XRD diffractograms. It can also be a conclusion of large spacing between the layers, or in some cases, the nanocomposite does not present ordering anymore so that no peaks can be observed in the diffractograms [2].

X-ray diffraction (XRD) patterns of organoclays and nanocomposites were carried out at the Central Laboratuary of METU which generates a voltage of 40 kV and current 40 mA from Cu Kα radiation source ($\lambda = 1.5418$). The diffraction angle 2θ was scanned from 1°

to 40° with scanning rate of 2°/min and a step size of 0.01°. The distances between the silicate layers were calculated by using Bragg' s equation which is given as;

$$n\lambda = 2d \sin\theta$$

where, n is degree of diffraction, λ is wavelength, d is the interlayer spacing and θ is the measured diffraction angle. For the purpose of X-Ray analysis, tensile bars were used while the analyses of the organoclay were done in powder form.

3.3.5.2 Scanning Electron Microscopy (SEM) Analysis

SEM analysis is another method which is used to get information about the morphology of the nanocomposites. This method can be basically explained as the scanning of a fine beam of electrons across the surface of an opaque specimen to which a light conducting gold film has been applied by evaporation.

For this study, a low voltage scanning electron microscope at the METU Central Laboratuary was used for the SEM analysis.

3.3.5.3 Transmission Electron Microscopy (TEM) Analysis

In order to confirm the morphology of the nanocomposites, TEM analyses were performed since it yields information on the internal structure of materials. TEM is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. Views of the defect structure through direct visualization at atomic dimensions, polymer-clay interaction and distribution of the various phases can be understood by TEM Analysis.
For the preparation of the samples, firstly, ultra thin sections with 100 nm in thickness were cryogenically cut with a diamond knife at a temperature of -100 ºC. After that, the samples prepared were examined at an acceleration rate of 80 kV at UNAM.

3.4 Organoclays

For the preparation and synthesis of nanocomposites, two different clays were used, namely, Cloisite 30 B and Modified Clay.

Modified clay was synthesized by using the procedure in the study of Ozkoc et. al. [56] at Kocaeli University. As surfactant, Tributylhexadecylphosphonium bromide ($C_{28}H_{60}BrP$) was used.

CHAPTER 4

RESULTS AND DISCUSSION

In this thesis, two different procedures were performed for the purpose of synthesis of PEEs and PEE Nanocomposites. Before discussing the effect of soft segment length and hard segment length on PEEs and addition of organoclay into polymers, the details of the determination of reaction conditions will be given.

4.1 Determination of Reaction Conditions for Synthesis of Poly(ether/ester)s Based on Poly(butylene terephthalate) and Poly(ethylene glycol)

For the purpose of determination of optimum reaction conditions, temperatures of transesterification and polycondensation were studied first.

4.1.1 Determination of Transesterification Temperature

The transesterification temperature was determined by observing the reaction mixture during the experiment. In the beginning, the temperature was set to 145 ^{0}C as mentioned in Fakirov's study [13], but it was seen that at this temperature only DMT starts to melt and transesterification does not occur no matter how much time elapsed. So, in order to determine the temperature, it was gradually increased and the temperature at which transesterification starts was observed. A few experiments were carried out and it was concluded that 175 ^{o}C is a suitable temperature for the transesterification, since it is possible to observe the release of the side product, methanol, from the reaction mixture at this temperature. The graph of Temperature vs. Volume of Methanol which was obtained during the synthesis of PEE/1000/75 wt% PBT (2) is shown Figure 4.1.

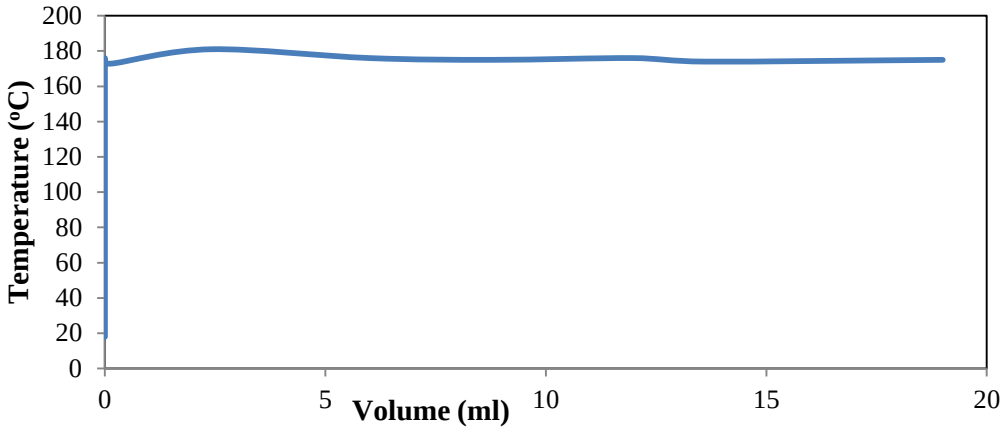


Figure 4.1 Temperature vs. Volume of Methanol Collected in the Synthesis of PEE/1000/75 wt% PBT (2)

4.1.2 Determination of Polycondensation Temperature

In the beginning of the thesis, the polycondensation temperature was decided as 260 °C which was declared in Fakirov's study [13] and few syntheses were performed at this temperature. The mechanical properties of the polymers which were synthesized according to the procedure were low, so in order to investigate the effect of higher temperature in the polycondensation step, the temperature of the reaction mixture was gradually increased, and it was observed that at 280 °C, the torque of the reaction mixture increased dramatically due to increase in molecular weight and viscosity. Then, it was decided to have two polycondensation temperatures in the reaction procedure as 260 °C and 280 °C, respectively. At 260 °C, the polycondensation step began and the reaction mixture stayed at this temperature for about one hour. When the volume of the excess 1,4-BD which was collected in the graduated tube did not change or when the desired amount of methanol volume was reached, the temperature of the reaction mixture is increased to 280°C and it stays at this temperature until the end of the reaction. In Figure 4.2, "Temperature vs. Torque" which was observed during the synthesis of PEE/1000/75wt% PBT (3) shows the effect of 280 °C in terms of increase in torque.

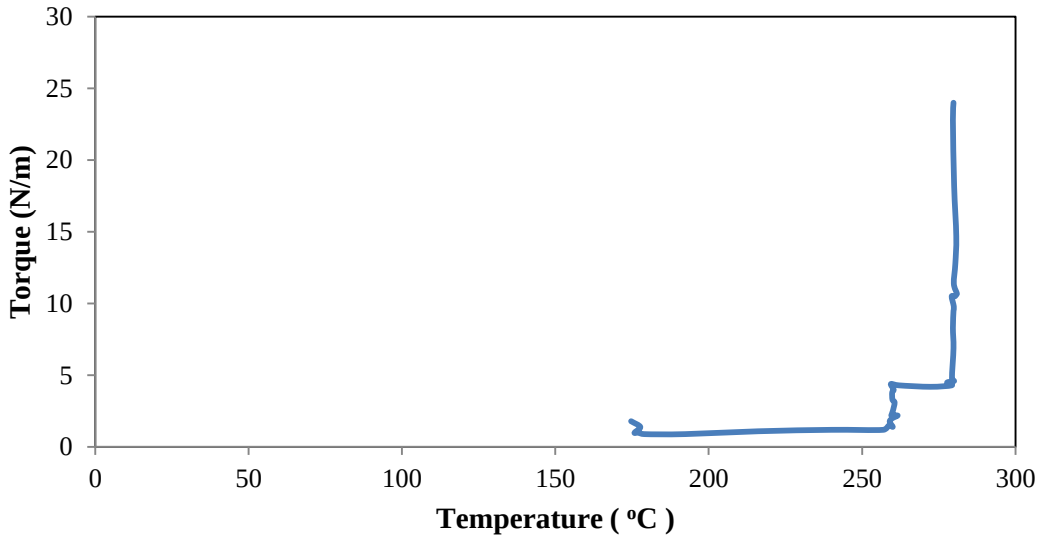


Figure 4.2 Temperature vs. Torque Graph of PEE/1000/75wt% PBT (3)

4.1.3 Determination of Transesterification and Polycondensation Time

In the literature [13, 46], since transesterification time is not mentioned, it was ascertained by performing a series of experiments at different reaction conditions, namely, the transesterification time. Through the reactions, it was observed that the molecular weights of polymers which had 45 minutes of transesterification time were higher so that for the first procedure, 45 minutes were chosen as the transesterification time.

For the second procedure, instead of constant transesterification time, constant volume ratio of the side product which is methanol was determined as 88-92 %.

4.2 Determination of Reaction Conditions for the Synthesis of Poly(ether/ester) Nanocomposites Based on Poly(butylene terephthalate) and Poly(ethylene glycol)

Since one of the aims of this study is to discuss the effect of introduction of organoclay into polymer matrix, the syntheses of the nanocomposites were performed by using the same reaction conditions except for the organoclay addition.

4.2.1 Determination of Organoclay

In order to obtain the nanocomposites without thermal degradation during the processing, it is important to use a thermally stable organoclay. In this thesis, two different organoclays, Cloisite® 30B and a Modified Clay were studied by TGA analysis.

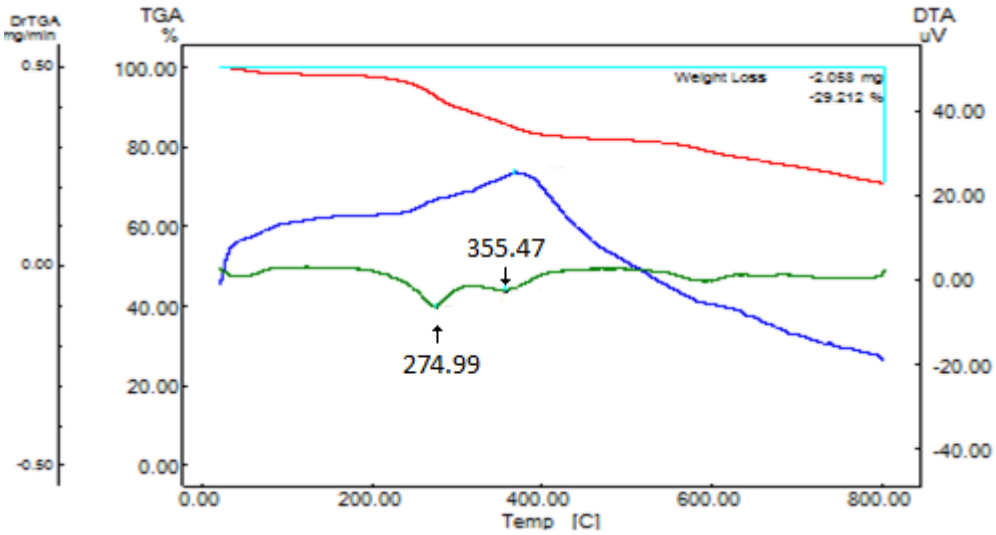


Figure 4.3 TGA Analysis of Cloisite 30B

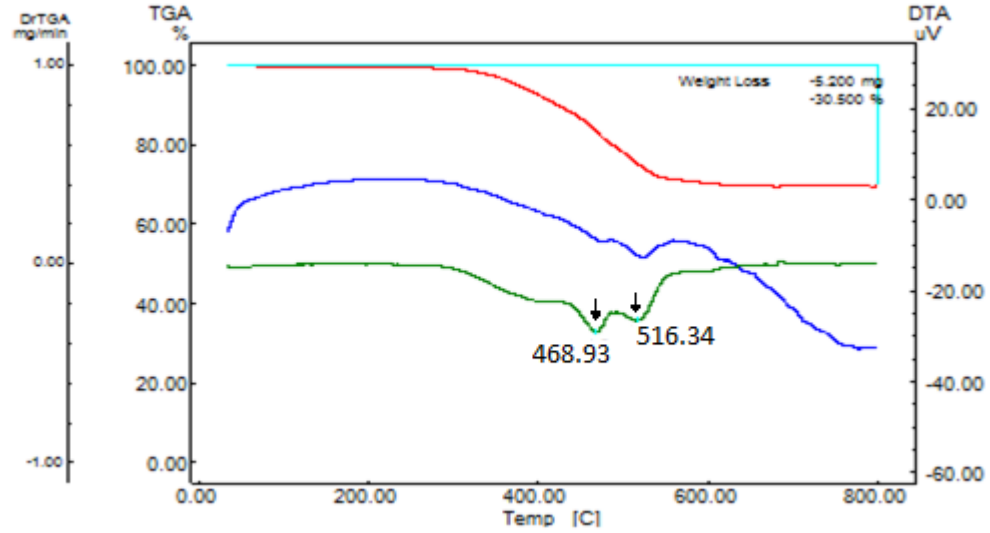


Figure 4.4 TGA Analysis of Modified Clay (TBHDP-MMT)

In both figures, there are two characteristic peaks. In the case of Cloisite 30B, the degradation temperatures are 274.99 ^{o}C and 355.47 ^{o}C, respectively. When modified clay is concerned, it is obviously clear that there is a significant increase in terms of degradation temperatures, namely 468.93 ^{o}C and 516.34 ^{o}C.

In the research of Ozkoc [56], thermal stability of Cloisite 30 B and modified organoclay were studied by TGA analysis, and it was observed that cumulative % weight loss at 280 ^{o}C for Cloisite 30 B and modified organoclay are 7% and 1%, respectively.

As mentioned in the previous parts, the highest temperature value during the synthesis of PEE nanocomposites is 280 ^{o}C. Since this temperature value is higher than the first

degradation temperature and very close to the second degradation temperature of Cloisite 30B, for the syntheses, modified clay was preferred.

4.3 Synthesis of PEEs Based on Poly(butylene terephthalate) and Poly(ethylene glycol) and Influence of Hard Segment Length on Structure

In the study, two different procedures were used in order to get PEEs; i.e. constant transesterification time and constant collected methanol volume ratio. In the beginning of the study, all PEEs were synthesized at constant transesterification time and mechanical properties were studied. However, since the results were not good, a second procedure was needed and was applied as mentioned in the previous parts. After the synthesis has been completed, first mechanical properties and molecular weight determination were studied and since the results were better compared to the first group, for the second group thermal analyses were performed in addition to spectroscopic analysis.

As mentioned in the experimental part, for each group having different hard segment lengths, more than two experiments were performed, but in this section, the ones that were synthesized at the same reaction conditions, namely at constant transesterification time and constant methanol volume ratio, are discussed.

4.3.1. Synthesis of PEEs with 37 wt % PBT

PEE/1000/37 wt % PBT (3) labeled polymer was synthesized at constant transesterification time, whereas PEE/1000/37 wt % PBT (5) labeled polymer was synthesized at constant methanol volume ratio.

Table 4.1 Reaction Conditions of PEEs with 37 wt % PBT

Sample Name	*Temp. of TE(^oC)*	*Duration of TE (min.)*	*Temp. of PC(^oC)*	*Duration of PC (min.)*	*Duration at 280 ^oC (min.)*
PEE/1000/37 wt%PBT(3)	175	45	260-280	195	121
PEE/1000/37 wt%PBT(5)	175-220	173	260-280	195	49

In Table 4.1, the first significant difference is the duration of transesterification time, the first one is 45 minutes while the second one is 173 minutes. During the synthesis of PEE/1000/37 wt % PBT (3), when the temperature was set to 260 ^oC, the ratio of methanol collected in the graduated cylinder to the theoretical volume of methanol was 67.5%. In the case of PEE/1000/37 wt % PBT (5), that ratio was 87.7 %, nearly 20 % higher.

Another difference between the reaction conditions is the duration at 280 ^{o}C. The duration of polycondensation time was kept constant but for PEE/1000/37 wt % PBT (3), duration at 280 ^{o}C is 121 minutes, while the duration at 280 ^{o}C is 49 minutes for PEE/1000/37 wt % PBT (5).

The effects of these two parameters were investigated in terms of mechanical properties and molecular weight determination in order to decide whether it is worth to synthesize PEE nanocomposites or not.

4.3.1.1. Tensile Tests

Since stress-strain curves provide information about the response of polymer to an applied stress, tensile stress-strain curves of PEEs with different PBT wt % are different from each other as shown in Figures 4.5-4.30.

Stress vs. Percentage Strain graphs for PEE/1000/37 wt % PBT (3) and PEE/1000/37 wt % PBT (5) are given Figure 4.5 and Figure 4.6.

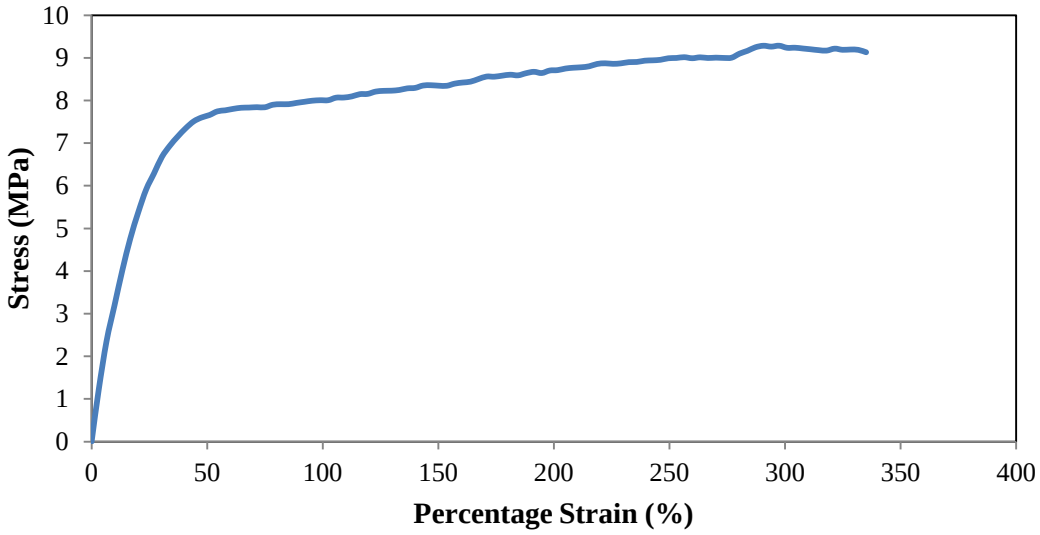


Figure 4.5 Stress vs. Percentage Strain Graph of PEE/1000/37wt % PBT (3)

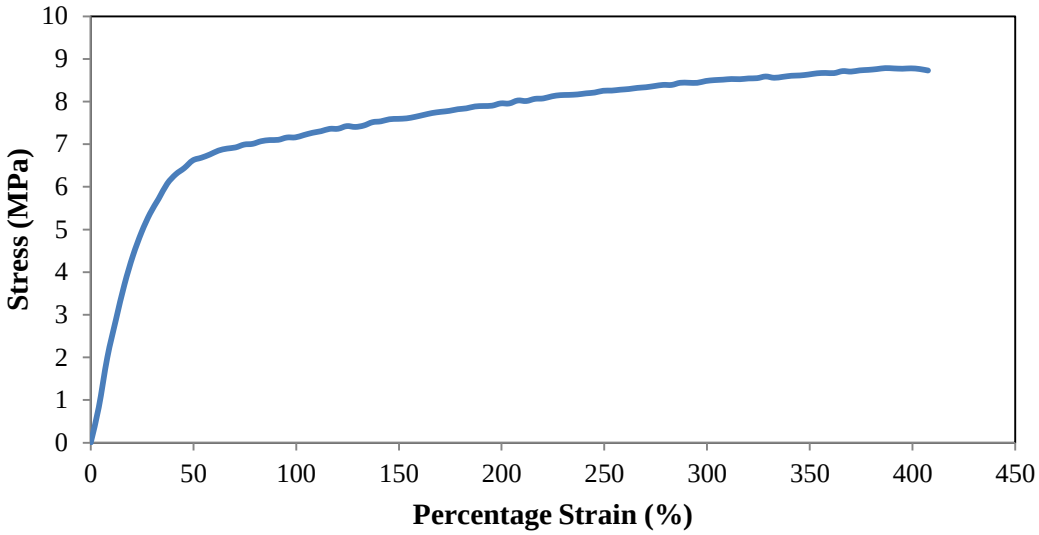


Figure 4.6 Stress vs. Percentage Strain Graph of PEE/1000/37 wt % PBT (5)

As shown in Table 4.2, two PEE samples have very close mechanical properties in terms of Young's modulus and tensile strength but PEE/1000/37 wt %PBT (5) sample has a higher extension value.

Table 4.2 Mechanical Properties of PEEs Having 37 wt % PBT

Sample Name	***Young's Modulus (MPa)***	***Tensile Strength (MPa)***	***Percentage Elongation at Fracture (%)***
PEE/1000/37 wt%PBT(3)	7.8	9.3	338
PEE/1000/37 wt%PBT(5)	7.0	8.8	412

4.3.1.2 GPC Results

Table 4.3 gives the weigth average molecular weight results of PEEs Having 37 wt % PBT.

Table 4.3 Weight Average Molecular Weight Results of PEEs Having 37 wt % PBT

Sample Name	***GPC Result (Mw)***
PEE/1000/37 wt%PBT(3)	$4.95x10^4$
PEE/1000/37 wt%PBT(5)	$1.23x10^5$

When the molecular weight is concerned, the one synthesized at constant volume ratio has better results as shown in Table 4.3. This result is related to the duration of transesterification step. As the ratio of methanol volume collected in the graduated cylinder increases, the molecular weight increases. For the other parameter, duration at 280 ^{o}C, it is difficult to give a general conclusion, but it is obvious that the effect of duration of transesterification is greater than the duration at 280 ^{o}C.

For PEEs having 37 wt% PBT, it is clear that both procedures resulted in poor mechanical properties. These results can be attributed to the low content PBT in PEE. It should be mentioned that when the ratio of hard segment is low, it is difficult to obtain thermoplastic elastomer with good mechanical properties as discussed in the studies in the literature [13].

4.3.2 Synthesis of PEEs with 49 wt % PBT

For this group of PEEs, PEE/1000/49 wt % PBT (7) poylmer was synthesized at constant transesterification time and PEE/1000/49 wt % PBT (8) polymer was synthesized at constant methanol volume ratio.

Table 4.4 Reaction Conditions of PEEs with 49 wt % PBT

Sample Name	***Temp. of TE(^{o}C)***	***Duration of TE (min.)***	***Temp. of PC(^{o}C)***	***Duration of PC (min.)***	***Duration at 280 ^{o}C (min.)***
PEE/1000/49 wt%PBT(7)	175	45	260 -280	195	121
PEE/1000/49 wt% PBT(8)	175-220	165	260-280	195	52

When the two reaction conditions are compared, the first significant difference is the duration of transesterification time, the first one is 45 minutes, while the second one is 165 minutes. For the synthesis of PEE/1000/49 wt % PBT (7), when the temperature was set to 260 ^{o}C, the ratio of methanol collected in the graduated cylinder to the theoretical volume of methanol was 65.1 %. In the case of PEE/1000/49 wt % PBT (8), that ratio was 88.6%, nearly 24% higher.

In addition, the durations at 280 ^{o}C are distinctly different. The duration of polycondensation time was kept constant as in the case of other synthesis, but for PEE/1000/49 wt% PBT (7), the duration at 280 ^{o}C is 121 minutes while the duration at 280 ^{o}C is 52 minutes for PEE/1000/49 wt % PBT (8).

The effects of these two parameters are analyzed in terms of mechanical properties and molecular weight determination.

4.3.2.1 Tensile Tests

Tensile test results are given in Figure 4.7 and 4.8.

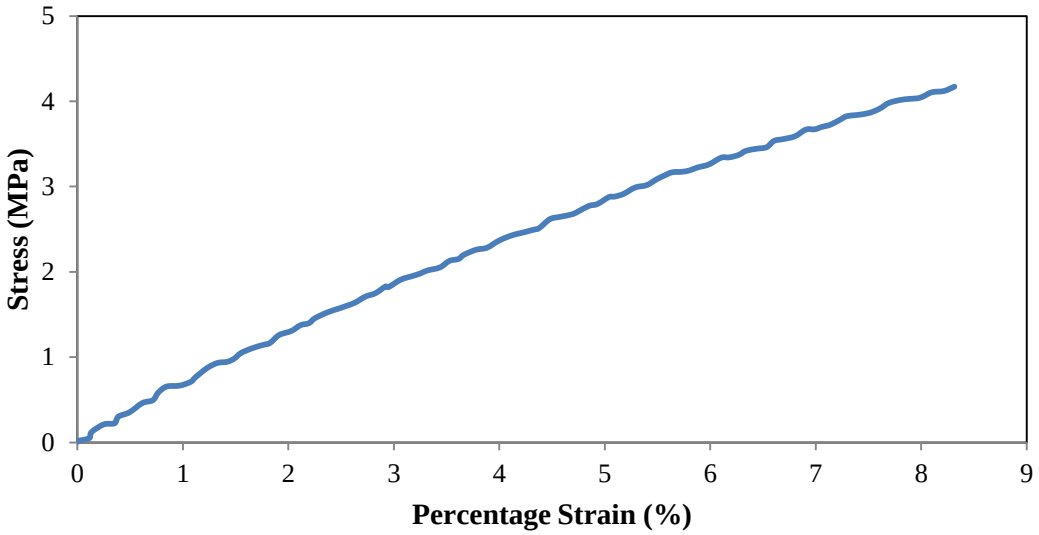


Figure 4.7 Stress vs. Percentage Strain Graph of PEE/1000/49 wt % PBT (7)

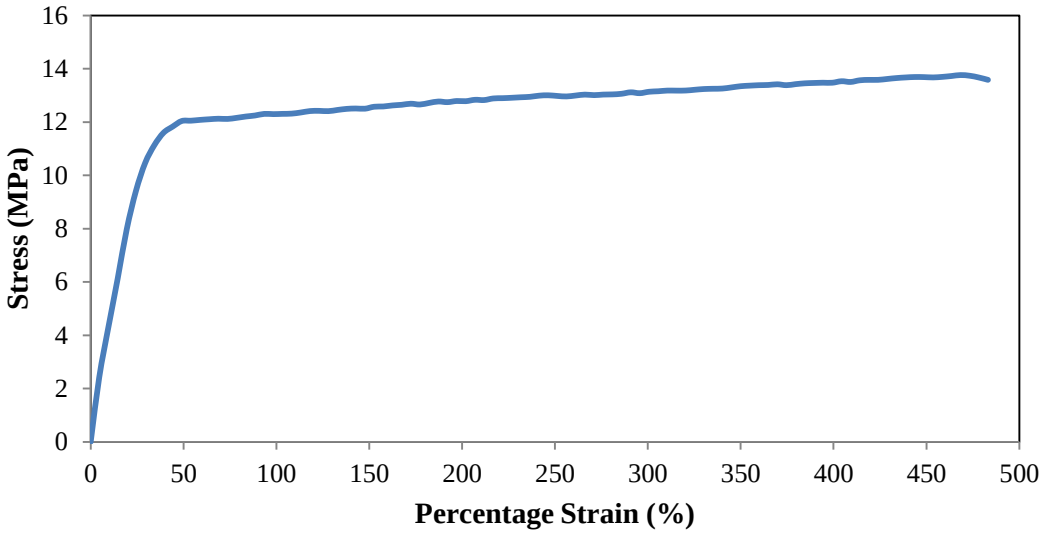


Figure 4.8 Stress vs. Percentage Strain Graph of PEE/1000/49 wt % PBT (8)

Table 4.5 Mechanical Properties of PEEs Having 49 wt % PBT

Sample Name	***Young's Modulus (MPa)***	***Tensile Strength (MPa)***	***Percentage Elongation at Fracture (%)***
PEE/1000/49 wt%PBT(7)	-	4.2	8.33
PEE/1000/49 wt% PBT(8)	11.95	13.77	488

From the Table 4.5, it is clear that PEE/1000/49 wt % PBT (8) which was synthesized at constant volume ratio has better mechanical properties when compared to PEE/1000/49 wt % PBT(7). The effect of duration of transesterification is obviously clear for PEEs having 49 wt % PBT.

4.3.2.2 GPC Results

Table 4.6 gives weight average molecular weights of PEEs with 49 wt % PBT.

Table 4.6 Weight Average Molecular Weight Results of PEEs Having 49 wt % PBT

Sample Name	***GPC Result (Mw)***
PEE/1000/49 wt%PBT(7)	-
PEE/1000/49 wt% PBT(8)	$3.955x10^4$

The mechanical properties of PEE/1000/49 wt % PBT (7) was very poor, thus the molecular weight determination was done only for PEE/1000/49 wt % PBT (8).

4.3.3 Synthesis of PEEs with 57 wt % PBT

Similar to other synthesis, although more than two reactions had been performed, only two samples, namely, PEE/1000/57 wt % PBT (2), at constant transesterification time, and PEE/1000/57 wt % PBT (3), at constant volume ratio, are discussed in this part.

Table 4.7 Reaction Conditions of PEEs Having 57 wt % PBT

Sample Name	*Temp. of TE(°C)*	*Duration of TE (min.)*	*Temp. of PC(°C)*	*Duration of PC (min.)*	*Duration at 280 °C (min.)*
PEE/1000/57 wt%PBT(2)	175	45	260 -280	195	116
PEE/1000/57 wt%PBT(3)	175-220	118	260-280	195	52

In terms of duration of transesterification time, there is a significant difference between the two syntheses, 45 min. and 118 min., respectively. For PEE/1000/57 wt % PBT (2), the ratio of methanol collected to the theoretical volume of methanol was 64% while it was 91.6% for PEE/1000/57 wt % PBT (3). As in the other synthesis, the polycondensation time was kept constant, but the duration at 280 °C is longer for the synthesis at constant transesterification time than the synthesis at constant volume ratio.

4.3.3.1 Tensile Tests

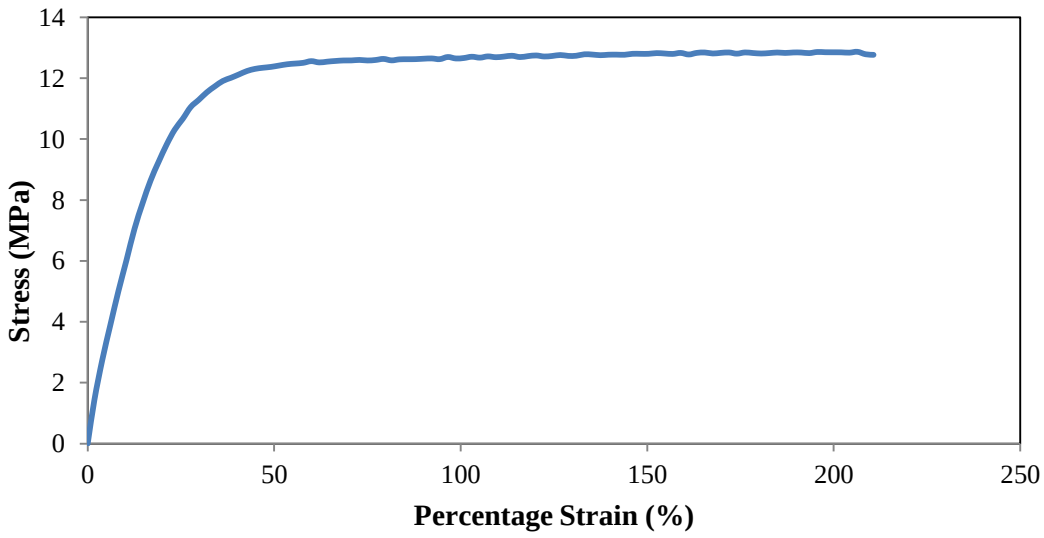


Figure 4.9 Stress vs. Percentage Strain Graph of PEE/1000/57 wt % PBT (2)

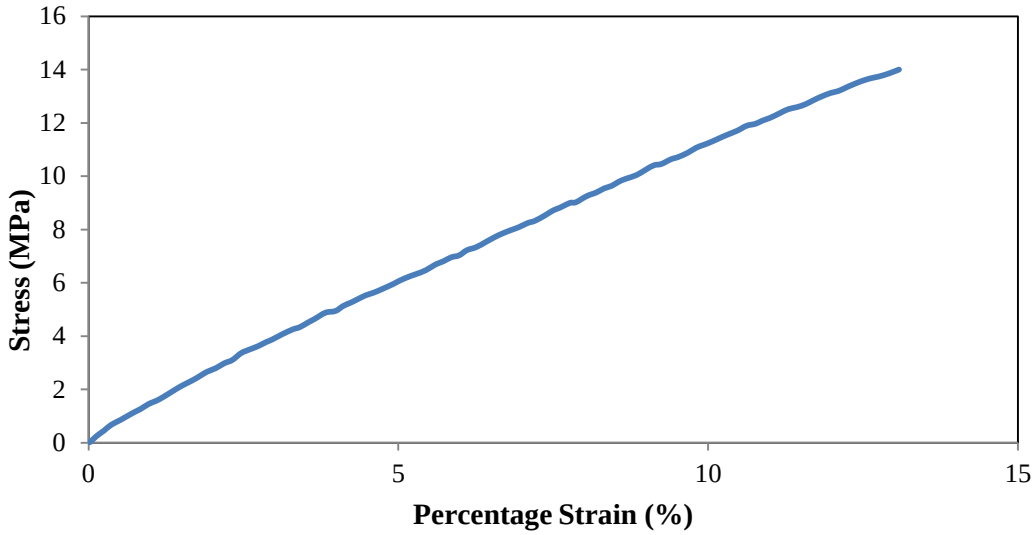


Figure 4.10 Stress vs. Percentage Strain Graph of PEE/1000/57 wt % PBT (3)

In the tensile analysis of PEE/1000/57 wt % PBT (3), the samples slipped out from the gaps for two times, so the mechanical properties are not given in Table 4.8

Table 4.8 Mechanical Properties of PEEs Having 57 wt % PBT

Sample Name	***Young's Modulus (MPa)***	***Tensile Strength (MPa)***	***Percentage Elongation at Fracture (%)***
PEE/1000/57 wt%PBT(2)	12.66	12.88	212

4.3.3.2 GPC Results

Although the mechanical analysis results of PEE/1000/57 wt % PBT(3) could not be obtained, from Table 4.9, it is clear that molecular weight of PEE/1000/57 wt % PBT(3) is approximately 2.5 times higher than PEE/1000/57 wt % PBT(2).

Table 4.9 Weight Average Molecular Weight Results of PEEs Having 57 wt % PBT

Sample Name	***GPC Result (Mw)***
PEE/1000/57 wt%PBT(2)	$5.357x10^4$
PEE/1000/57 wt% PBT(3)	$1.40x10^5$

4.3.4 Synthesis of PEEs with 75 wt % PBT

For this group of PEE, PEE/1000/75 wt % PBT (3) polymer is the one which is synthesized at constant transesterification time, whereas PEE/1000/75 wt % PBT (5) is the one synthesized at constant methanol volume ratio. The reaction conditions are given in Table 4.10.

Table 4.10 Reaction Conditions of PEEs with 75 wt % PBT

Sample Name	***Temp. of TE(^oC)***	***Duration of TE (min.)***	***Temp. of PC(^oC)***	***Duration of PC (min.)***	***Duration at 280 ^oC (min.)***
PEE/1000/75 wt%PBT(3)	175	45	260-280	195	116
PEE/1000/75 wt%PBT(5)	175-220	135	260-280	195	46

In Table 4.10, when the two reaction conditions are studied, the first significant difference is the duration of transesterification time, the first one is 45 minutes, while the second one is 135 minutes. During the synthesis of PEE/1000/75 wt % PBT (3), when the temperature was set to 260 ^oC, the ratio of methanol collected in the graduated cylinder to the theoretical volume of methanol was 72.30%. In the case of PEE/1000/75 wt % PBT (5), that ratio was 88.3%.

Another difference between the reaction conditions is the duration at 280 ^oC. The duration of polycondensation time was kept constant, but for PEE/1000/75 wt % PBT (3), the duration at 280 ^oC is 116 minutes, whereas the duration at 280 ^oC is 46 minutes for PEE/1000/75 wt % PBT (5).

The effects of these two parameters were investigated in terms of mechanical properties and molecular weight determination in order to decide on the synthesis of PEE nanocomposites.

4.3.4.1 Tensile Tests

Figure 4.11 and 4.12 show Stress vs. Strain (%) curves and test results are given in Table 4.11.

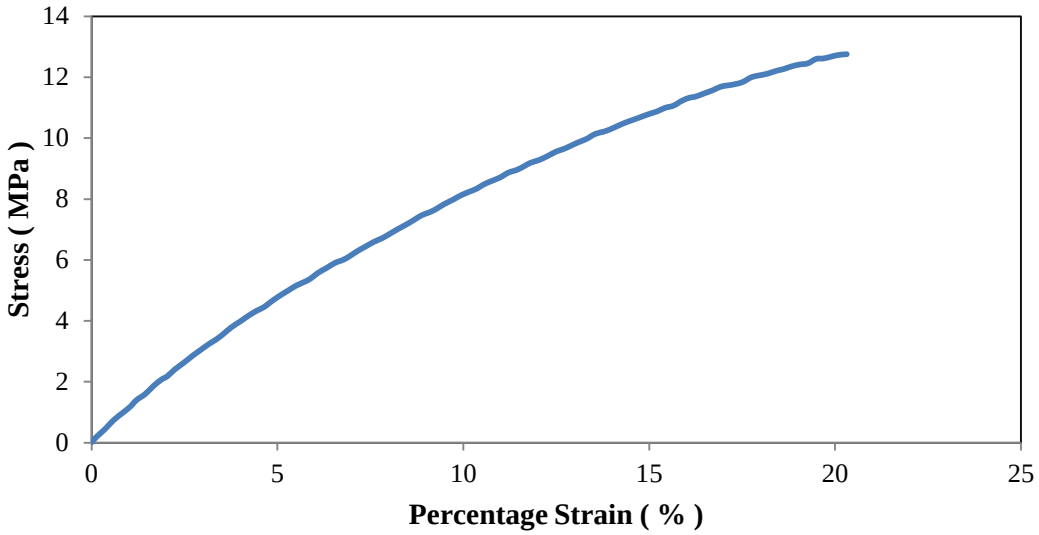


Figure 4.11 Stress vs. Percentage Strain Graph of PEE/1000/75 wt % PBT (3)

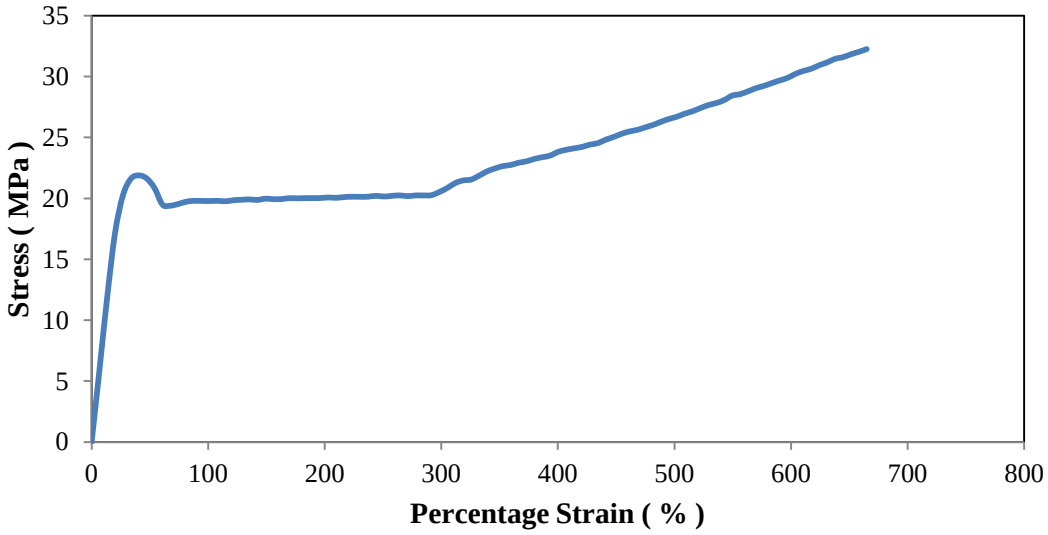


Figure 4.12 Stress vs. Percentage Strain Graph of PEE/1000/75 wt % PBT (5)

Table 4.11 Mechanical Properties of PEEs Having 75 wt % PBT

Sample Name	***Young's Modulus (MPa)***	***Tensile Strength (MPa)***	***Percentage Elongation at Fracture (%)***
PEE/1000/75 wt%PBT(3)	-	12.8	20
PEE/1000/75 wt%PBT(5)	19.49	32.4	672

In terms of mechanical behaviours, PEE/1000/75 wt % PBT (5) has superior properties compared to PEE/1000/75 wt % PBT (3). Quite obvious is the difference in the tensile strength and elongation at fracture data when compared with the ones in the study of Fakirov [13]. In that study, the tensile strength (in MPa) and the elongation at fracture (in %) are 27.8 and 499, respectively. For PEE/1000/75 wt % PBT (5), the strength is 32.4 MPa and elongation at fracture is 672%.

4.3.4.2 GPC Results

Table 4.12 gives the weight average molecular weight results of PEEs having 75 wt % PBT.

Table 4.12 Weight Average Molecular Weight Results of PEEs Having 75 wt % PBT

Sample Name	***GPC Result (Mw)***
PEE/1000/75 wt%PBT(3)	$4.88x10^4$
PEE/1000/75 wt% PBT(5)	$1.12x10^5$

4.3.5 Influence of Hard Segment Length on Structure of Poly(ether-ester) Based Thermoplastic Elastomers

In order to discuss the effect of hard segment length, a series of poly(ether-ester)s based on poly(butylene terephthalate) and poly(ethylene glycol) were synthesized according to the two different reaction conditions which were discussed in the previous parts. In the synthesis, the soft segment lengths were kept constant by using PEG with molecular weight of 1000 gr/mole, while the contents of hard segment were varied from 37 to 75 wt %.

4.3.5.1 Mechanical Properties

4.3.5.1.1 Tensile Tests

For PEEs which are synthesized at constant transesterification time, the effect of hard segment lenght is as expected and it is obviously clear that as the length of hard segment, in other words wt % of PBT, increases, tensile strength increases, but in the case of PEE/1000/49 wt % PBT (7), there is an unexpected decrease as shown in Figure 4.13.

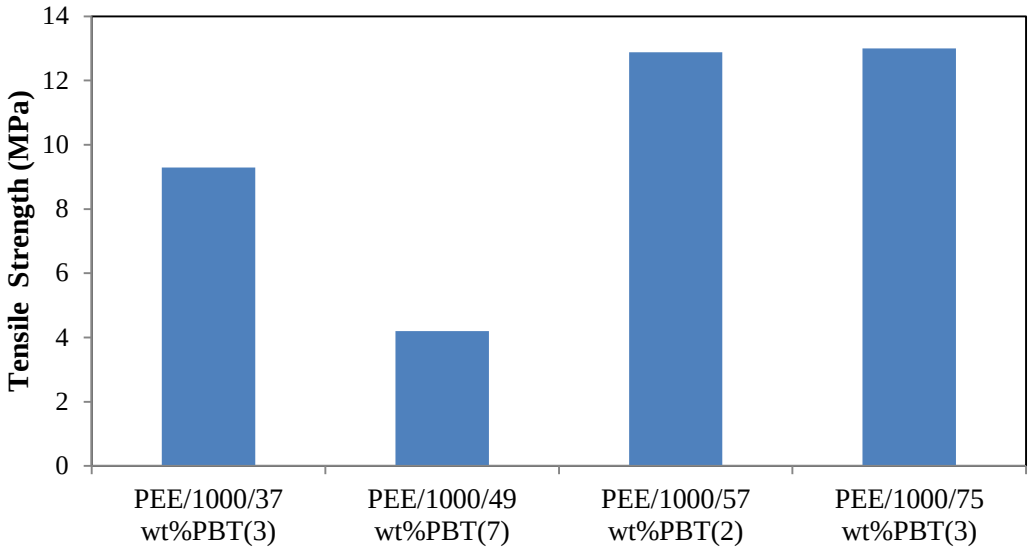


Figure 4.13 Tensile Strength of PEEs Having Different Hard Segment Length

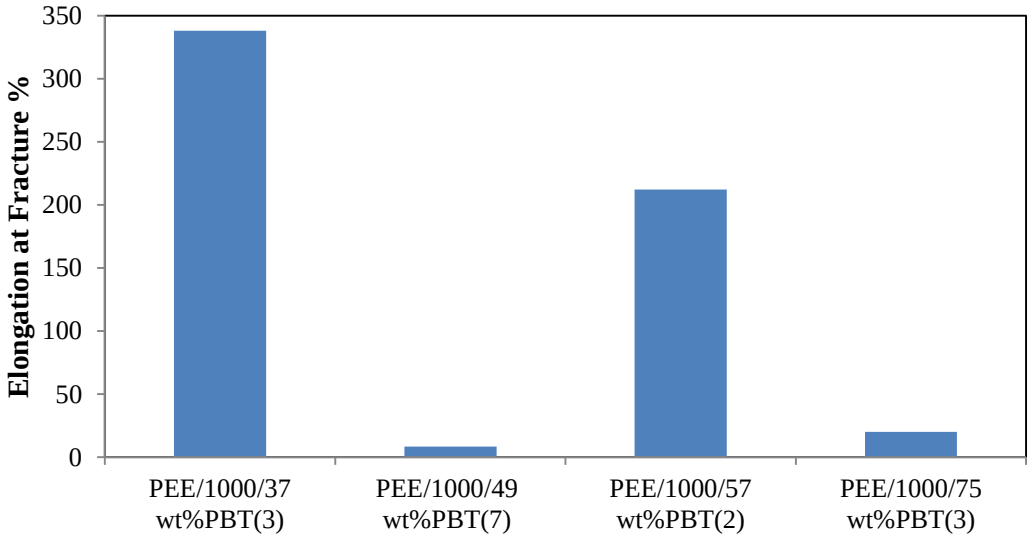


Figure 4.14 Elongation at Fracture of PEEs Having Different Hard Segment Length

With the increase of PBT wt %, % elongation at fracture decreases, but there is a sharp decrease which is not expected. This obvious difference can be explained by very low tensile strength of PEE having 49 wt % PBT.

When the second procedure, constant methanol volume ratio, was applied, the trend was in the same manner as in the studies of Szymczyk [47] and Fakirov [13]. In other words, the study showed that tensile strength values increased with the increase of hard segment content, since the degree of crystallinity increases as shown later. In addition, it should be

mentioned that weight average molecular weight of PEEs increase significantly when the second procedure was used.

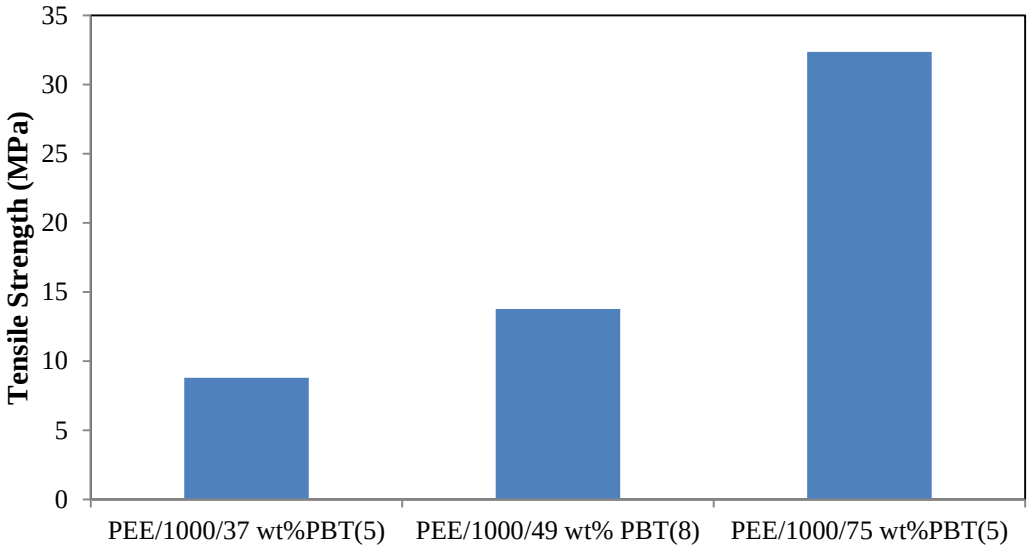


Figure 4.15 Tensile Strength of PEEs Having Different Hard Segment Length

The tensile strength of PEE with 75 wt % PBT has a value of 32.3 MPa which is about 3.5 times higher than the one with 37 wt % PBT.

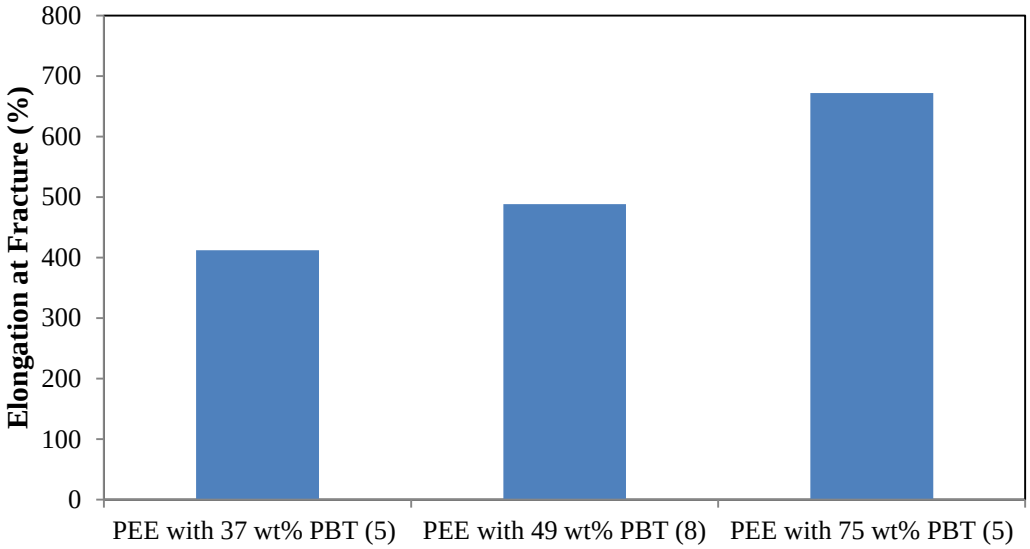


Figure 4.16 Elongation at Fracture of PEEs Having Different Hard Segment Length

In the study, the decrease of elongation at fracture was expected with the increase of PBT wt % as discussed in Fakirov's study [13]. However, the difference in elongation data is obvious. From Figure 4.16, it is clear that as the percentage of PBT increases, elongation at break also increases. This result may be explained in terms of the degree of crystallinity.

When mechanical analysis results are compared with the ones in Fakirov's study [13], it is seen that the tensile strength of PEE having 75 wt% PBT is greater and in terms of elongation at break, the percentage is better since it is 499 in Fakirov's study.

4.3.5.2 Thermal Analysis

4.3.5.2.1 DSC Analysis

The first cooling and second heating scans were used to determine the melting and crystallization peaks.

In the study of Fakirov [13], in order to study thermal properties of PEEs, DSC analysis was done and DSC traces are given in Figure 4.17.

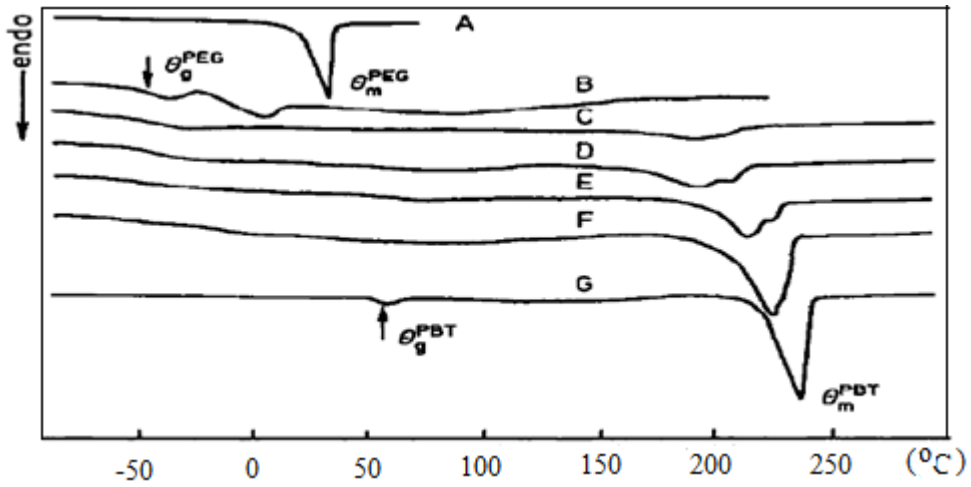


Figure 4.17 DSC traces of the homopolymers and poly(ether/ester)s synthesized with different contents of wt% PBT: 0(A); 24% (B); 49% (C); 57% (D); 75% (E); 79% (F); 100% (G) [13].

Table 4.13 DSC Data of Synthesized PEEs

Sample Name	*Tg (PEG) (^oC)*	*Tm (PEG) (^oC)*	*Tg (PBT) (^oC)*	*Tm (PBT) (^oC)*
PEE/1000/37 wt%PBT (5)	-47.3	7.3	-	175.2
PEE/1000/49 wt% PBT (8)	-48.0	-	-	191.9
PEE/1000/57 wt%PBT (3)	-46.8	-	-	208.6
PEE/1000/75 wt %PBT (5)	-36.3	-	-	213.0

From Table 4.13, although the values for 37 wt % PBT and 49 wt % PBT are very close, it is possible to observe the shift of glass transition temperatures of PEG towards higher values. This result can be explained by the increase of soft amorphous phase of amorphous PBT segments resulting in a restriction of the polyether segment mobility [13]. Another reason for the decrease can be the increase of the crystalline PBT fraction. In other words, the heat capacity values at Tg increase as hard segment content imcreases since the degree of phase separation increases when PBT segment content increases [45].

The only melt temperature of PEG was observed in the DSC curve of the PEE with 37 wt % PBT as 7.3 ^oC. Since the melt temperature of pure PEG is 34 ^oC [13], it is in the accepted range. On the other DSC curves, no melting peak was detected for PEG. This result indicated that PEG units cannot aggregate to form crystalline region as they were present in low concentration.

As the PBT segment length increases, melting point of PBT increases dramatically owing to higher degree of crystallization.

4.3.5.3 Spectroscopic Analysis

4.3.5.3.1 FTIR-ATR Analysis

The synthesized PEEs were characterized by FTIR-ATR measurements. The signals at 2900 cm^{-1} are due to the presence of methylene bonds and since the length of PEG was kept constant, intensities of the spectra are the nearly the same. Absorption bands at 1718 cm^{-1} are attributed to carbonyl groups in the structure. The multiplets in the region between 1300 and 1100 cm^{-1} are assigned to skeletal vibrations of ester and ether fragments. The bands at 1520 cm^{-1} are due to stretching vibrations of carbon-carbon bonds of terephthalic benzene ring. The aromatic carbon-hydrogen bonds are observed at 1000 cm^{-1}.

In the studies of Fakirov [13, 48], it was claimed that the increase of PBT content in the structures results in abrupt increase in the intensity of bands at 1520 and 1000 cm^{-1} and it was added that the change could be used to prove the presence of hard segment fraction in the structure. The change in the intensities of bands at 1000 cm^{-1} are observed here as well, but the changes in 1520 cm^{-1} can not be detected in Figure 4.18.

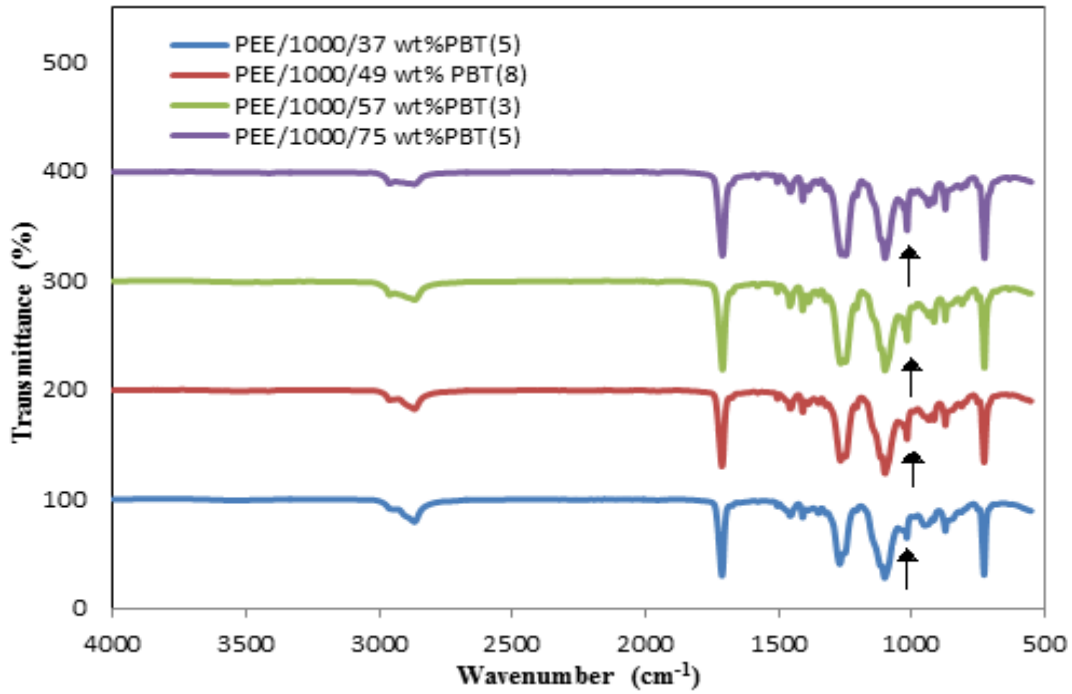


Figure 4.18 ATR Spectra of PEEs with Different PBT wt%

4.4 Synthesis and Preparation of PEE Nanocomposites Based on Poly(butylene terephthalate) and Poly(ethylene glycol)

4.4.1 PEE Nanocomposites with 37 wt % PBT

For PEEs having 37 wt % PBT, in-situ synthesis of nanocomposites was not performed instead, its nanocomposites were prepared only by melt intercalation.

In order to get nanocomposites of PEE/1000/37 wt % PBT (5), polymer and predetermined amount of modified organoclay (TBHDP-MMT), 0.1%, 0.3% and 0.5% (all wt %), respectively, were mixed with a twin-screw extruder and then injection molded. The results of the tensile tests on these materials are shown in Figure 4.19 through 4.21.

4.4.1.1 Tensile Tests

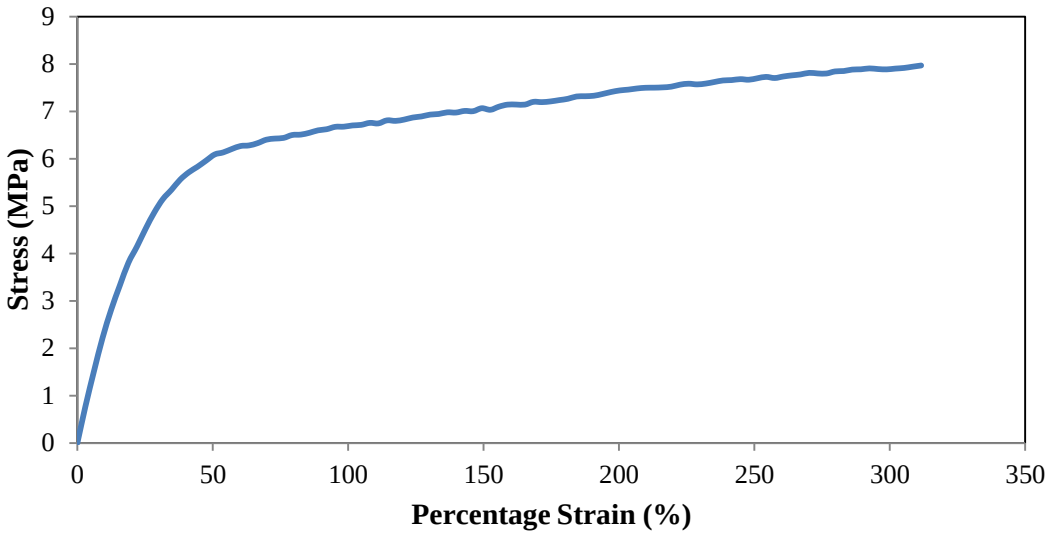


Figure 4.19 Stress vs. Percentage Strain Graph of PEE/1000/37 wt % PBT (5) +0.1% TBHDP-MMT

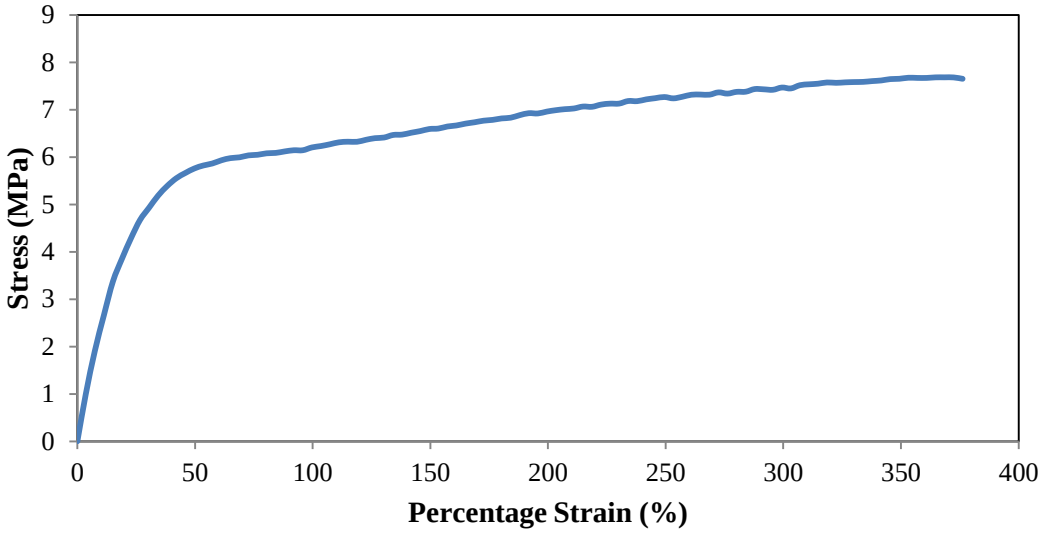


Figure 4.20 Stress vs. Percentage Strain Graph of PEE/1000/37 wt % PBT (5) +0.3% TBHDP-MMT

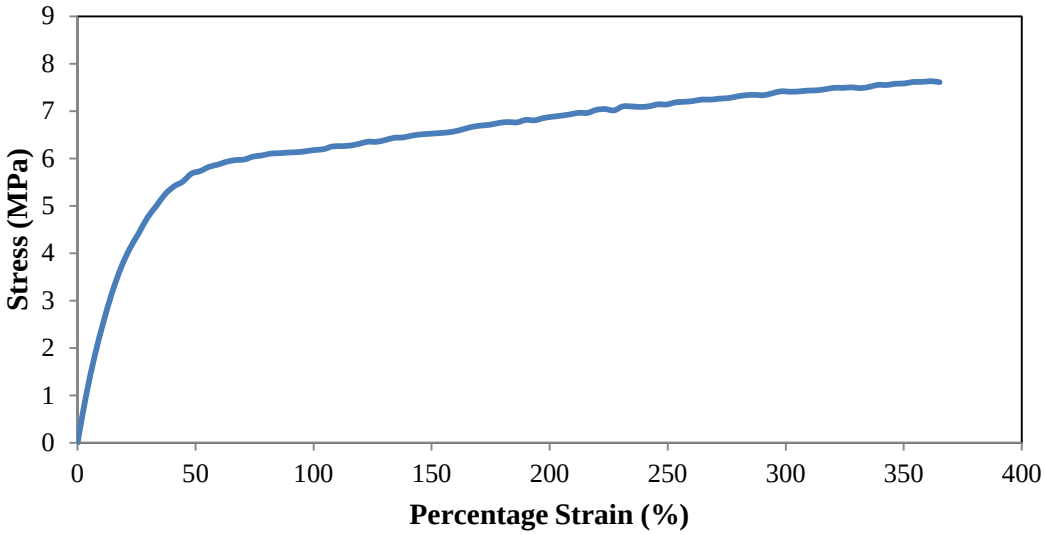


Figure 4.21 Stress vs. Percentage Strain Graph of PEE/1000/37 wt % PBT (5) +0.5% TBHDP-MMT

4.4.2 PEE Nanocomposites with 49 wt % PBT

Since tensile test results of PEE/1000/49 wt % PBT (8) were not so good, only melt intercalation method was used to obtain PEE nanocomposites having 49 wt % PBT and the effects of addition of organoclay are discussed.

4.4.2.1 Tensile Tests

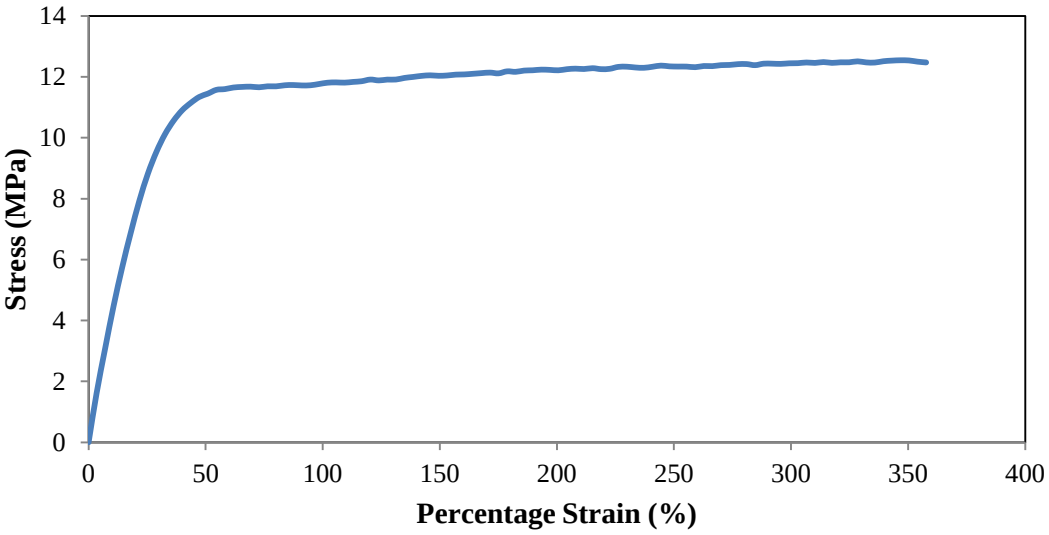


Figure 4.22 Stress vs. Percentage Strain Graph of PEE/1000/49 wt % PBT (8) + 0.1% TBHDP-MMT

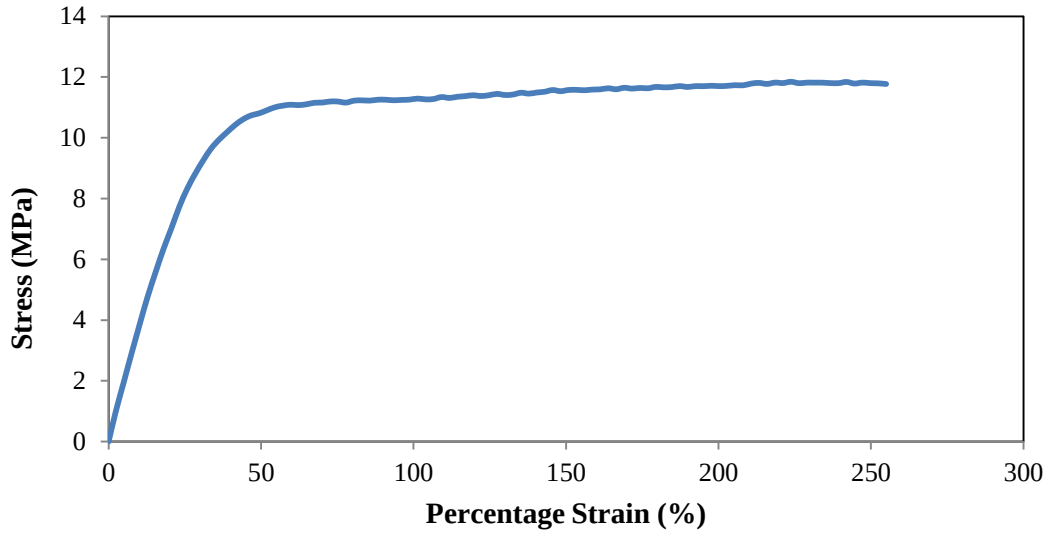


Figure 4.23 Stress vs. Percentage Strain Graph of PEE/1000/49 wt % PBT (8) + 0.3% TBHDP-MMT

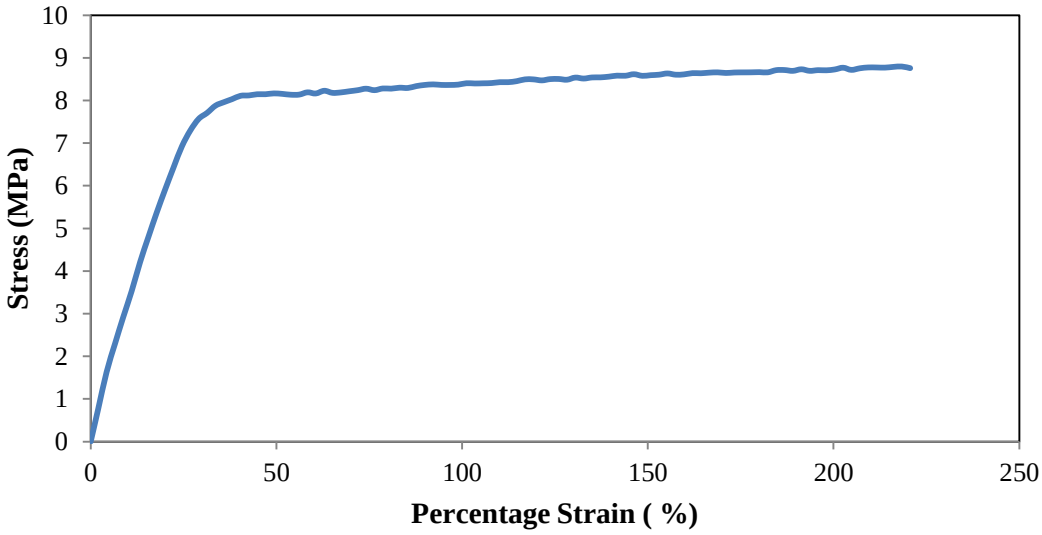


Figure 4.24 Stress vs. Percentage Strain Graph of PEE/1000/49 wt % PBT (8) + 0.5% TBHDP-MMT

4.4.3 PEE Nanocomposites Having 57 wt% PBT

PEE/1000/57 wt % PBT (3) gave better results than the other two groups, i.e. PEEs with 37% and 49%, so, for this group of PEE, both in-situ polymerization and melt intercalation methods were used in order to get PEE nanocomposites.

4.4.3.1 Synthesis of PEE Nanocomposites Having 57 wt % PBT

Synthesis of PEE nanocomposites were performed by using the same procedure of PEE/1000/57 wt % PBT (3) except for the addition of the organoclay. Different from the neat polymer synthesis, in the beginning of the experiment, 1,4-BD and organoclay were mixed at room temperature for 30 minutes in the ultrasonic bath in order to disperse the organoclay. Then, the other reactants were added and the same procedure was followed to synthesize the nanocomposites.

The reaction conditions are shown in Table 4.14.

Table 4.14 Reaction Conditions of PEE Nanocomposites Having 57 wt % PBT

Sample Name	***Temp. of TE(^oC)***	***Duration of TE (min.)***	***Temp. of PC(^oC)***	***Duration of PC (min.)***	***Duration at 280^oC (min.)***
PEE/1000/57 wt%PBT-0.1%	175	108	260-280	195	46
PEE/1000/57 wt%PBT-0.3%	175	98	260-280	195	47
PEE/1000/57 wt%PBT-0.5%	175	162	260-280	195	47

For the synthesis of PEE/1000/57 wt % PBT-0.1 %, when the temperature was set to 260 ^oC in order to begin polycondensation step, the ratio of volume of methanol collected to the volume of theoretical one was 91.7%, whereas it was 90.7% for the case of PEE/1000/57 wt % PBT-0.3%. When these two ratios are taken into consideration, duration of transesterification times for two nanocomposites were not so different, but it should be mentioned that for the nanocomposite having 0.5% organoclay, with the increase of organoclay content, duration of transesterification increases significantly because the same ratio of methanol was collected for PEE/1000/57 wt % PBT-0.5% (90.7%) nearly one hour later compared to that of PEE/1000/57 wt % PBT-0.3%.

Except for the duration of transesterification time, the other reaction conditions are nearly kept constant for the synthesis of nanocomposites in order to discuss the effect of organoclay content.Stress vs. Strain (%) curves for this set of samples are shown in Figures 4.25 through 4.27.

4.4.3.1.1 Tensile Tests of Synthesized PEE Nanocomposites

Tensile analysis results of PEE nanocomposites are given through Figure 4.25, 4.26 and 4.27.

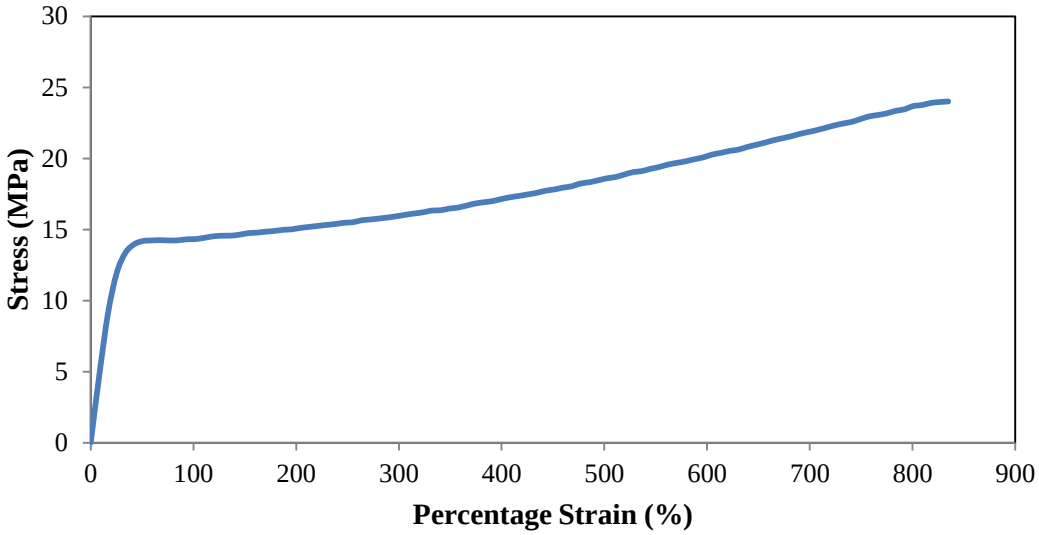


Figure 4.25 Stress vs. Percentage Strain Graph of PEE/1000/57 wt % PBT-0.1 % TBHDP-MMT

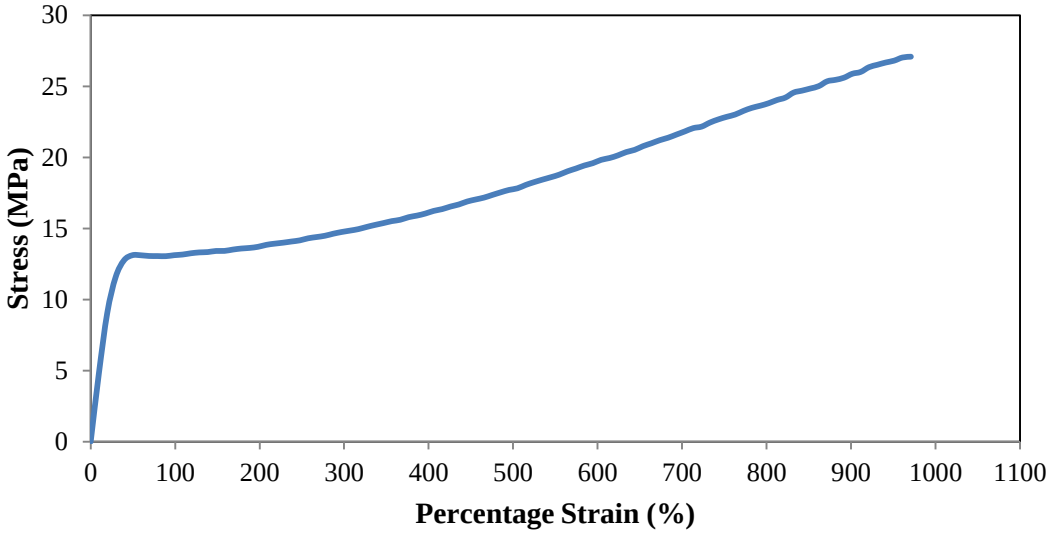


Figure 4.26 Stress vs. Percentage Strain Graph of PEE/1000/57 wt % PBT-0.3% TBHDP-MMT

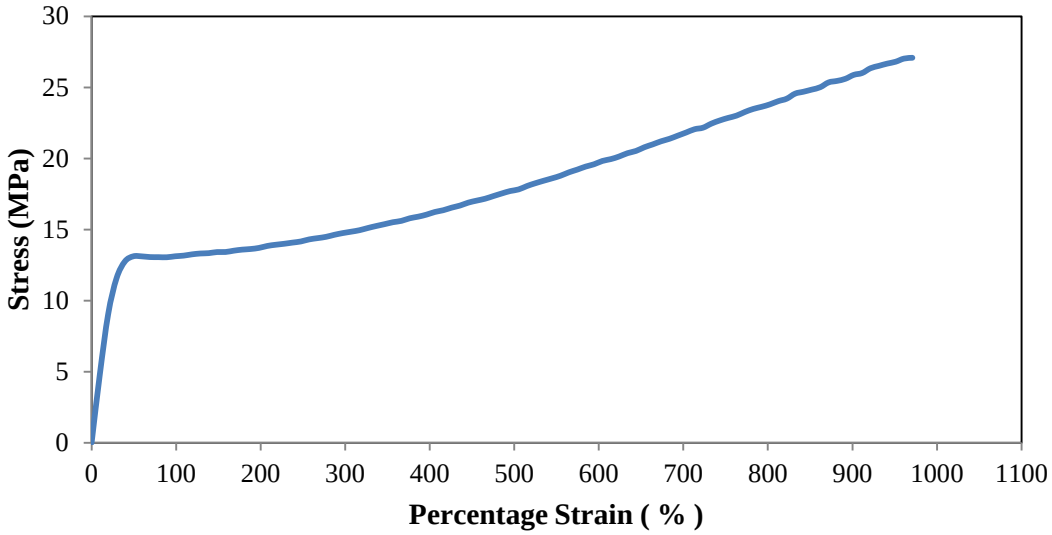


Figure 4.27 Stress vs. Percentage Strain Graph of PEE/1000/57 wt % PBT-0.5% TBHDP-MMT

4.4.3.2 Preparation of PEE Nanocomposites Having 57 wt % PBT by Melt Compounding

PEE/1000/57 wt % PBT (3) and predetermined amount of organoclay, 0.1%, 0.3% and 0.5%, were mixed by using the twin-screw extruder in order to observe the effects of melt compounding vs. in-situ polymerization. The results of the tensile tests on melt compounded materials are displayed in Figures 4.28 through 4.30. These results are compared later.

4.4.3.2.1 Tensile Tests of Melt Compounded PEE Nanocomposites

Tensile analysis results of PEE nanocomposites are given through Figure 4.28, 4.29 and 4.30.

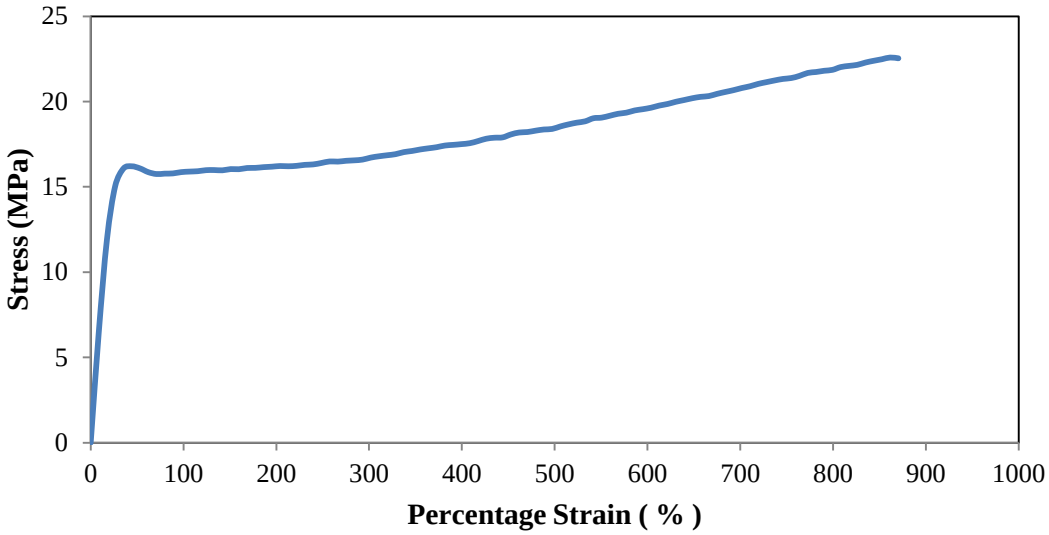


Figure 4.28 Stress vs. Percentage Strain Graph of PEE/1000/57 wt % PBT (3) +0.1% TBHDP-MMT

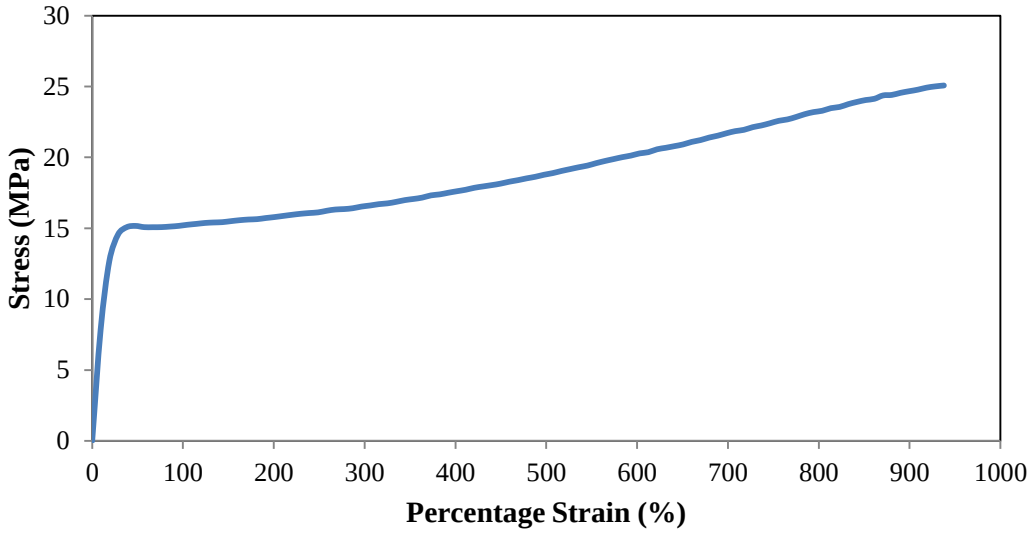


Figure 4.29 Stress vs. Percentage Strain Graph of PEE/1000/57 wt % PBT (3) +0.3% TBHDP-MMT

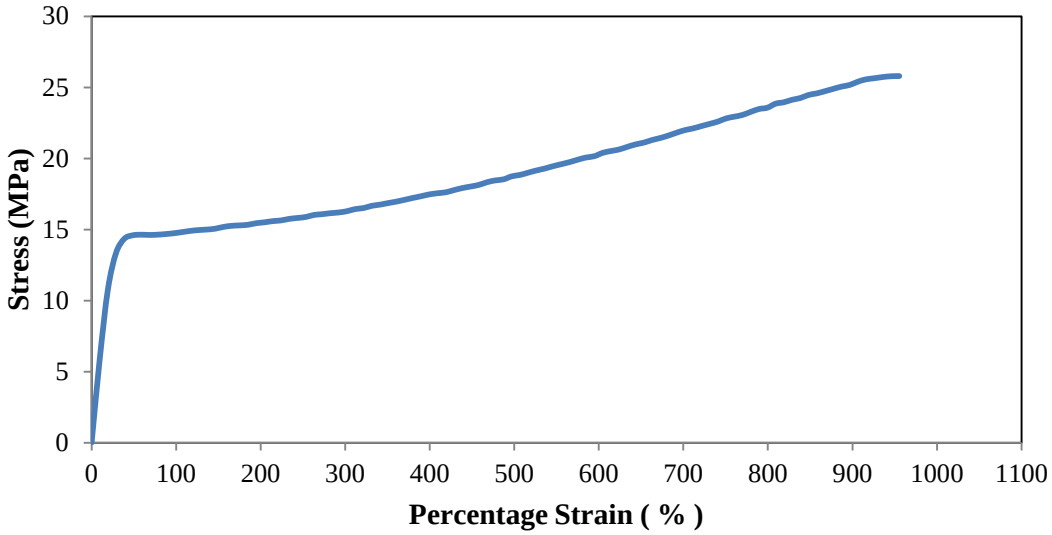


Figure 4.30 Stress vs. Percentage Strain Graph of PEE/1000/57 wt % PBT (3) +0.5% TBHDP-MMT

4.4.4 PEE Nanocomposites having 75 wt % PBT

As shown in the previous part, mechanical properties of PEE/1000/75 wt % PBT(5) gave good results, so as in the case of PEEs having 57 wt % PBT, both in-situ polymerization and melt intercalation methods were used in order to obtain PEE nanocomposites and compare the effects of the process method.

4.4.4.1 Synthesis of PEE Nanocomposites having 75 wt % PBT

Synthesis of PEE nanocomposites were perfomed by applying the same procedure of PEE/1000/75 wt % PBT (5) except for the organoclay addition. Before starting the experiment, 1,4-BD and organoclay were mixed at room temperature for 30 minutes in the ultrasonic bath in order to disperse the clay. Then, the other reactants were added and the same procedure was followed to get the PEE nanocomposites.

The reaction conditions are shown in the Table 4.15.

Table 4.15 Reaction Conditions of PEE Nanocomposites Having 75 wt % PBT

Sample Name	*Temp. of TE(°C)*	*Duration of TE (min.)*	*Temp. of PC(°C)*	*Duration of PC (min.)*	*Duration at 280°C (min.)*
PEE/1000/75 wt%PBT-0.1%	175	123	260-280	195	47
PEE/1000/75 wt%PBT-0.3%	175	143	260-280	195	62
PEE/1000/75 wt%PBT-0.5%	175	126	260-280	195	48

For the synthesis of PEE/1000/75 wt % PBT-0.1% and PEE/1000/75 wt % PBT-0.3% when the temperature was set to 260 °C in order to begin polycondensation step, the ratio of volume of methanol collected to the volume of theoretical one was 85%, whereas it was 88.3% for PEE/1000/75 wt % PBT-0.5 %.

Except for duration of transesterification time, the other reaction conditions were nearly kept constant for the synthesis of nanocomposites in order to compare the effect of organoclay ratios. The results of the tensile tests on these samples are shown in Figures 4.31 through 4.33. The results are compared later.

4.4.4.1.1 Tensile Tests of Synthesized PEE Nanocomposites

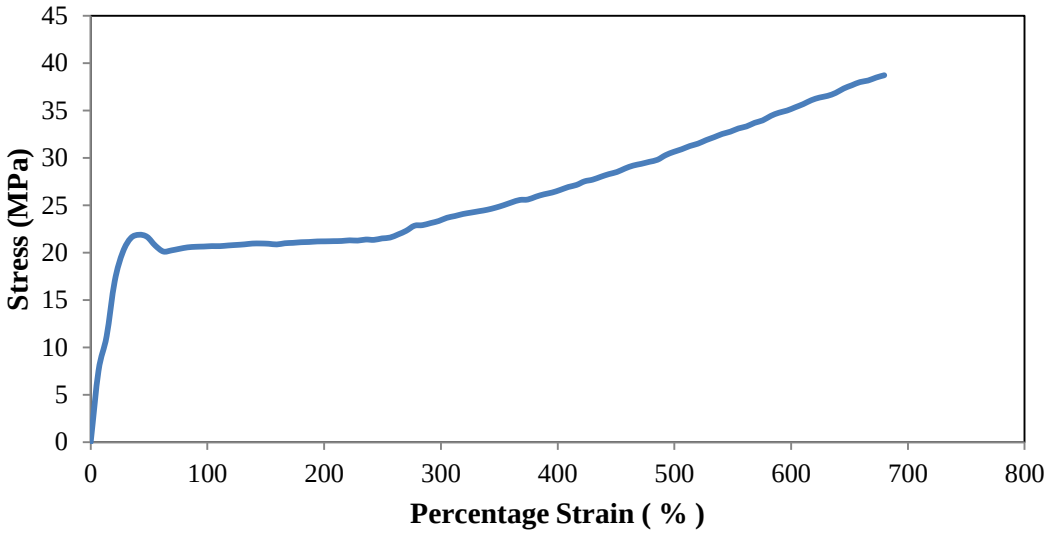


Figure 4.31 Stress vs. Percentage Strain Graph of PEE/1000/75 wt % PBT-0.1% TBHDP-MMT

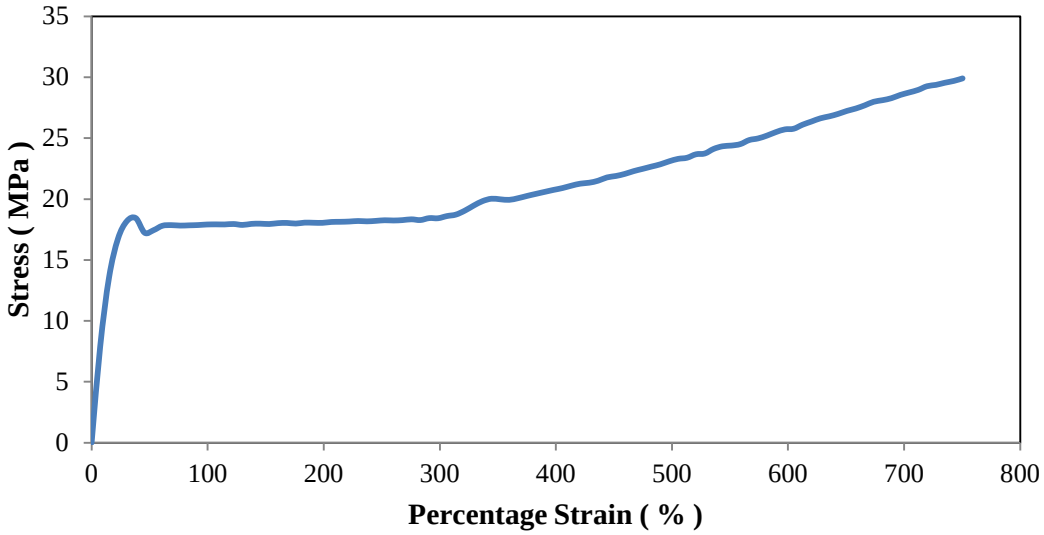


Figure 4.32 Stress vs. Percentage Strain Graph of PEE/1000/75 wt % PBT-0.3% TBHDP-MMT

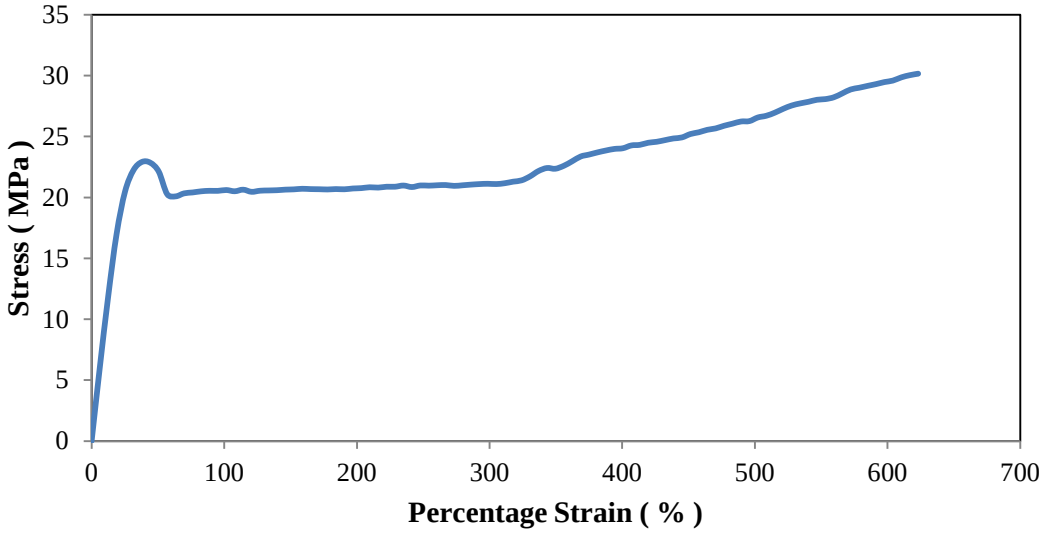


Figure 4.33 Stress vs. Percentage Strain Graph of PEE/1000/75 wt % PBT-0.5% TBHDP-MMT

4.4.4.2 Preparation of PEE Nanocomposites Having 75 wt % PBT by Melt Compounding

PEE/1000/75 wt % PBT (5) and predetermined amount of organoclay, 0.1%, 0.3% or 0.5%, were mixed by using the twin-screw extruder and then injection molded in order to

compare the effects of process method. The stress-strain curves of the materials are displayed in Figures 4.34 through 4.36. The results are compared later.

4.4.4.2.1 Tensile Tests of Synthesized Nanocomposites Having 75 wt % PBT

Tensile analysis results of PEE nanocomposites are given through Figure 4.34, 4.35 and 4.36.

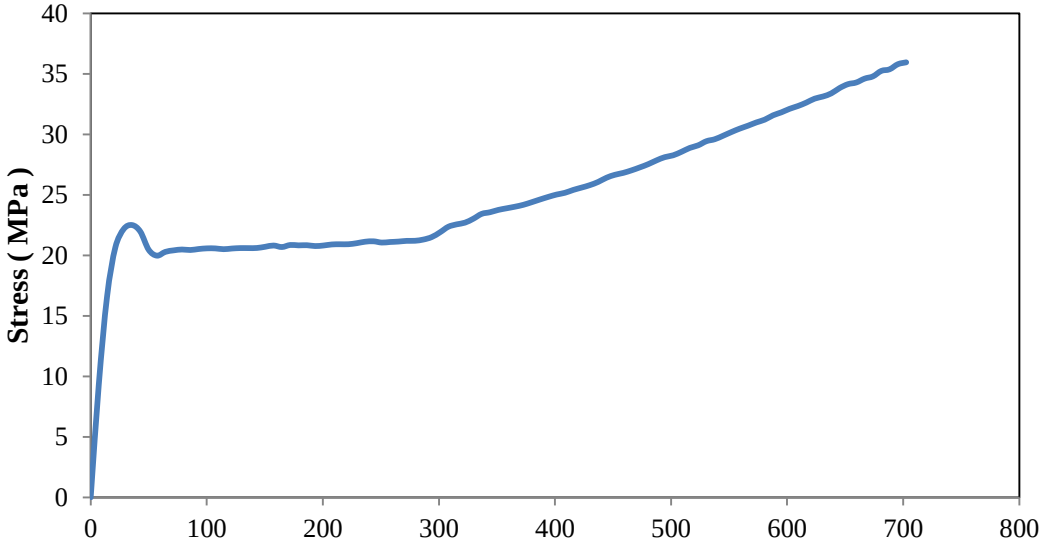


Figure 4.34 Stress vs. Percentage Strain Graph of PEE/1000/75 wt% PBT (5) + 0.1% TBHDP-MMT

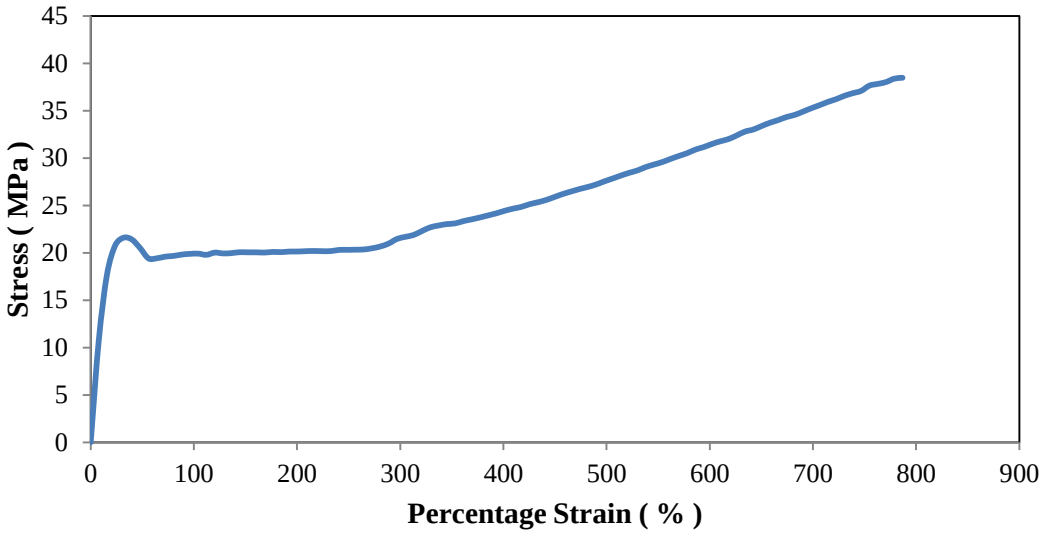


Figure 4.35 Stress vs. Percentage Strain Graph of PEE/1000/75 wt % PBT (5) + 0.3% TBHDP-MMT

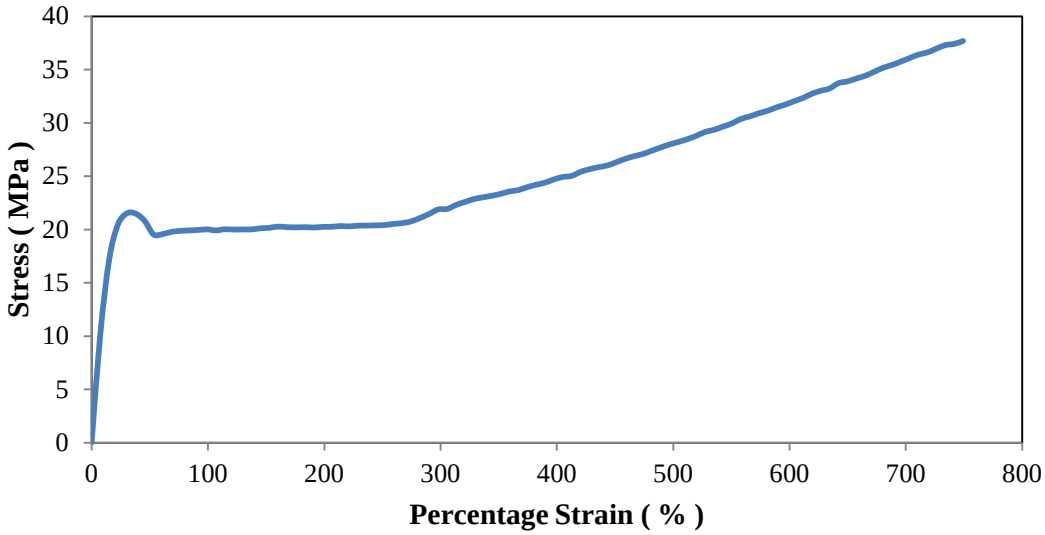


Figure 4.36 Stress vs. Percentage Strain Graph of PEE/1000/75 wt % PBT (5) + 0.5% TBHDP-MMT

4.4.5 Influence of Organoclay Content on the Structure of Poly(ether-ester) Based Thermoplastic Elastomers

4.4.5.1 Mechanical Analysis

4.4.5.1.1 Tensile Tests

As in the study of Szymczyk [55], in 2012, it was expected that the polymers having different organoclay ratios would show better results in terms of Tensile Strength compared to that of neat polymers but in the present study, with the increase of organoclay, the tensile strength decreased as shown in Table 4.16 and Figures 4.37 and 4.38.

Elongation at fracture data led to a conclusion which is not surprising. There is a gradual decrease in elongation at fracture decrease with the increase of organoclay content.

Table 4.16 Mechanical properties of Melt Compounded PEE Nanocomposites Having 37 wt % PBT

Sample Name	***Young's Modulus (MPa)***	***Tensile Strength (MPa)***	***Percentage Elongation at Fracture (%)***
PEE/1000/37 wt%PBT(5)	7.0	8.8	412
PEE/1000/37 wt%PBT(5) + 0.1%	6.7	8.2	346
PEE/1000/37 wt%PBT(5) + 0.3%	6.0	7.7	380
PEE/1000/37 wt%PBT(5) + 0.5%	6.18	7.6	369

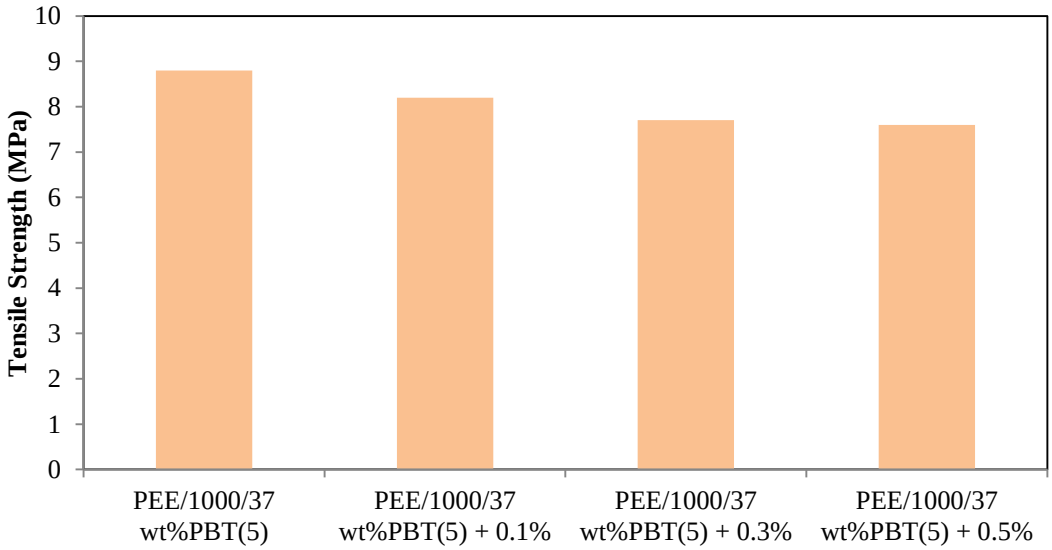


Figure 4.37 Tensile Strength of PEE and Melt Compounded PEE Nanocomposites Having 37 wt % PBT

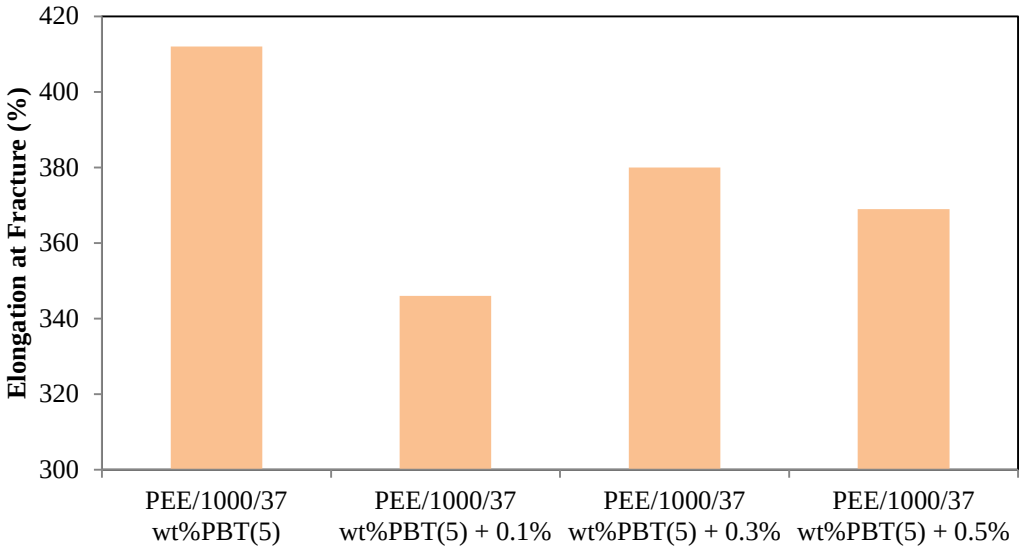


Figure 4.38 Elongation at Fracture (%) of PEE and Melt Compounded PEE Nanocomposites Having 37 wt % PBT

Table 4.17 Mechanical Properties of Melt Compounded PEE Nanocomposites Having 49 wt % PBT

Sample Name	***Young's Modulus (MPa)***	***Tensile Strength (MPa)***	***Percentage Elongation at Fracture (%)***
PEE/1000/49 wt% PBT(8)	11.95	13.7	488
PEE/1000/49 wt% PBT(8) + 0.1%	11.58	12.5	361
PEE/1000/49 wt% PBT(8) + 0.3%	11.15	11.8	257
PEE/1000/49 wt% PBT(8) + 0.5%	8.31	8.8	222

According to Table 4.17, when the organoclay content increases, tensile strength decreases. Considering the elongation at fracture, as the organoclay content increases, the elongation at fracture decreases as expected. These results are displayed in Figures 4.39 and 4.40.

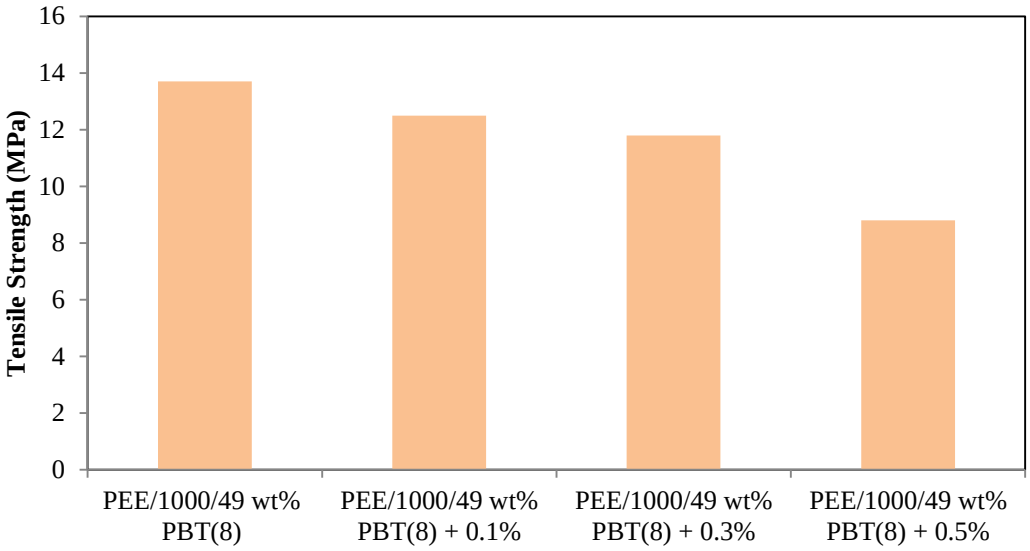


Figure 4.39 Tensile Strength of PEE and PEE Nanocomposites Having 49 wt % PBT

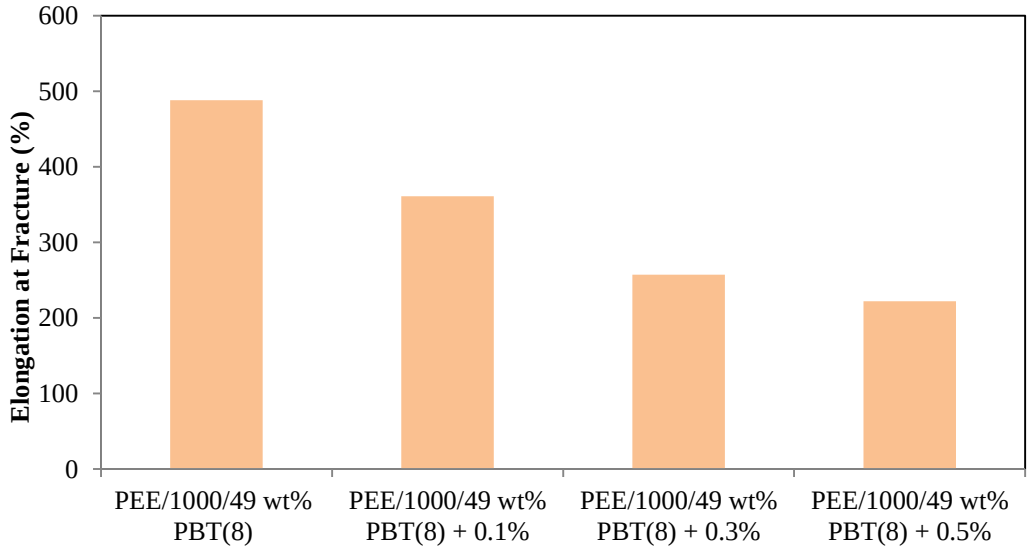


Figure 4.40 Elongation at Fracture (%) of PEE and PEE Nanocomposites Having 49 wt % PBT

The mechanical properties for in-situ polymerized PEE nanocomposites having 57 wt % PBT are shown in Table 4.18, and Figures 4.41 and 4.42.

Table 4.18 Mechanical properties for In-Situ Polymerized PEE Nanocomposites Having 57 wt % PBT

Sample Name	***Young's Modulus (MPa)***	***Tensile Strength (MPa)***	***Percentage Elongation at Fracture (%)***
PEE/1000/57 wt%PBT-0.1%	14.06	24.0	843
PEE/1000/57 wt%PBT-0.3%	12.10	27.1	980
PEE/1000/57 wt%PBT-0.5%	12.11	28.9	991

As shown in Table 4.18, with the increase of organoclay content, tensile strength increases as expected. A surprising result was obtained when the elongation at fracture data were compared, because contrary to the other results of nanocomposites prepared by melt intercalation, nanocomposites of PEEs having 57 wt % PBT displayed improved results. When the organoclay ratio was increased from 0.3% to 0.5%, elongation of the nanocomposite is slightly influenced, but the change from 0.1% to 0.3% led to an important difference.

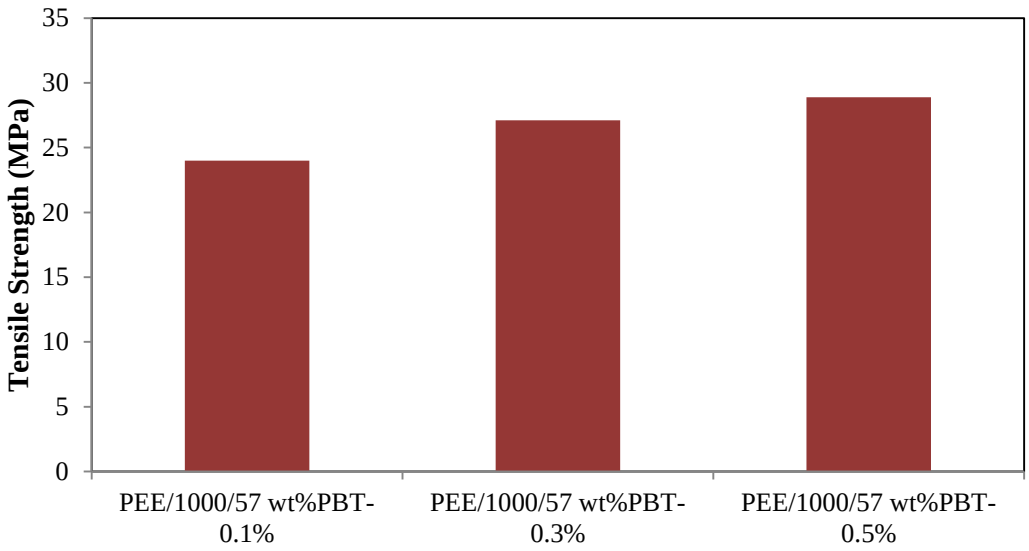


Figure 4.41 Tensile Strength of In-Situ Polymerized PEE Nanocomposites Having 57 wt % PBT

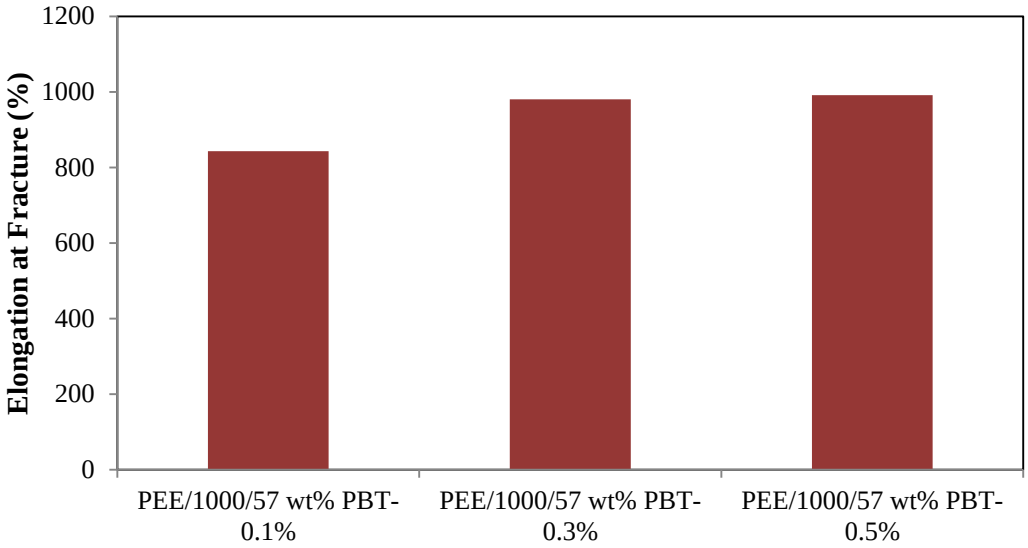


Figure 4.42 Elongation at Fracture (%) of In-Situ Polymerized PEE Nanocomposites Having 57 wt % PBT

Table 4.19 Mechanical Properties of Melt Compounded PEE Nanocomposites Having 57 wt % PBT

Sample Name	***Young's Modulus (MPa)***	***Tensile Strength (MPa)***	***Percentage Elongation at Fracture (%)***
PEE/1000/57 wt%PBT(3)+0.1%	14.94	22.6	879
PEE/1000/57 wt%PBT(3)+0.3%	14.52	25.1	947
PEE/1000/57 wt%PBT(3)+0.5%	13.85	25.8	965

As shown in Table 4.19 and Figures 4.43 and 4.44, there is a slight increase between PEE/1000/57 wt % PBT+ 0.3 % and PEE/1000/57 wt % PBT+ 0.5% in terms of tensile strength and elongation, but when the nanocomposites having 0.1% and 0.3% organoclay are concerned, a significant difference is observed.

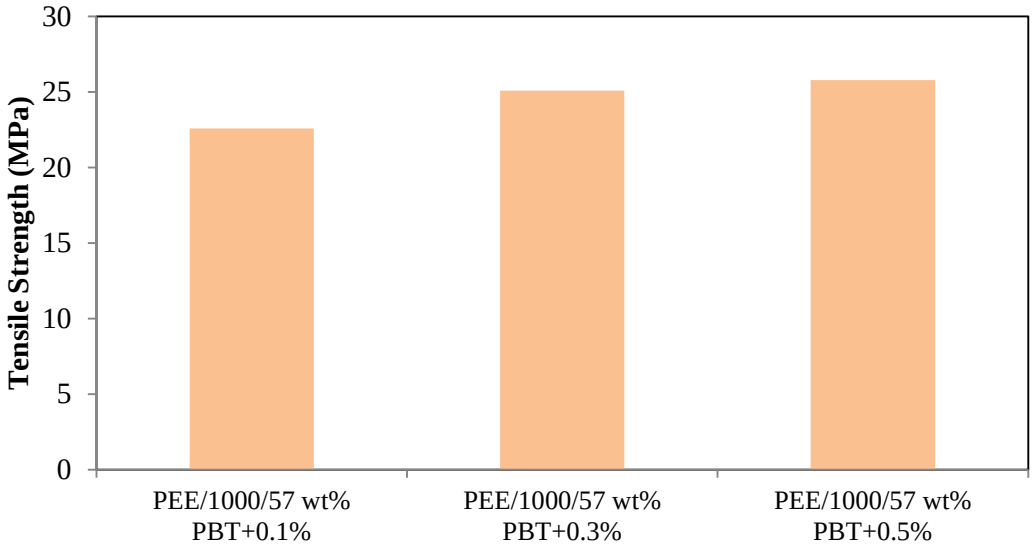


Figure 4.43 Tensile Strength of Melt Compounded PEE Nanocomposites Having 57 wt % PBT

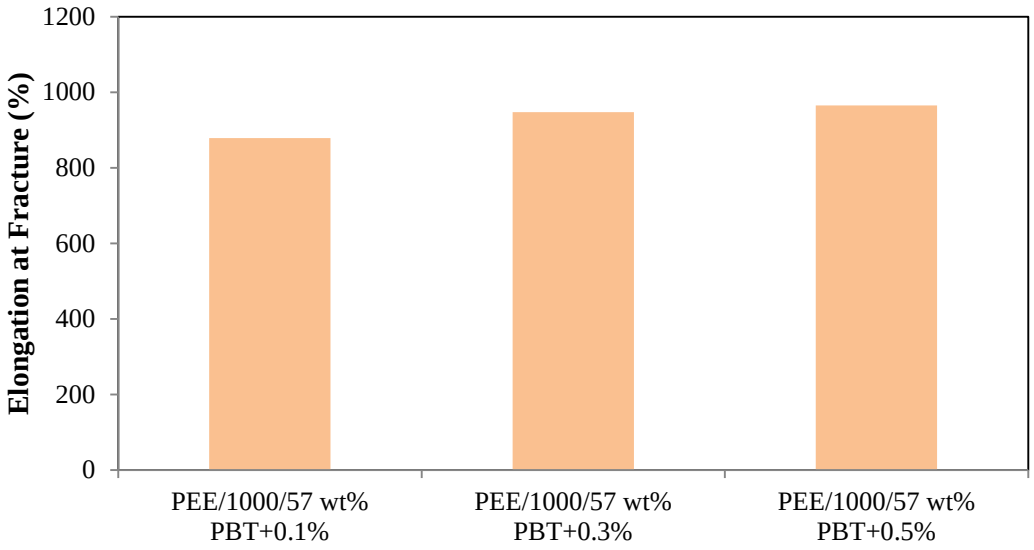


Figure 4.44 Elongation at Fracture (%) of Melt Compounded PEE Nanocomposites Having 57 wt % PBT

Table 4.20 and Figures 4.45 and 4.46 display the results on mechanical properties of in-situ polymerized PEE nanocomposites having 75 wt % PBT.

Table 4.20 Mechanical Properties of In-Situ Polymerized PEE Nanocomposites Having 75 wt % PBT

Sample Name	***Young's Modulus (MPa)***	***Tensile Strength (MPa)***	***Percentage Elongation at Fracture (%)***
PEE/1000/75 wt%PBT(5)	19.5	32.4	672
PEE/1000/75 wt%PBT-0.1%	19.9	38.7	687
PEE/1000/75 wt%PBT-0.3%	16.7	30.0	758
PEE/1000/75 wt%PBT-0.5%	20.3	30.3	629

It is obvious that in terms of tensile strength and elongation at break, there is not a general trend. Considering the tensile strength, PEE/1000/75 wt % PBT-0.3% and PEE/1000/75 wt % PBT-0.5% have nearly the same values, and they are lower than that of neat polymer's. The PEE/1000/75 wt % PBT-0.1% nanocomposite is the only one which has higher tensile strength than that of the neat polymer. As shown in the Table 4.20, PEE/1000/75 wt % PBT-0.3% has the highest elongation at fracture while PEE/1000/75 wt % PBT-0.5% has the lowest.

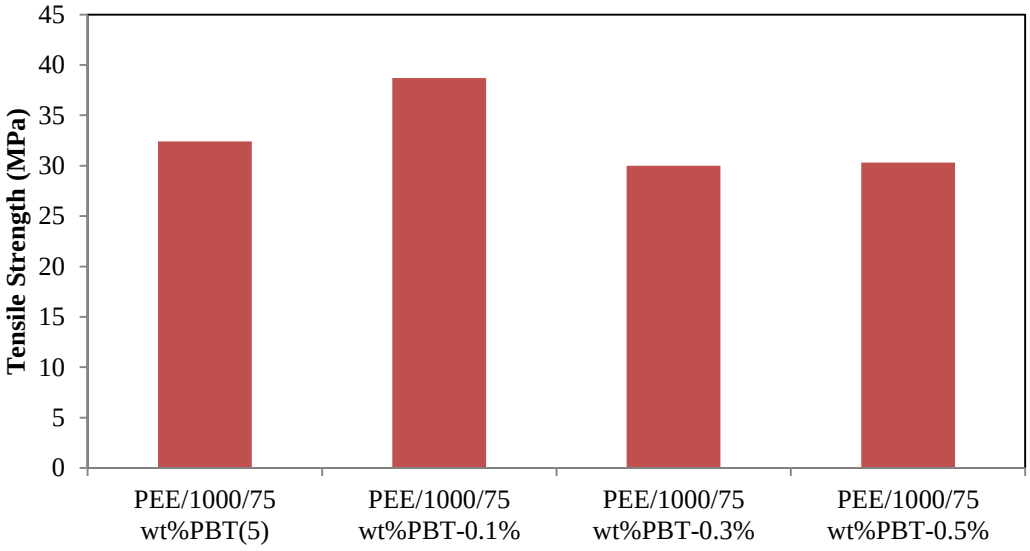


Figure 4.45 Tensile Strength of PEE and In-Situ Polymerized PEE Nanocomposites Having 75 wt % PBT

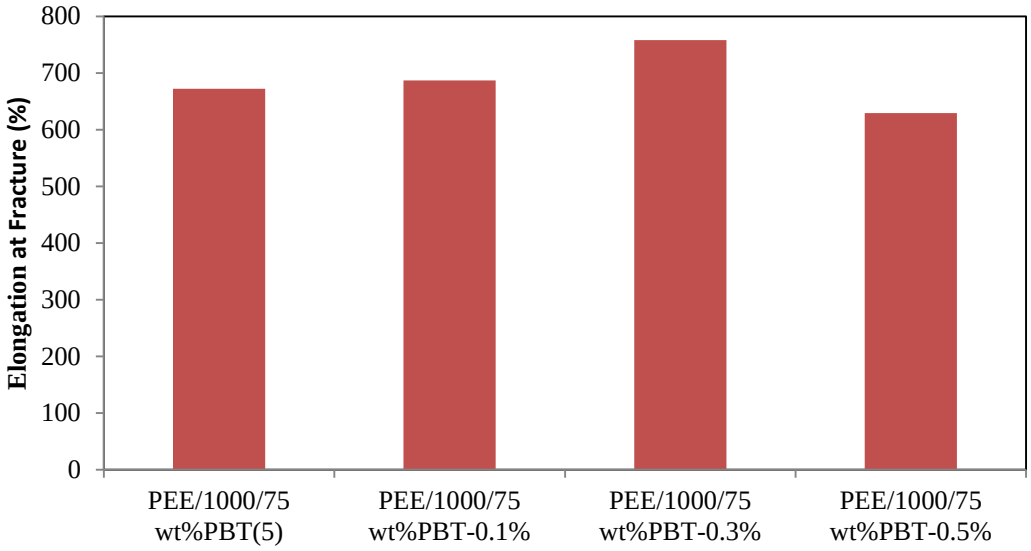


Figure 4.46 Elongation at Fracture (%) of PEE and In-Situ Polymerized PEE Nanocomposites Having 75 wt % PBT

Table 4.21 and Figures 4.47 and 4.48 display the results on mechanical properties of pee and melt compounded nanocomposites having 75 wt % PBT.

Table 4.21 Mechanical Properties of PEE and Melt Compounded Nanocomposites Having 75 wt % PBT

Sample Name	***Young's Modulus (MPa)***	***Tensile Strength (MPa)***	***Percentage Elongation at Fracture (%)***
PEE/1000/75 wt%PBT(5)	19.5	32.4	672
PEE/1000/75 wt%PBT(5)+0.1%(1)	20.6	36.0	710
PEE/1000/75 wt%PBT(5)+0.3%(1)	19.2	38.6	795
PEE/1000/75 wt%PBT(5)+0.5%(1)	18.7	37.9	757

The nanocomposites of PEE/1000/75 wt % PBT (5) which are prepared by melt mixing have higher tensile strength values than that of neat polymer's. For this group of nanocomposites, it is clear that with the increase of tensile strength, elongation at fracture also increases.

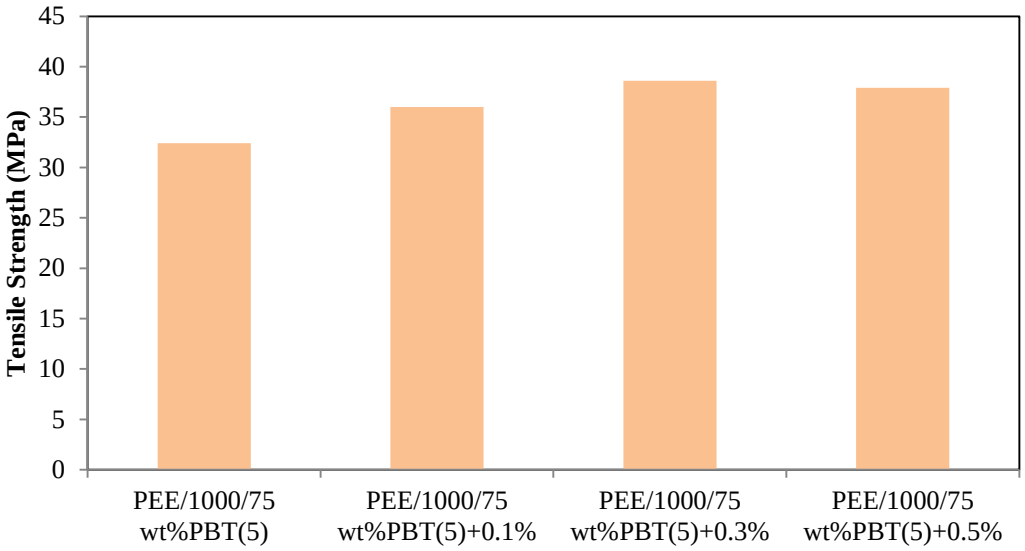


Figure 4.47 Tensile Strength of PEE and Melt Compounded PEE Nanocomposites Having 75 wt % PBT

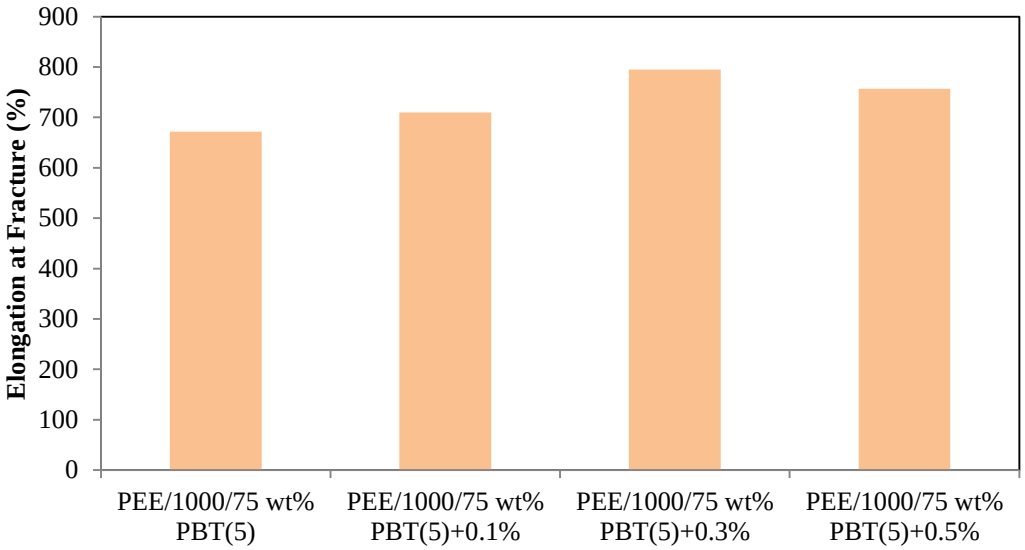


Figure 4.48 Elongation at Fracture (%) of PEE and Melt Compounded PEE Nanocomposites Having 75 wt% PBT

4.4.5.2 Thermal Analysis

4.4.5.2.1 DSC Analysis

4.4.5.2.1.1 PEE and PEE Nanocomposites Having 37 wt% PBT

Considering thermal behaviours, it was concluded that silicate layers of the organoclays do not affect glass transition temperature and melting temperature of the PEG-rich soft segment [55].

In the case of melting temperature of the PBT hard segment, the neat polymer and nanocomposite having 0.1% TBHDP-MMT showed approximately the same Tm value, but as shown in Table 4.22, it is obvious that the melting point of hard segment decreases as the content of organoclay increases. This result indicates that the addition of organoclay disturbs the crystallinity of PBT hard segment and decreases the Tm value.

Table 4.22 DSC Data of PEE and Melt Compounded PEE Nanocomposites Having 37 wt % PBT

Sample Name	***Tg (PEG) (^oC)***	***Tm (PEG) (^oC)***	***Tg (PBT) (^oC)***	***Tm (PBT) (^oC)***
PEE/1000/37 wt%PBT (5)	-47.3	7.3	-	175.2
PEE/1000/37 wt%PBT (5) +0.1%	-46.9	8.2	-	173.3
PEE/1000/37 wt%PBT (5) +0.3%	-48.2	7.5	-	163.8
PEE/1000/37 wt%PBT (5) +0.5%	-46.9	8.2	-	163.0

4.4.5.2.1.2 PEE and PEE Nanocomposites Having 49 wt % PBT

The glass transition temperature due to PEG decreases slightly with increasing organoclay content as shown in Table 4.23. These changes are essentially caused by increasing contribution of organoclay content since the organoclay restricts the motion of the PEG soft segment.

When the melting temperature of PBT hard segment is concerned, a decrease is observed as expected, since crystallinity of PBT decreases with the addition of organoclay. On the other hand, the Tm of PBT increases with increasing PBT content when Table 4.22 and Table 4.23 are compared.

Table 4.23 DSC Datas of PEE and Melt Compounded PEE Nanocomposites Having 49 wt % PBT

Sample Name	***Tg (PEG) (°C)***	***Tm (PEG) (°C)***	***Tg (PBT) (°C)***	***Tm (PBT) (°C)***
PEE/1000/49 wt%PBT (8)	-48.0	-	-	191.9
PEE/1000/49 wt%PBT (8) +0.1%	-49.0	-	-	189.0
PEE/1000/49 wt%PBT (8) +0.3%	-49.4	-	-	186.5
PEE/1000/49 wt%PBT (8) +0.5%	-49.9	-	-	186.7

4.4.5.2.1.3 PEE and PEE Nanocomposites Having 57 wt % PBT

As shown in Tables 4.24 and 4.25, both for melt intercalation and in-situ polymerization, DSC curves did not show significant differences in terms of Tg temperature of PEG in PEE nanocomposites with different organoclay ratios. Since the PEG content was low, it was not possible to observe melting temperature for the PEG segment.

In terms of melting temperature of the PBT hard segment, the same result was observed due to the addition of organoclay which restricts the crystallization of the PBT segment.

Table 4.24 DSC Data of PEE and Melt Compounded PEE Nanocomposites Having 57 wt % PBT

Sample Name	***Tg (PEG) (°C)***	***Tm (PEG) (°C)***	***Tg (PBT) (°C)***	***Tm (PBT) (°C)***
PEE/1000/57 wt%PBT (3)	-46.7	-	-	208.6
PEE/1000/57 wt%PBT (3) +0.1%	-45.5	-	-	198.0
PEE/1000/57 wt%PBT (3) +0.3%	-45.8	-	-	196.4
PEE/1000/57 wt%PBT (3) +0.5%	-46.4	-	-	195.0

Table 4.25 DSC Data of PEE and In-Situ Polymerized PEE Nanocomposites Having 57 wt % PBT

Sample Name	***Tg (PEG) (°C)***	***Tm (PEG) (°C)***	***Tg (PBT) (°C)***	***Tm (PBT) (°C)***
PEE/1000/57 wt%PBT (3)	-46.7	-	-	208.6
PEE/1000/57 wt%PBT (3) -0.1%	-45.7	-	-	195.0
PEE/1000/57 wt%PBT (3) -0.3%	-45.7	-	-	194.0
PEE/1000/57 wt%PBT (3) -0.5%	-44.7	-	-	194.9

4.4.5.2.1.4 PEE and PEE Nanocomposites Having 75 wt % PBT

The DSC results of the nanocomposites having 75 wt % PBT are shown in Table 4.26 and 4.27. For both melt intercalation and in-situ polymerization methods, the nanocomposite which has lower glass transition temperature than the neat polymer is PEE with 0.3% organoclay content. For others, it is possible to say that silicate layers of the organoclays do not affect the glass transition temperature. The Tg values of these nanocomposites are the highest owing to the lowest PEG content.

In the case of melting temperature of the PBT segment, a significant difference was not observed in contrast to the other PEE nanocomposites with lower PBT wt %. This result may be due to the PBT content. In other words, the effect of organoclay became of secondary importance compared to the effect of PBT hard segment content. For this reason, the mechanical properties of these group materials do not decrease with increasing organoclay content.

Table 4.26 DSC Data of PEE and Melt Compounded PEE Nanocomposites Having 75 wt % PBT

Sample Name	***Tg (PEG) (^oC)***	***Tm (PEG) (^oC)***	***Tg (PBT) (^oC)***	***Tm (PBT) (^oC)***
PEE/1000/75 wt%PBT (5)	-36.2	-	-	213.6
PEE/1000/75 wt%PBT (5) +0.1%	-34.6	-	-	214.3
PEE/1000/75 wt%PBT (5) +0.3%	-38.1	-	-	213.6
PEE/1000/75 wt%PBT (5) +0.5%	-35.2	-	-	212.6

Table 4.27 DSC Data of PEE and In-Situ Polymerized PEE Nanocomposites Having 75 wt % PBT

Sample Name	***Tg (PEG) (^oC)***	***Tm (PEG) (^oC)***	***Tg (PBT) (^oC)***	***Tm (PBT) (^oC)***
PEE/1000/75 wt%PBT (5)	-36.2	-	-	213.6
PEE/1000/75 wt%PBT (5) -0.1%	-35.0	-	-	213.4
PEE/1000/75 wt%PBT (5) -0.3%	-45.4	-	-	212.0
PEE/1000/75 wt%PBT (5) -0.5%	-37.0	-	-	213.6

4.4.5.3 Morphological Analysis

4.4.5.3.1 XRD Analysis

XRD analysis is an important tool for nanocomposite research studies since it gives valuable information about the dispersion of the organoclay into the polymer matrix. With the help of XRD analysis, it is possible to determine intercalated and exfoliated

structures by dealing with the position, shape and intensity of the basal reflections from the silicate layers of the organoclay.

As mentioned in the introduction part, there are three main types of composites when a layered clay is associated with a polymer; namely, phase separated, intercalated and exfoliated structures.

In the case of phase separated composites, since the polymer matrix is not present in the clay galleries, basal spacing shows no difference in the XRD patterns.

When intercalated composites are concerned, since polymer matrix flows into the clay platelets, the platelets are periodically aligned and a reflection from the clay platelets is observed. As the number of polymer chains in the clay galleries increase, interlayer spacing increases and this results as a shift of the clay peak to lower angles.

For exfoliated nanocomposites, no clay peak is determined in XRD patterns as polymer matrix forces the clay galleries to disarrange and cause random dispersion of clay platelets.

As mentioned in the previous parts, nanocomposites of PEEs having 37 wt % PBT and 49 wt % PBT were prepared by melt intercalation and PEEs having 57 wt % PBT and 75 wt % PBT were prepared both by melt intercalation and in-situ polymerization.

XRD analyses were carried out for all the samples in the angle 2Θ range of 1-40 ^{o}. XRD patterns of both 1-10^{o} and 1-40^{o} are shown in the current study since in some cases it is difficult to determine small peaks in the angle 2Θ range of 1-10^{o}.

4.4.5.3.1.1 XRD Analysis of Modified Clay

Modified clay (TBHDP-MMT) has four diffraction peaks at 2Θ=3.98^{o}, 2Θ=7.88^{o}, 2Θ=19.76^{o}, 2Θ=24.41^{o} with basal spacing of d_1=2.22, d_2=1.12, d_3= 0.45, d_4=0.37 nm, respectively. Figure 4.49 shows the X-Ray diagram of the modified clay.

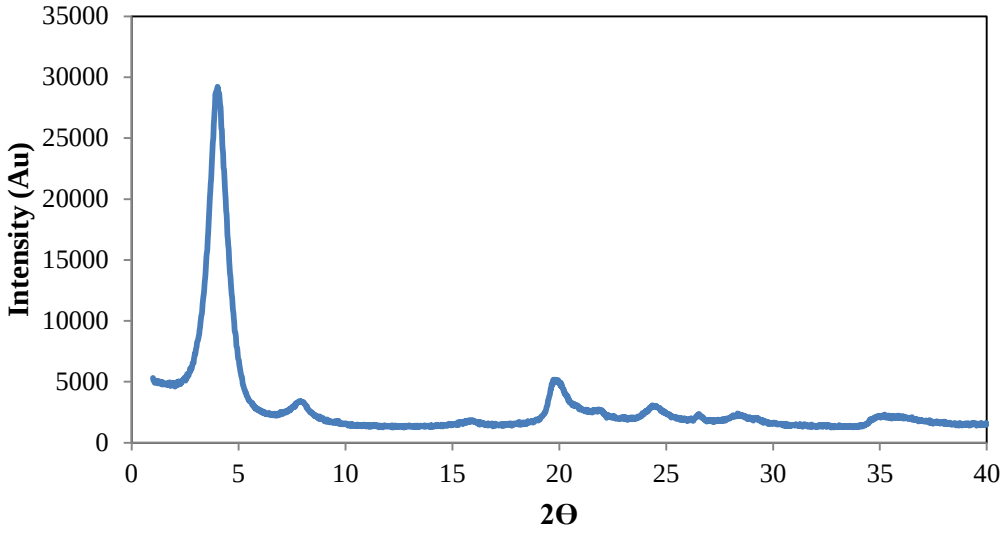


Figure 4.49 XRD Patterns of TBHDB-MMT Clay

The interlayer spacing results of organoclay are in accordance with the data obtained from the previous study [56].

4.4.5.3.1.2 XRD Analysis Results of PEE Nanocomposites Having 37 wt % PBT

Since the mechanical properties of PEE synthesized at constant transesterification time were poor, nanocomposites of PEE synthesized at constant methanol volume ratio were prepared by melt intercalation method and analyzed.

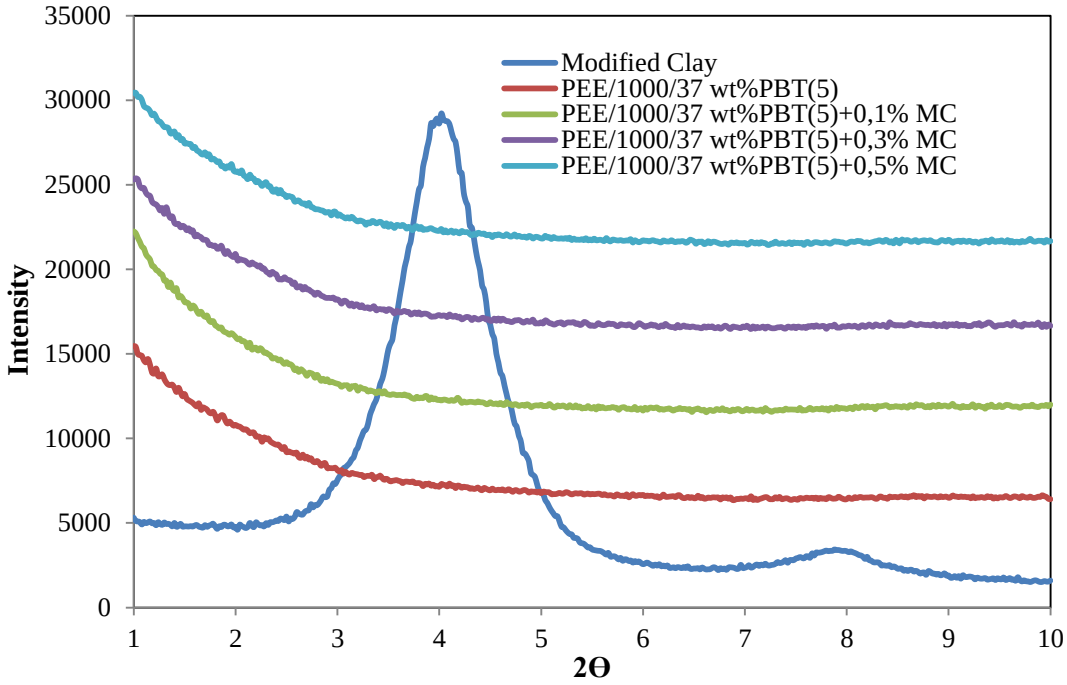


Figure 4.50 XRD Patterns of Melt Compounded Nanocomposites of PEE/1000/37 wt % PBT (5)

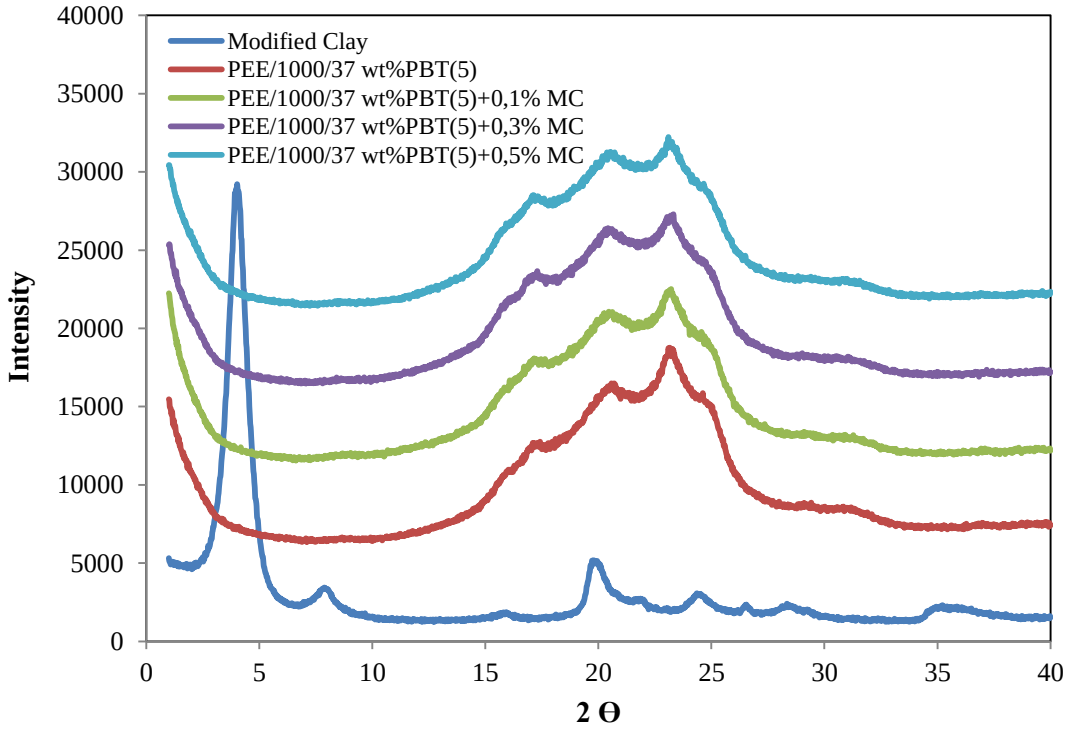


Figure 4.51 XRD Patterns of Melt Compounded Nanocomposites of PEE/1000/37 wt % PBT

Figure 4.50 and 4.51 give the X-Ray diffraction curves of pure PEE and PEE/1000/37 wt % PBT nanocomposites with 0.1-0.5 wt%organoclay loading. The curves show no characteristic organoclay peaks in the range of 2 Θ= 3-8 °, in other words, the peaks corresponding to the basal spacing have disappeared, meaning that the exfoliation of the organoclay occurred in the PEE matrix.

4.4.5.3.1.3 XRD Analysis Results of PEE Nanocomposites having 49 wt % PBT

As in the case of 37 wt% PBT, nanocomposites of PEEs having 49 wt % PBT were obtained by melt intercalation.

From Figure 4.52 and 4.53, it is possible to say that characteristic peaks of organoclay have disappeared which indicates the exfoliation of the organoclay.

Both PEE nanocomposites with 37 wt % and 49 wt % PBT were poor in terms of mechanical properties, so the organoclay dispersion in PEE were not crosschecked further by performing SEM and TEM analysis.

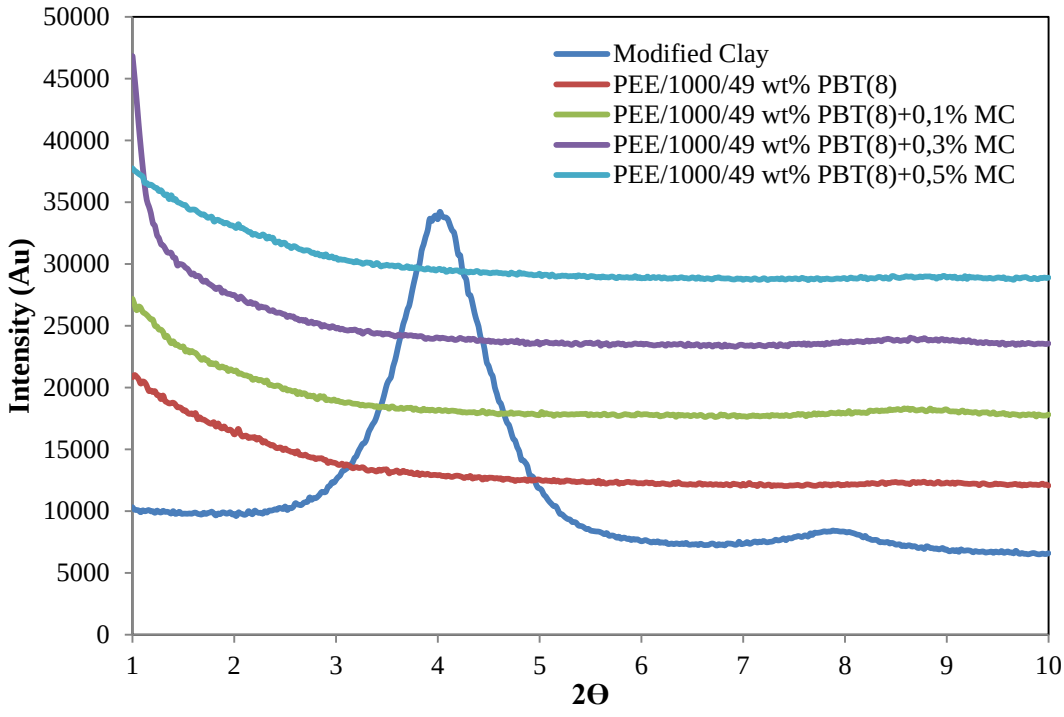


Figure 4.52 XRD Patterns of Melt Compounded Nanocomposites of PEE/1000/49 wt % PBT

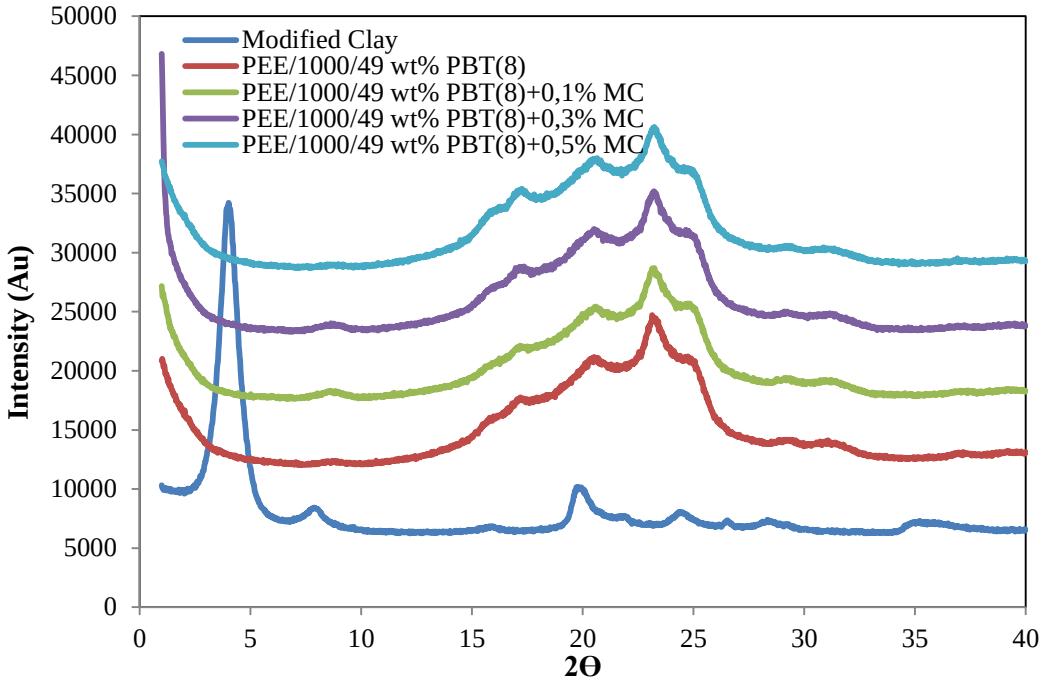


Figure 4.53 XRD Patterns of Melt Compounded Nanocomposites of PEE/1000/49 wt % PBT

4.4.5.3.1.4 XRD Analysis Results of PEE Nanocomposites having 57 wt % PBT

PEE nanocomposites having 57 wt % PBT were prepared by two methods namely by melt intercalation and by in-situ polymerization.

In Figure 4.54 and Figure 4.55, for PEE with 0.1-0.5 wt % organoclay loadings, small d_2 peaks which were shifted to the right are observed at $2\Theta = 9^{o}$ (d=0.98 nm), at $2\Theta = 8.74^{o}$ (d=1.01 nm) and at $2\Theta = 8.74^{o}$ (d=1.01 nm), respectively. These results indicate that agglomeration of a small part of the clay has occurred in the PEE matrix. The reason of the agglomeration may be stacking of organoclay galleries during the injection molding. In addition, it is more obvious in Figure 4.55 that as the ratio of organoclay increases, the shape of the peak changes from sharp to broad. Broader peaks refer to the several intercalated structures with different interlayer spacings that were formed during the melt blending process.

Figure 4.56 and 4.57 show the X-Ray diffraction curves of pure PEE and PEE nanocomposites with 0.1-0.5 wt % organoclay loading which were synthesized by in-situ polymerization. For the one with 0.1 wt %, characteristic peaks of organoclay has disappeared which implies the exfoliation of organoclay in the PEE matrix. When PEE nanocomposites with 0.3 and 0.5 wt % are considered, a small d_2 peak was detected at 2Θ=6.24 (d=1.41 nm) and at 2Θ=6.20 (d=1.43 nm), respectively, referring to intercalated structures, but since only XRD patterns are not persuasive enough to characterize the

structure of nanocomposites, SEM and TEM analysis were also performed for PEE nanocomposites which are prepared by different methods, namely, melt intercalation and in-situ polymerization.

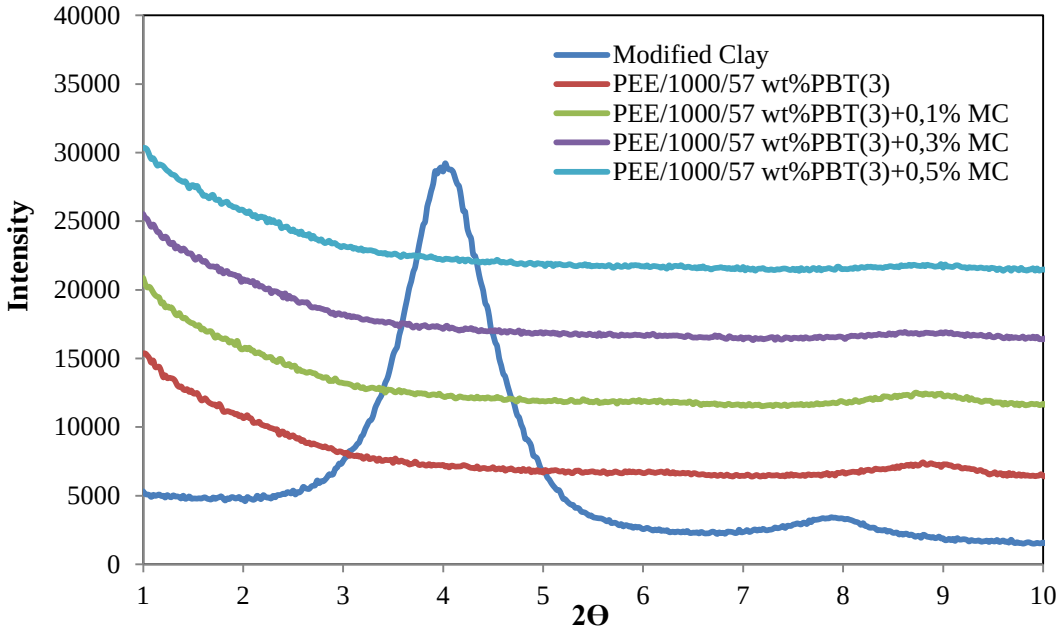


Figure 4.54 XRD Patterns of Melt Compounded Nanocomposites of PEE/1000/57 wt % PBT

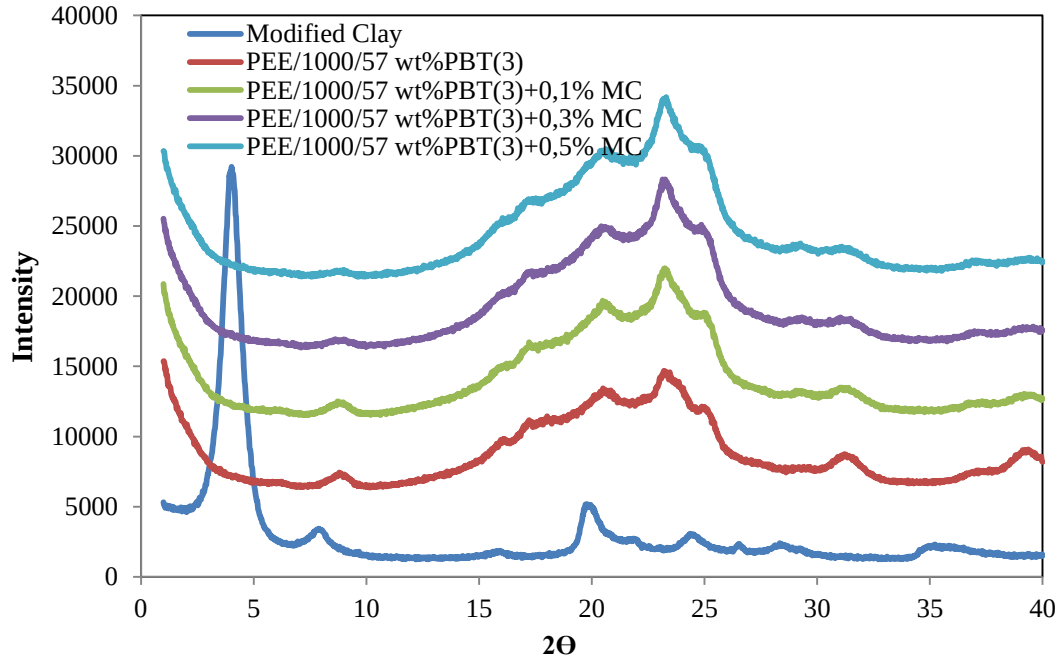


Figure 4.55 XRD Patterns of Melt Compounded Nanocomposites of PEE/1000/57 wt % PBT

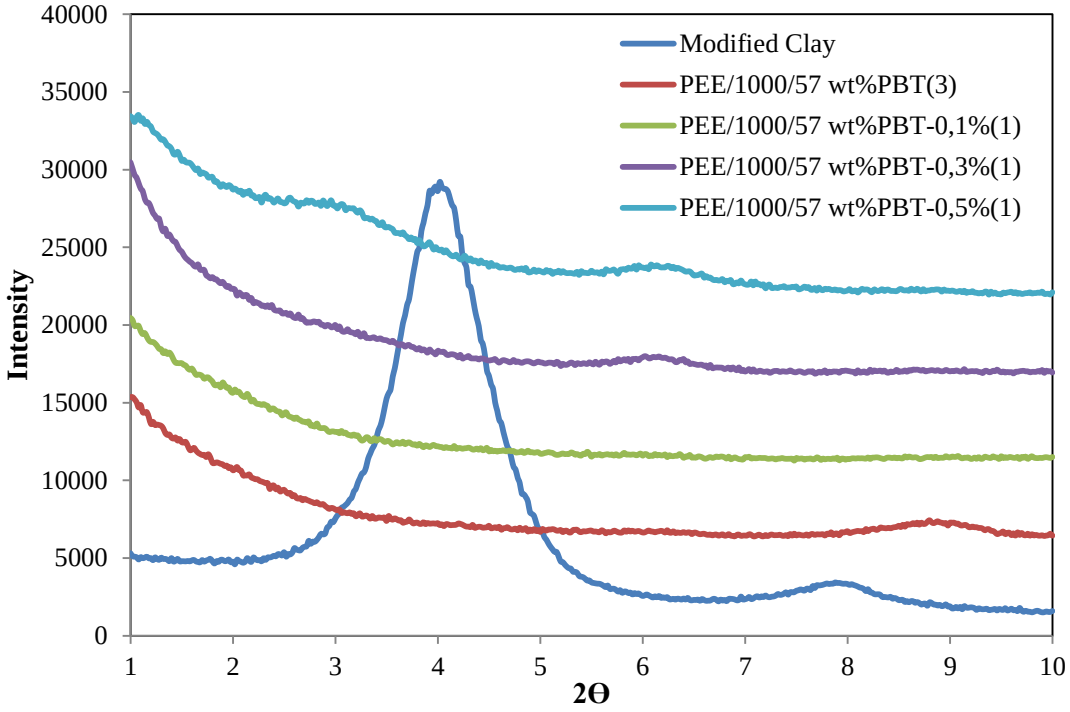


Figure 4.56 XRD Patterns of In-Situ Polymerized Nanocomposites of PEE/1000/57 wt % PBT

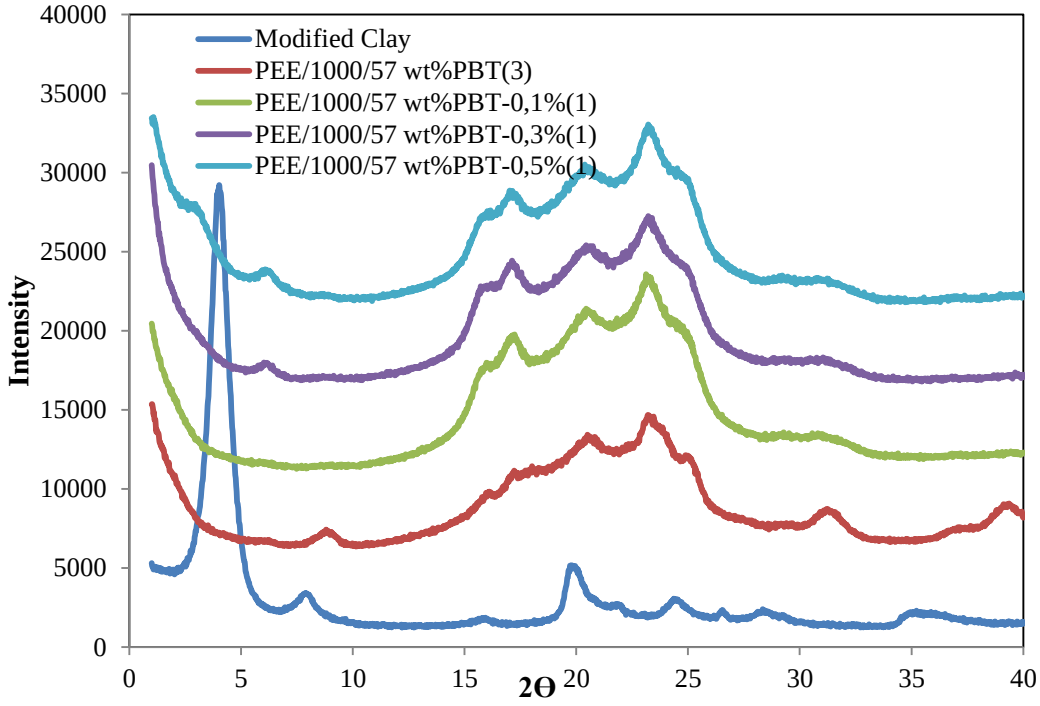


Figure 4.57 XRD Patterns of In-Situ Polymerized Nanocomposites of PEE/1000/57 wt % PBT

4.4.5.3.1.5 XRD Analysis Results of PEE Nanocomposites having 75 wt % PBT

In case of PEE nanocomposites having 75 wt % PBT which were prepared both by melt intercalation and in-situ polymerization, characteristic organoclay peaks disappeared as shown in Figures 4.58-4.61.

Altough the lack of organoclay peaks in XRD patterns refers to exfoliated structures in Figure 4.58 and 4.60, it is known that an immisicible or disordered samples may also give a XRD pattern without any peak. For that reason, TEM analysis of these nanocomposites was also performed to provide a qualitative understanding of the internal structure.

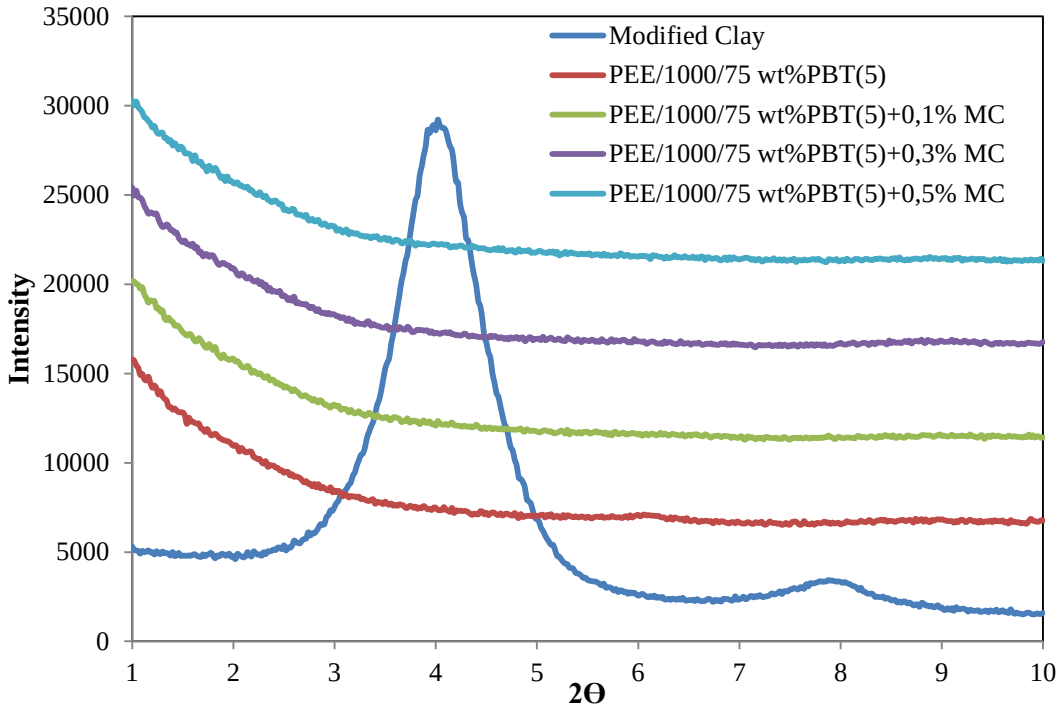


Figure 4.58 XRD Patterns of Melt Compounded Nanocomposites of PEE/1000/75 wt % PBT

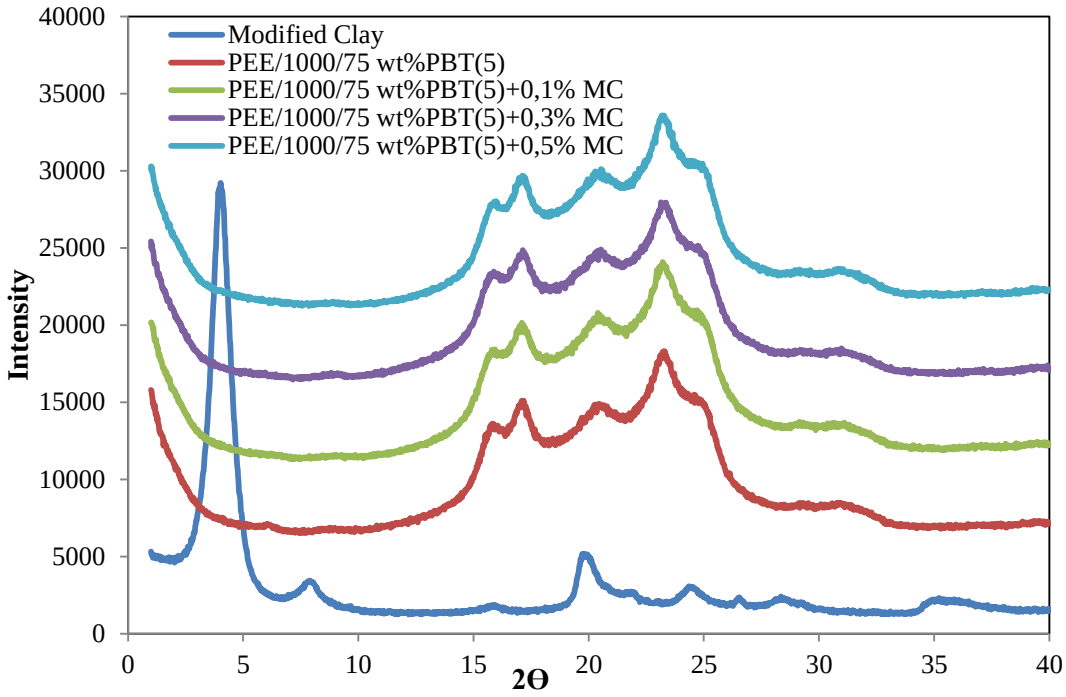


Figure 4.59 XRD Patterns of Melt Compounded Nanocomposites of PEE/1000/75 wt % PBT

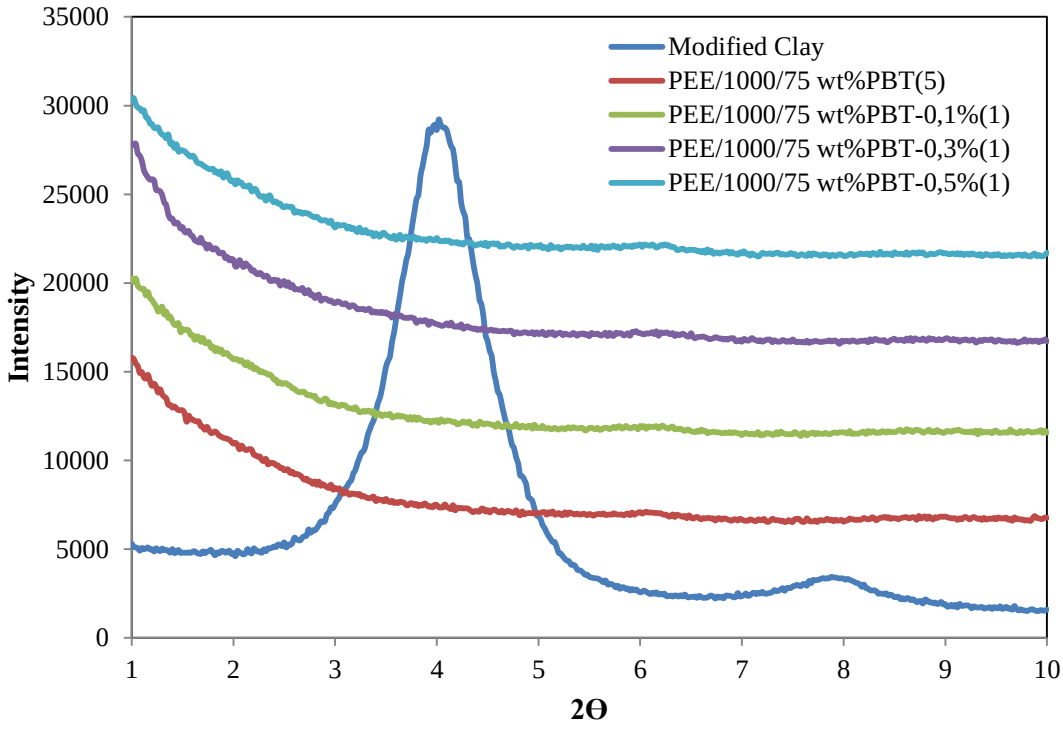


Figure 4.60 XRD Patterns of In-Situ Polymerized Nanocomposites of PEE/1000/75 wt % PBT

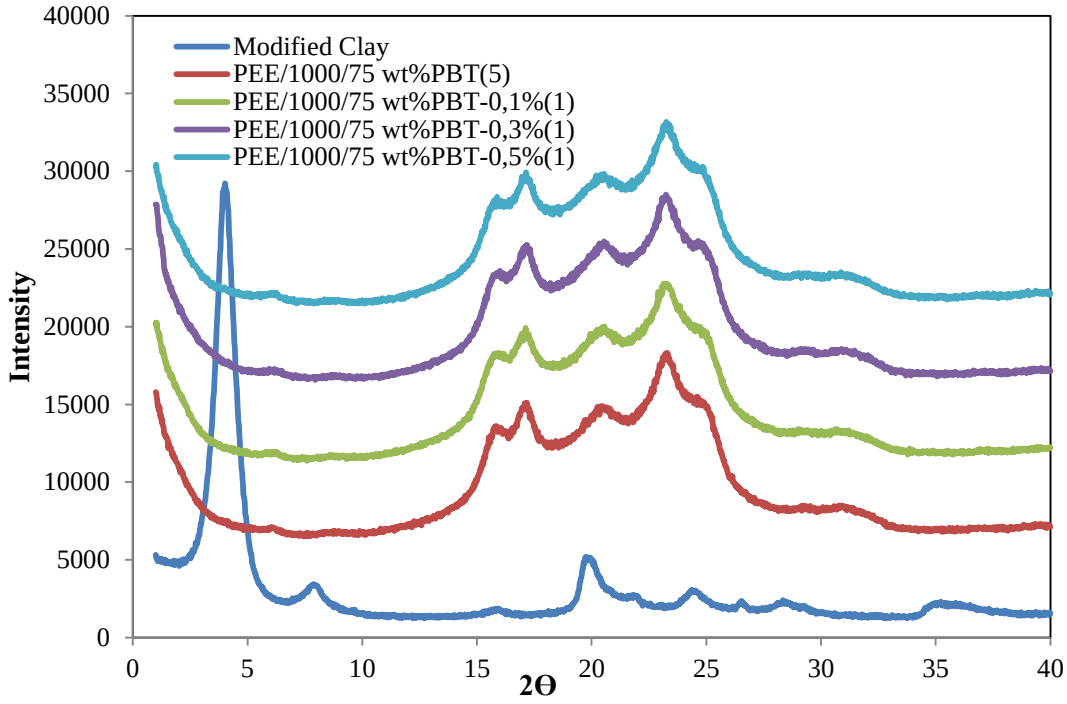


Figure 4.61 XRD Patterns of In-Situ Polymerized Nanocomposites of PEE/1000/75 wt % PBT

4.4.5.3.2 SEM Analysis

It is well known that XRD is most useful tool for the measurement of the d-spacing of ordered intercalated polymer nanocomposites with clay [52] but SEM and TEM analyses are needed to see the whole picture.

For this purpose, first SEM analyses were done on fractured surfaces of neat polymers and nanocomposites to discuss the morphology, in other words, the dispersion of the modified organoclay. The fractured surfaces were prepared by breaking the samples using liquid nitrogen for all the samples. SEM micrographs of all the samples are shown in the thesis with magnification of x1000 and x10000.

4.4.5.3.2.1 PEE and PEE Nanocomposites with 57 wt % PBT

Figure 4.62 shows the micrographs of neat PEE/1000/57 wt % PBT (3). Smooth surfaces are observed with few crack propagation lines.

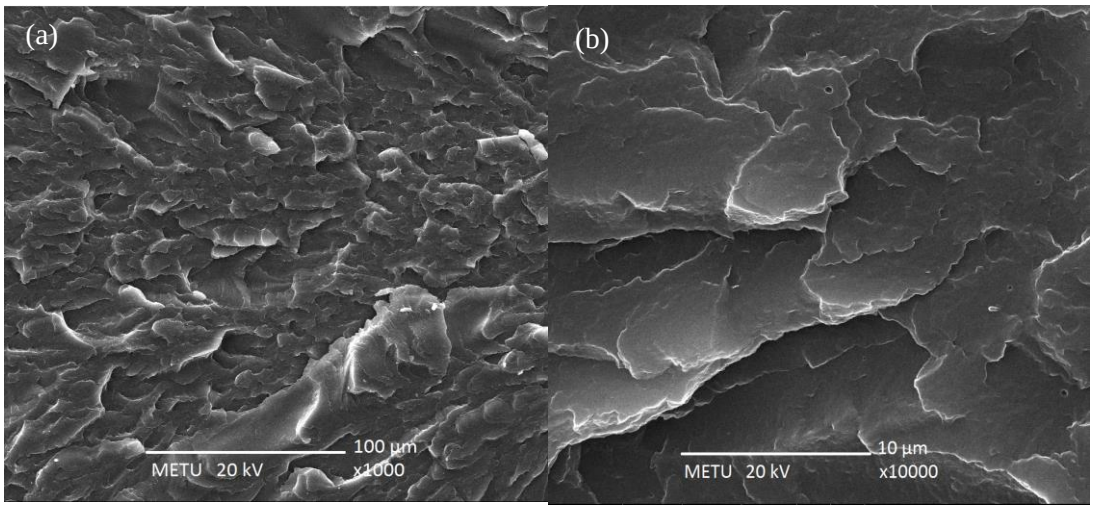


Figure 4.62 SEM Micrographs of PEE/1000/57 wt % PBT(3) (a) x 1000 magnification, (b) x10000 magnification

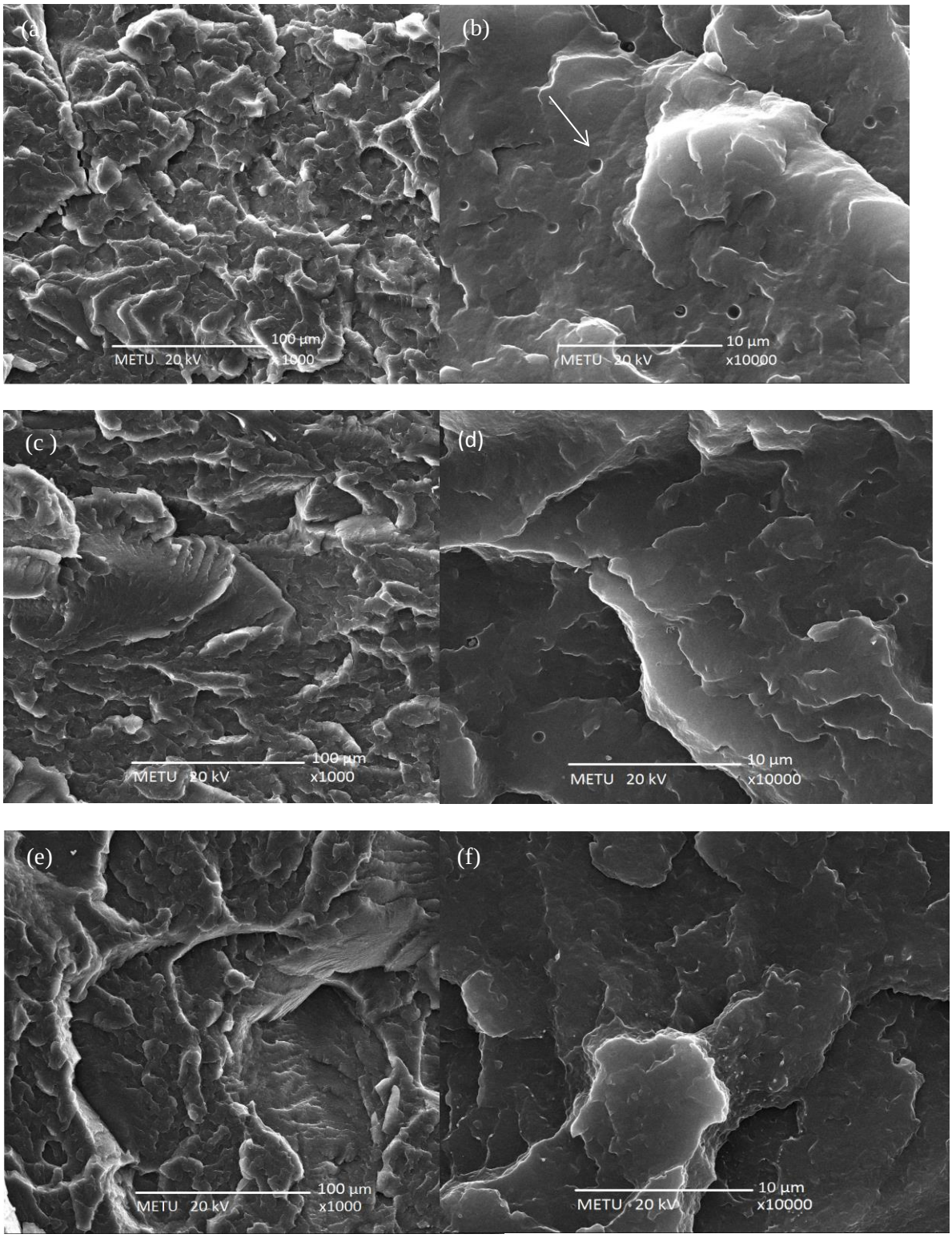


Figure 4.63 SEM Micrographs of In-Situ Polymerized PEE Nanocomposites (a) PEE/1000/57 wt % PBT-0.1 x1000 magnification, (b) PEE/1000/57 wt % PBT-0.1 % x10000 magnification (c) PEE/1000/57 wt % PBT-0.3 % x1000 magnification (d) PEE/1000/57 wt % PBT-0.3 % x10000 magnification (e) PEE/1000/57 wt % PBT-0.5 % x1000 magnification, (f) PEE/1000/57 wt % PBT-0.5 % x10000 magnification

In Figure 4.63 (a-f), fractured surfaces of nanocomposites with different organoclay ratios which are synthesized by in-situ polymerization are shown. From the SEM images, it can be concluded that modified nanoclays are randomly dispersed in the polymer matrix, since the smooth surfaces indicate the dispersed clay particles [52].

In addition, it is possible to observe some domains in Figure 4.63 (b) and (d) which shows the presence of hard blocks in polymer matrix.

Fractured surfaces of nanocomposites which are prepared by melt intercalation are shown in Figure 4.64 (a-f). The micrographs of Figure 4.64 (b) and (d) containing 0.1% and 0.3% show smooth surfaces which indicates the dispersion of clay but in the case of Figure 4.64 (f), it is difficult say that there is a homogeneous dipersion of clay in the polymer matrix.

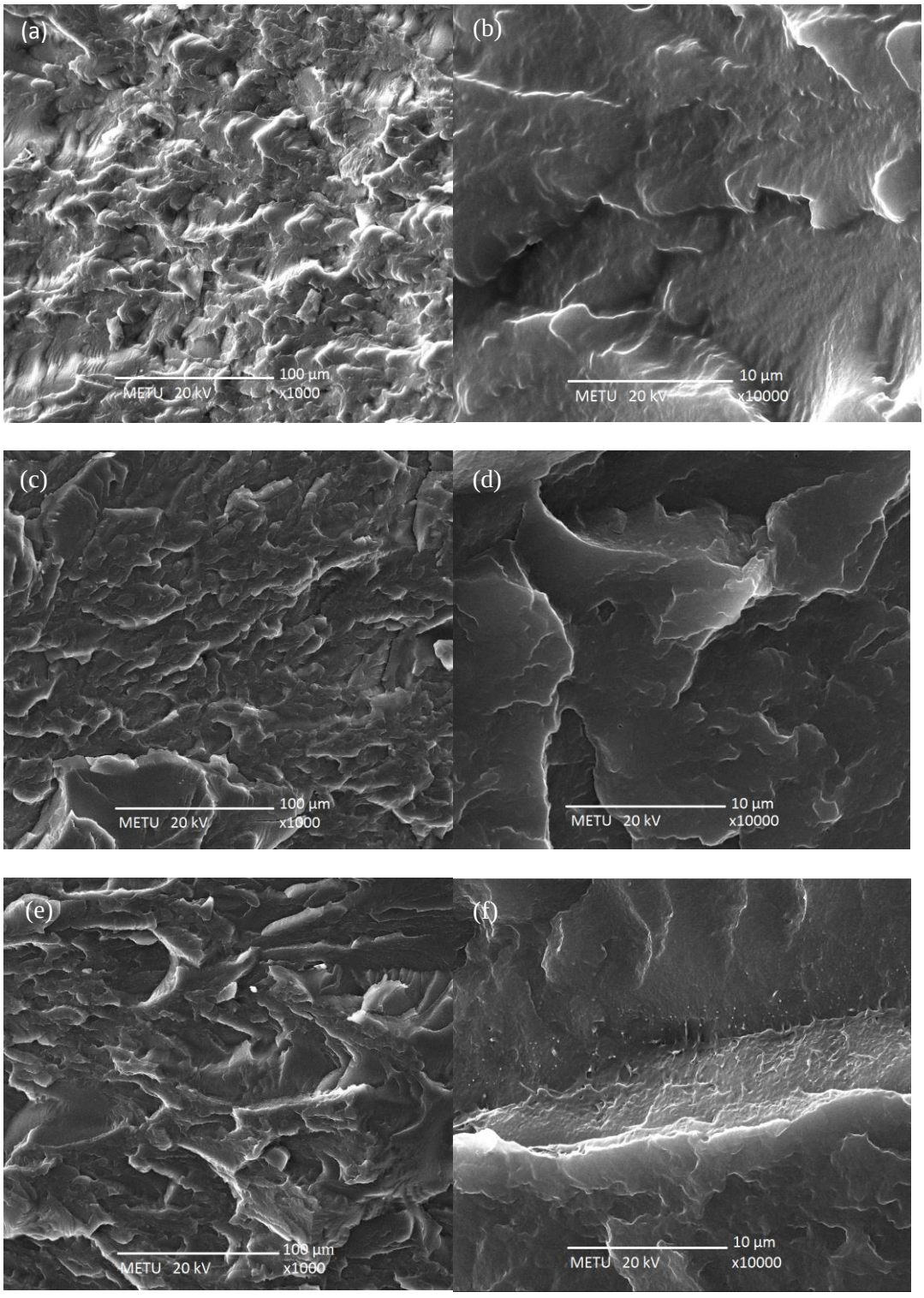


Figure 4.64 SEM Micrographs of Melt Compounded PEE Nanocomposites (a) PEE/1000/57 wt % PBT(3)+ 0.1 % x1000 magnification, (b) PEE/1000/57 wt % PBT(3)+0.1% x10000 magnification (c) PEE/1000/57 wt % PBT(3)+0.3% x1000 magnification (d) PEE/1000/57 wt % PBT(3)+0.3 % x 10000 magnification (e) PEE/1000/57 wt % PBT(3)+ 0.5% x1000 magnification, (f) PEE/1000/57 wt % PBT(3)+0.5 % x10000 magnification.

4.4.5.3.2.2 PEE and PEE Nanocomposites with 75 wt % PBT

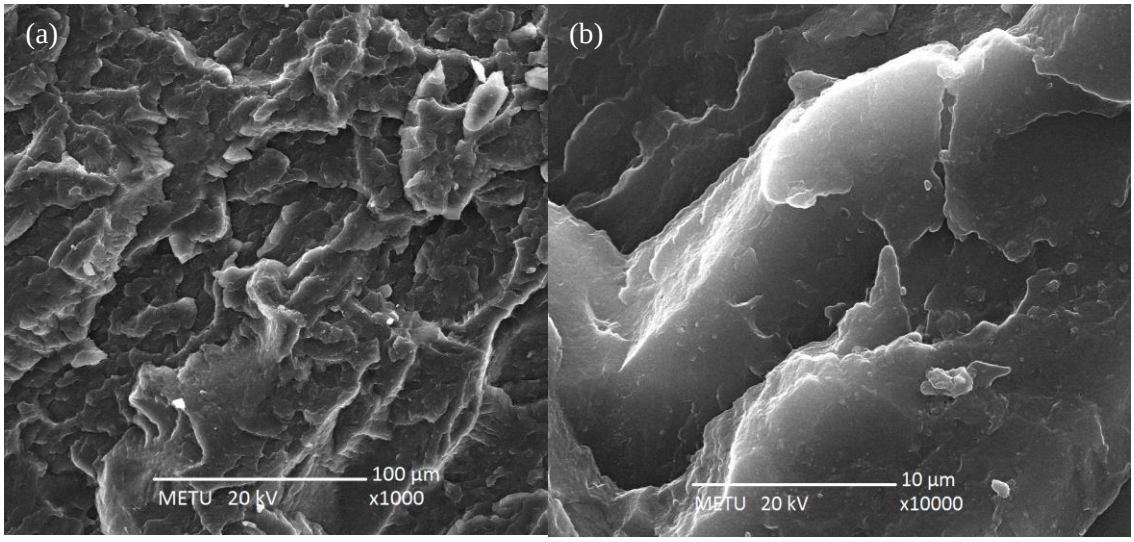


Figure 4.65 SEM Micrographs of PEE/1000/75 wt % PBT(5) (a) x1000 magnification, (b) x10000 magnification

In Figure 4.65 (a-b), the fractured surfaces of neat polymer are shown while Figure 4.66 (a-f) represent the fractured surfaces of PEEs with organoclay loading varying from 0.1% to 0.5% which are obtained by in-situ polymerization. Homogeneity of the surface disappeared due to poor organoclay dispersion. Agglomerates of organoclay were not observed in the images. Fractured surfaces of melt compounded PEE nanocomposites are shown in Figure 4.67 (a-f), showing the same trend as in situ nanocomposites.

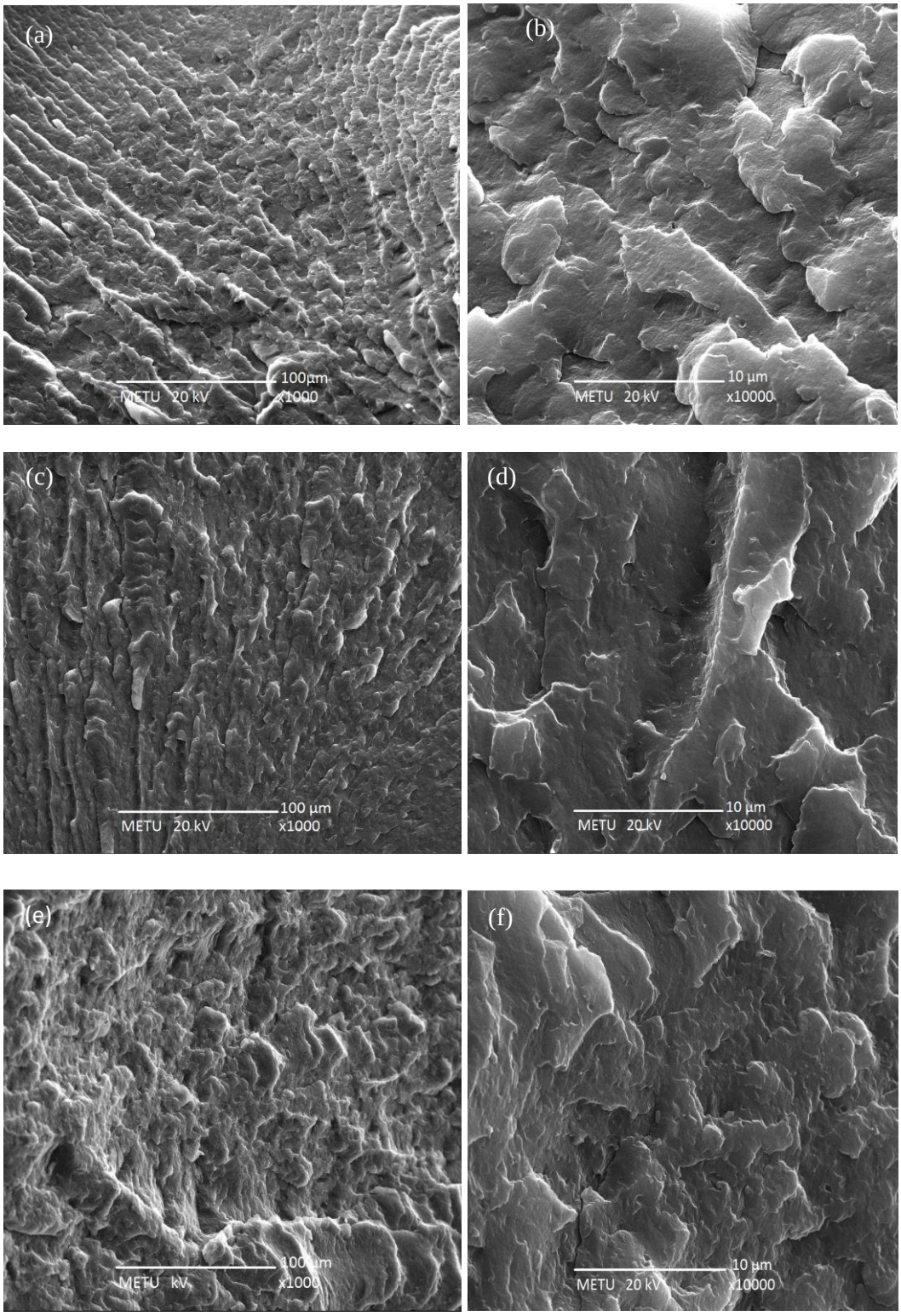


Figure 4.66 SEM Micrographs of In-Situ Polymerized PEE Nanocomposites (a) PEE/1000/75 wt % PBT-0.1 % x1000 magnification, (b) PEE/1000/75 wt % PBT-0.1 % x10000 magnification (c) PEE/1000/75 wt % PBT-0.3 % x1000 magnification (d) PEE/1000/75 wt % PBT-0.3 % x10000 magnification (e) PEE/1000/75 wt % PBT-0.5 % x1000 magnification, (f) PEE/1000/75 wt % PBT-0.5 % x10000 magnification

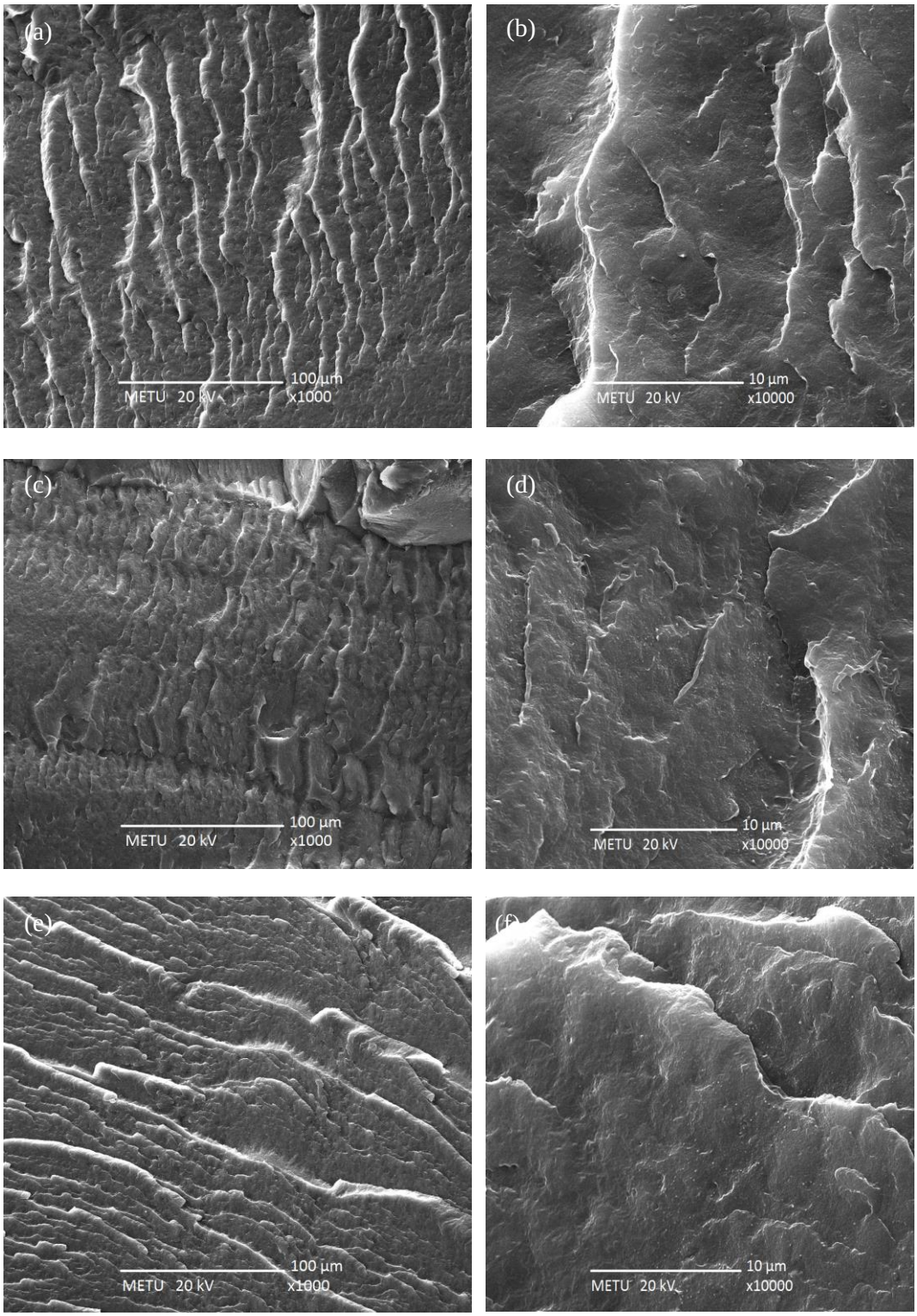


Figure 4.67 SEM Micrographs of Melt Compounded PEE Nanocomposites (a) PEE/1000/75 wt% PBT(5)+ 0.1% x 1000 magnification, (b) PEE/1000/75 wt % PBT(5)+ 0.1% x10000 magnification (c) PEE/1000/75 wt% PBT(5)+ 0.3% x1000 magnification (d) PEE/1000/75 wt % PBT(5)+ 0.3% x 10000 magnification (e) PEE/1000/75 wt % PBT (5)+ 0.5% x 1000 magnification, (f) PEE/1000/75 wt % PBT (5)+ 0.5% x10000 magnification

4.4.5.3.3 TEM Analysis

TEM studies were conducted in order to discuss the precise dispersion of modified organoclay layers within the polymer matrix.

4.4.5.3.3.1 PEE and PEE Nanocomposites with 57 wt % PBT

In Figure 4.68 (a), the PBT hard segments are observed as a bunch of grapes as well as single domains.

Figure 4.68 (b-d) shows the TEM micrographs of Melt Compounded PEE nanocomposites with 57 wt % PBT loading 0.1 wt %, 0.3 wt % and 0.5 wt % , respectively. The dark lines refer to silicate layers while gray/white areas are polymer matrix. Considering the XRD patterns, agglomeration was detected in all the three nanocomposites and it was concluded that the degree of agglomeration decreases, as the ratio of organoclay increases. TEM images also supported these results and in Figure 4.68 (c) and (d), partial intercalation of silicate layers were detected in TEM micrographs.

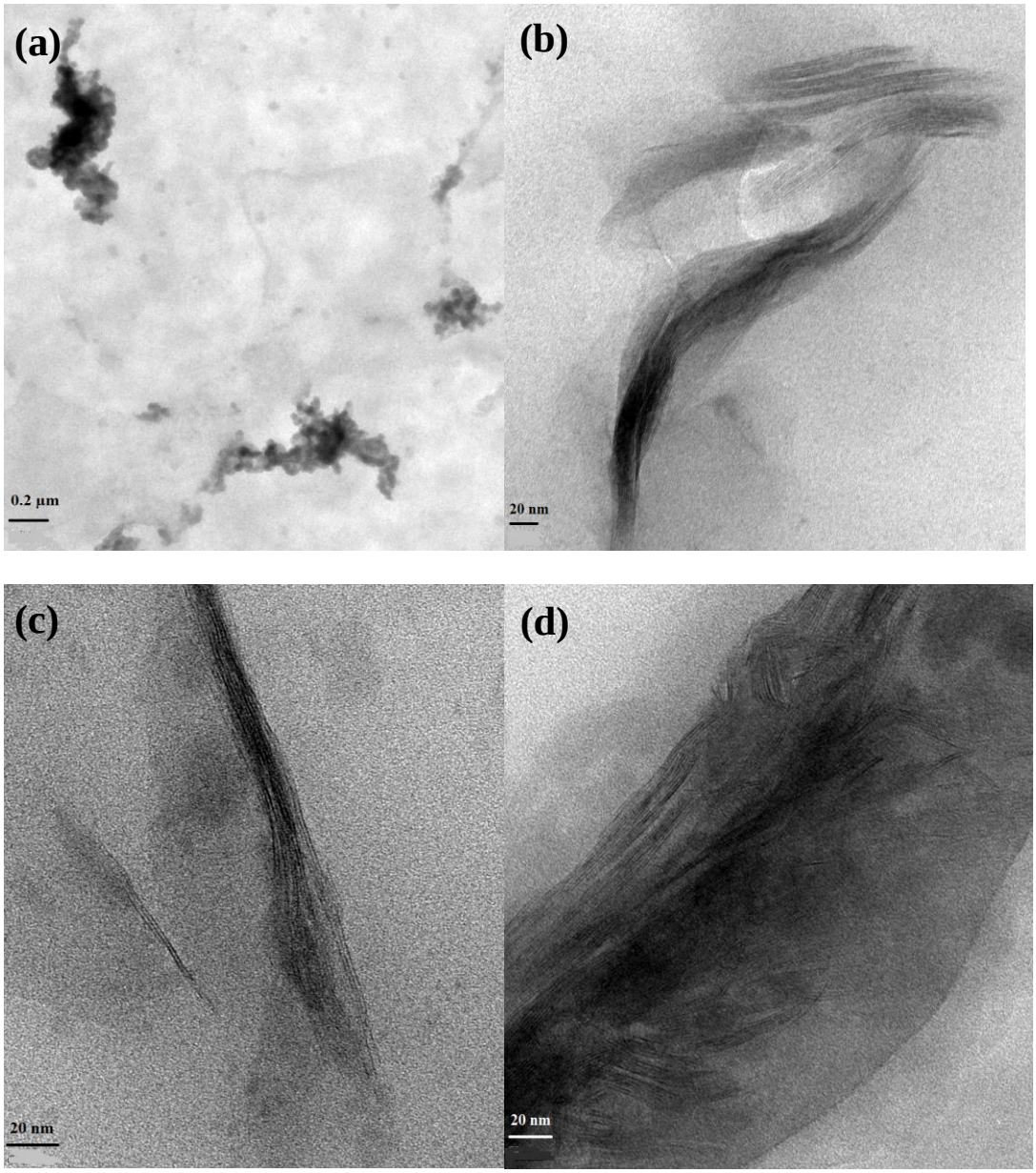


Figure 4.68 TEM Micrographs of Melt Compounded PEE Nanocomposites (a) PEE/1000/57 wt % PBT(3), (b) PEE/1000/57 wt % PBT(3)+0.1% (c) PEE/1000/57 wt % PBT(3)+0.3% (d) PEE/1000/57 wt % PBT(3)+0.5%

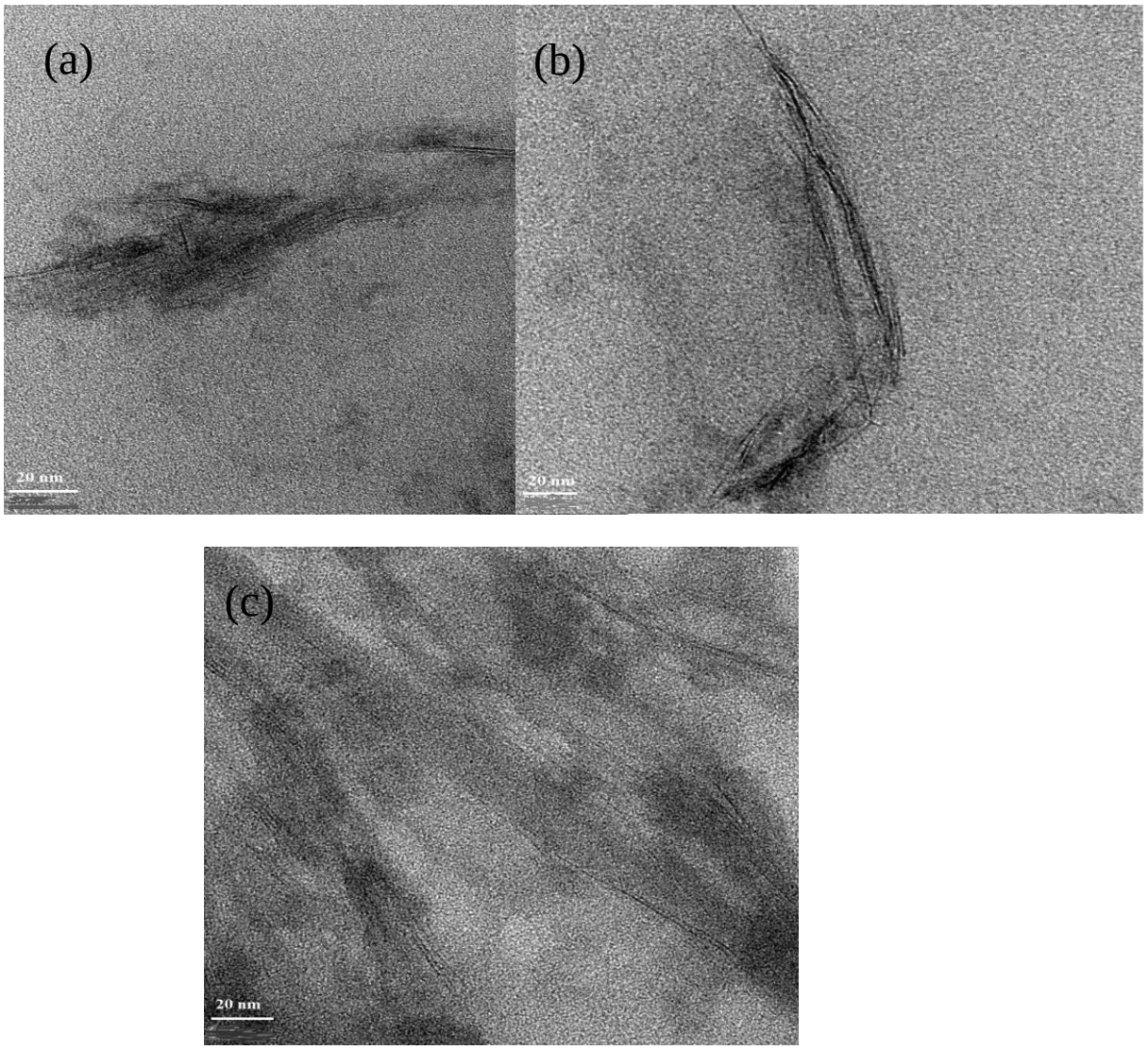


Figure 4.69 TEM Micrographs of In-Situ Polymerized PEE Nanocomposites (a) PEE/1000/57 wt % PBT-0.1%, (b) PEE/1000/57 wt % PBT-0.3%, (c) PEE/1000/57 wt % PBT-0.5%

Figure 4.69 (a-c) shows the TEM micrographs of PEE/1000/57 wt % PBT nanocomposites which are synthesized by in-situ polymerization. In these figures, both intercalated and exfoliated structures are detected. XRD analysis results implied that PEE nanocomposite with 0.1 wt % organoclay loading showed better organoclay dispersion compared to 0.3 wt % and 0.5 wt % organoclay loading, however, from TEM images, it apparent that good dispersion of organoclay was achieved also for PEE/1000/57 wt % PBT-0.3% and PEE/1000/57 wt % PBT-0.5%.

4.4.5.3.3.2 PEE and PEE Nanocomposites with 75 wt % PBT

Figure 4.70 (a) shows the neat polymer, PEE with 75 wt % PBT, while (b), (c) and (d) show melt compounded PEE nanocomposites with 0.1 wt %, 0.3 wt % and 0.5 wt % organoclay loading, respectively.

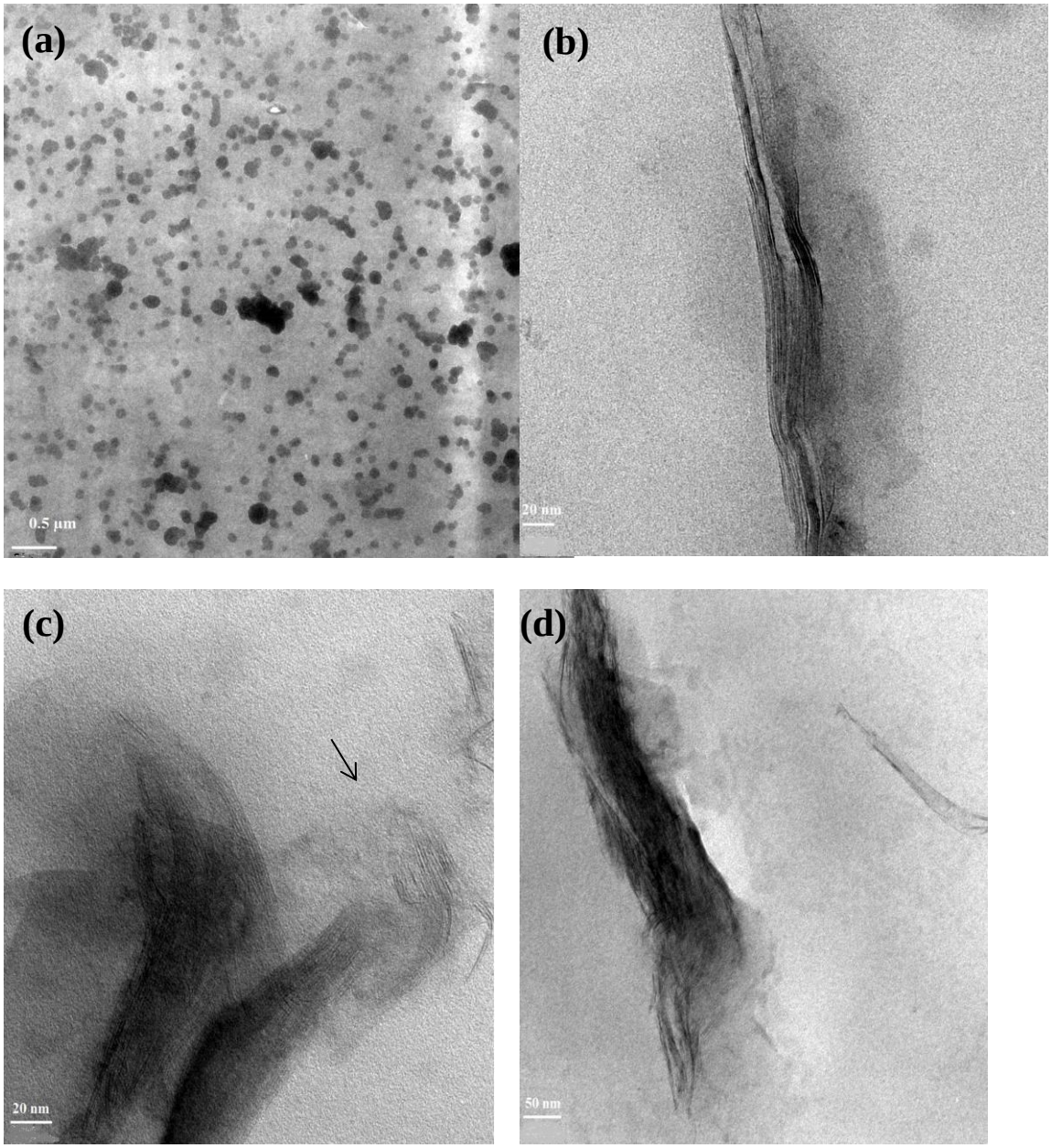


Figure 4.70 TEM Micrographs of Melt Compounded PEE Nanocomposites (a) PEE/1000/75 wt % PBT(5), (b) PEE/1000/75 wt % PBT(5)+0.1 % (c) PEE/1000/75 wt % PBT(5)+0.3 % (d) PEE/1000/75 wt % PBT(5)+0.5 %

From XRD analysis, it is difficult to understand whether an exfoliated or phase separated structure was obtained, since there was no peak in the patterns, but considering TEM micrographs in Figure 4.70, it is obvious that exfoliation of silicate layers was not achieved. Among the nanocomposites with different organoclay ratios, the best intercalation and partial exfoliation were observed in the micrograph of nanocomposite with 0.3 wt % organoclay which also explains the mechanical properties of the nanocomposites since the tensile strength increases in the order of 0.3 wt %, 0.5 wt % and 0.1 wt %.

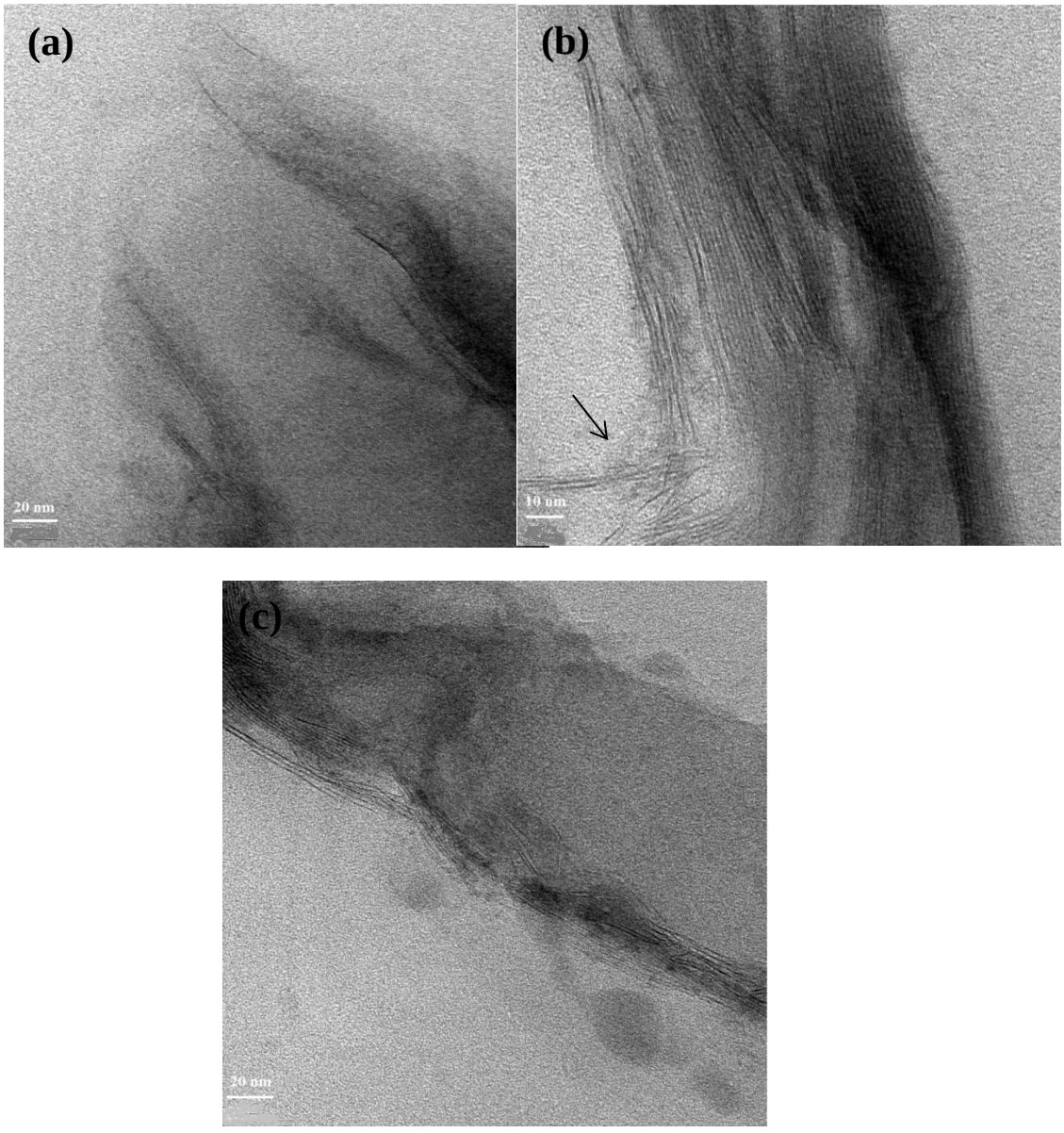


Figure 4.71 TEM Micrographs of In-Situ Polymerized PEE Nanocomposites (a) PEE/1000/75 wt % PBT-0.1% (b) PEE/1000/75 wt % PBT-0.3% (c) PEE/1000/75 wt % PBT-0.5%

In Figures 4.71 (a-c), TEM micrographs of PEE/1000/75 wt % PBT nanocomposites with different organoclay contentS which are synthesized by in-situ polymerization are given. In the case of PEE/1000/75 wt % PBT-0.1 %, it is possible to observe intercalated silicate layers in addition to partially exfoliated ones which supports the XRD analysis. For PEE with 0.3 wt% organoclay, the exfoliated and intercalated silicate layers are clearly observed, however, a small agglomeration was also detected in the micrograph. Maybe, this agglomeration led to the decrease in the tensile strength. In addition to the intercalated and exfoliated silicate layers, it is also possible to observe hard domains in Figure 4.71 (c).

4.5 Influence of Nanocomposite Preparation Methods on PEEs

As mentioned in the experimental part, two different methods for the preparation of nanocomposites were performed; namely, in-situ polymerization and melt intercalation.
In this part, these two methods will be compared only in terms of mechanical and morphological properties since characterization and thermal analysis details are given in the previous parts.

4.5.1 Mechanical Properties

The mechanical properties are shown in Figures 4.72 through 4.75. For PEEs with 57 wt % PBT, mechanical properties of nanocomposites which are synthesized by in-situ polymerization gave better results in terms of tensile strength than nanocomposites which are obtained by melt intercalation. The results are not too different but from Figure 4.72, it is clear that as the ratio of organoclay increases, the difference increases. For both two series, with the wt% of organoclay increase, tensile strength becomes better as expected, however, it should be mentioned that the possibility of stacking organoclay galleries during melt intercalation increases as the organoclay content increases which can be the reason of this gap in tensile strength.

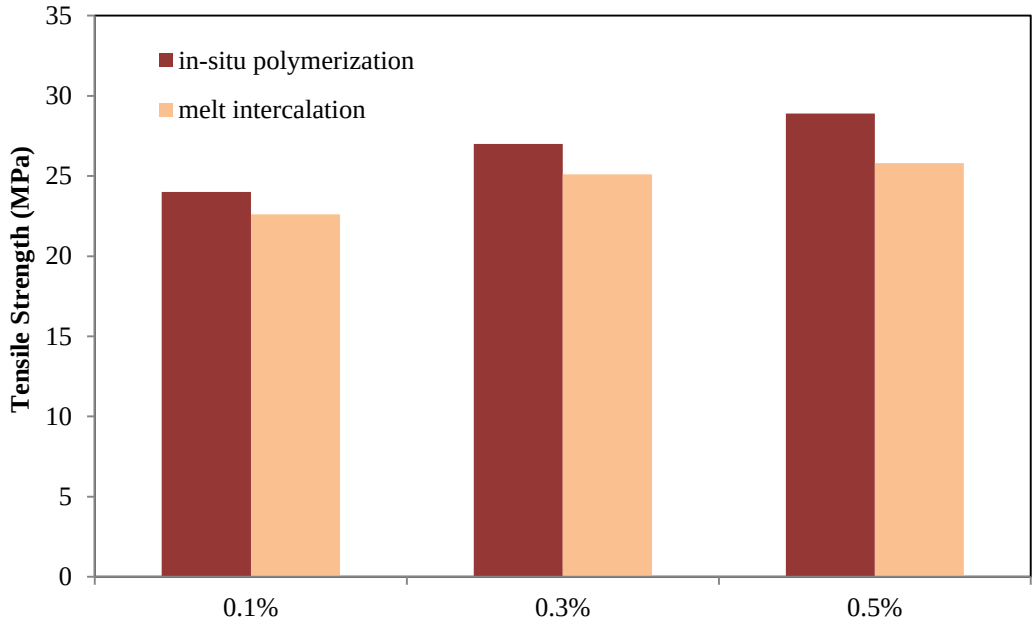


Figure 4.72 Tensile Strength of In-Situ Polymerized and Melt Compounded PEE Nanocomposites Having 57 % PBT

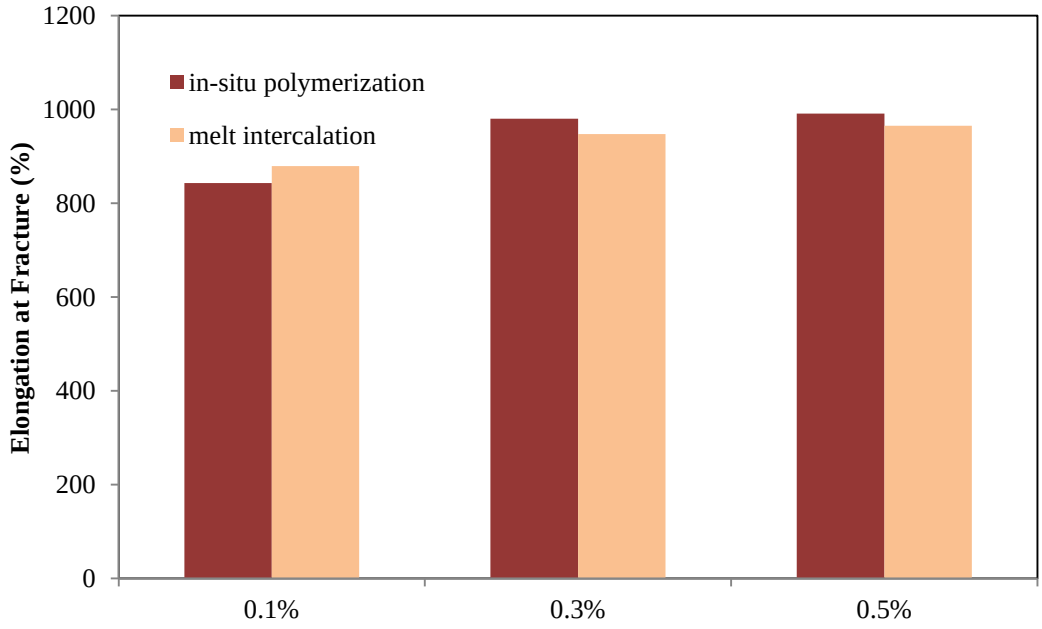


Figure 4.73 Elongation at Fracture of In-Situ Polymerized and Melt Compounded PEE Nanocomposites Having 57% PBT

In Figure 4.73 it is observed that, in terms of elongation at fracture, except for 0.1 wt % organoclay, the ones which are synthesized by in-situ polymerization showed better results.

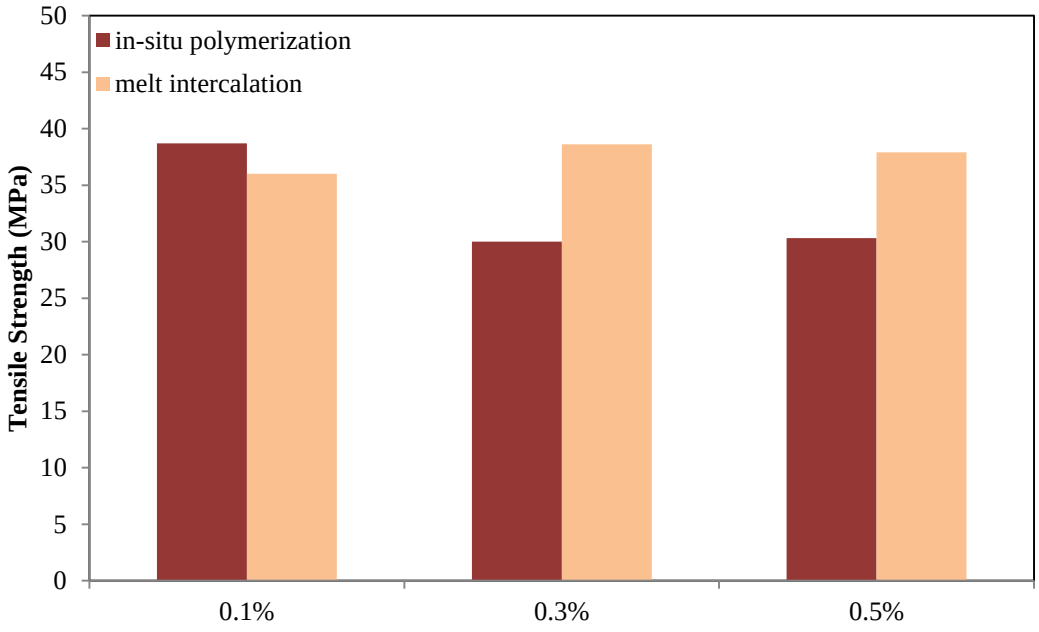


Figure 4.74 Tensile Strength of In-Situ Polymerized and Melt Compounded PEE Nanocomposites Having 75 % PBT

In nanocomposites with 75 wt % PBT, as seen in Figure 4.74, except for PEE with 0.1 wt % organoclay loading, with the increase of PBT wt %, nanocomposites prepared by melt intercalation gave better results in terms of tensile strength. Figure 4.75 shows that, in case of elongation at fracture, the data showed that the nanocomposites prepared by melt intercalation have better elastomeric character.

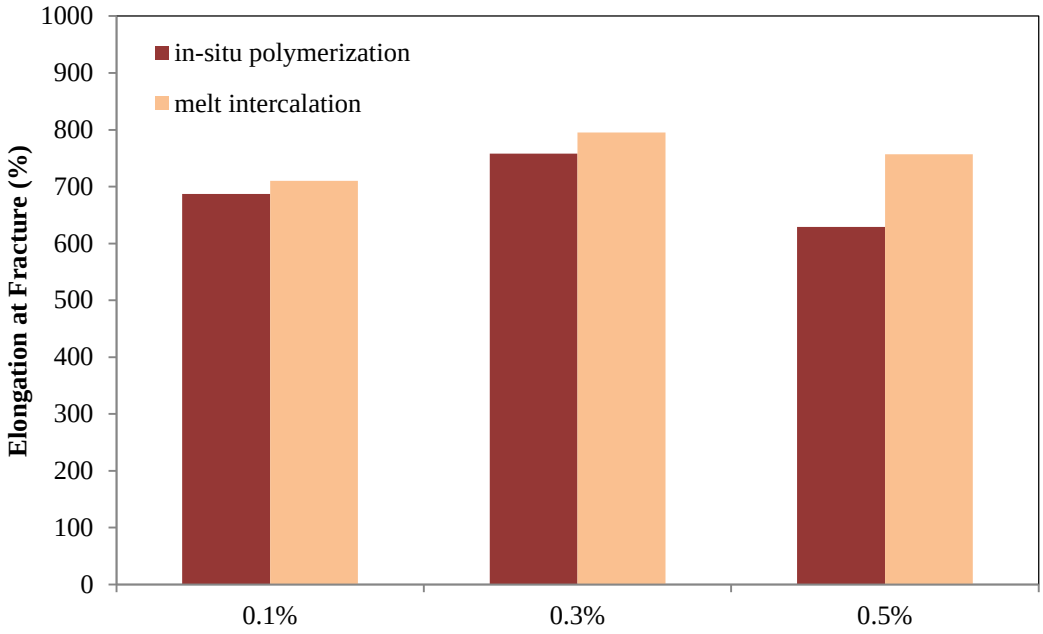


Figure 4.75 Elongation at Fracture (%) of In-Situ Polymerized and Melt Compounded PEE Nanocomposites PEEs Having 75 % PBT

4.5.2 Morphology of the Nanocomposites

In order to discuss the dispersion of organoclay, XRD, SEM and TEM analysis were performed for PEE and PEE nanocomposites. In the end of the analysis, it was concluded that better dispersion of organoclay was achieved by in-situ polymerization.

In the case of in-situ polymerization, organoclay and 1,4-butane diol were mixed in ultrasonic bath for 30 minutes prior to reaction so that the swelling of layered silicates in the 1,4- butane diol was achieved. As observed in XRD patterns and TEM micrographs, for nanocomposites synthesized by in-situ polymerization, d-spacing between clay layers were greater than d-spacing of nanocomposites prepared by melt intercalation.

CHAPTER 5

CONCLUSIONS

For the synthesis of PEEs with different PBT weight ratios varying from 37 wt % to 75 wt %, two different procedures were used and it was concluded that the transesterification time and the volume of methanol which is collected as a side product play great role to obtain polymers with better mechanical properties and higher molecular weights.

In terms of mechanical properties, increasing tensile strength and elongation at fracture was observed with increasing wt % PBT, and the best results were obtained for PEE with 75 wt % PBT, as 32.35 MPa and 672%, respectively. Considering the thermal behavior, DSC analysis showed that as the PBT segment length increases, melting point of PBT increases dramatically due to higher degree of crystallization.

Nanocomposites based on PEE (37 wt % and 49 wt % PBT) and modified organoclay (0.1, 0.3 and 0.5 wt %) were prepared only by melt intercalation. Mechanical properties did not increase with the addition of organoclay. When the thermal analysis is concerned, the results indicate that the addition of organoclay disturbs the crystallinity of PBT hard segment and causes the decrease of Tm value at these PBT contents.

PEE nanocomposites with 57 wt % PBT and 75 wt % PBT were obtained by two different methods used namely, in-situ polymerization and melt intercalation.

For PEE/1000/57 wt % PBT nanocomposites, the mechanical analysis indicated that as the wt % of organoclay ratio increases, tensile strength and elongation (%) increase for both methods. However, nanocomposites synthesized by in-situ polymerization showed better mechanical properties. The addition of organoclay did not affect the glass transition temperature of PEG, but resulted in decrease of the melting point of PBT, since the organoclay restricts the crystallization in PEE. From morphological analysis, it was concluded that in-situ polymerization method provides better dispersion of organoclay silicate layers within the PEEs. In addition, with the contribution of XRD and SEM analysis, TEM analysis proved the strong relationship between morphological and mechanical properties of the nanocomposites. Especially in the case of in-situ polymerization, the dispersion of organoclay through PEE had significant effects on the mechanical behaviour.

In the case of 75 wt % PBT, for the nanocomposites which were synthesized by in-situ polymerization, 0.1 wt % organoclay addition improved the tensile strength significantly compared to that of neat PEE, but as the wt % of organoclay was increased, the tensile strength decreased. The highest tensile strength was obtained in the mechanical analysis

of PEE with 0.3 wt % organoclay loading for the melt intercalation method. In thermal analysis, different from the other series, the addition of organoclay did not decrease the melting point of PBT, probably due to the increase of PBT content in PEE nanocomposites. This was observed for both methods of preparation. As in the case of PEE/1000/57 wt %PBT, the results of XRD, SEM and TEM analysis showed that better dispersion of organoclay is achieved with the in-situ polymerization method.

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APPENDIX A

EXPERIMENTAL DETAILS FOR THE SYNTHESIS OF PEEs and PEE NANOCOMPOSITES

1. Synthesis of PEE/1000/ 37 wt % PBT (1)

The reactants, 1,4-BD (0.30 mole, 27.00 gr), PEG (0.06 mole, 60 gr), DMT (0.24 mole, 46.56 gr), catalyst (0.116 gr, 121 μl) and stabilising agent (0.139 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. 25 minutes later, the temperature was set 260 ^{o}C, and after one hour, the vacuum was applied and the pressure was decreased to 2.7 mbar in 95 minutes. The duration time at 260 ^{o}C was 182 minutes and accordingly, the temperature was set 275 ^{o}C. The reaction mixture stayed at these conditions for 43 minutes to get the target polymer.

2. Synthesis of PEE/1000/ 37 wt % PBT (2)

The reactants, 1,4-BD (0.30 mole, 27.00 gr), PEG (0.06 mole, 60 gr), DMT (0.24 mole, 46.56 gr), catalyst (0.116 gr, 121 μl) and stabilising agent (0.139 gr) were mixed in a 150 ml recation vessel and heated to 175 ^{o}C. When the temperature raised 175 ^{o}C, reflux started. 25 minutes later, the temperature was set to 260 ^{o}C. The reaction mixture was stirred and heated at this temperature for 255 minutes to get the desired compound. The vacuum was applied after 35 minutes and the pressure was decreased to 3 mbar in 115 minutes.

3. Synthesis of PEE/1000/ 37 wt % PBT (3)

The reactants, 1,4-BD (0.275 mole, 24.75 gr), PEG (0.055 mole, 55 gr), DMT (0.22 mole, 42.68 gr), catalyst (0.1067 gr, 111 μl) and stabilising agent (0.128 gr) were mixed in a 150 ml reaction vessel and heated up to 175 ^{o}C. After stirring for 61 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the volume of MeOH collected to theoretical total volume of MeOH was 67.49%. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 76.2 % when it was set to 280 ^{0}C. After 14 minutes, the temperature was increased to 280 ^{o}C and the vacuum was applied.The pressure was decreased to 2.4 mbar in 44 minutes. The reaction mixture was stirred at this temperature for 121 minutes and when the reaction was over, the ratio of the volume collected to the theoretical one was 86%.

4. Synthesis of PEE/1000/ 37 wt % PBT (4)

The reactants, 1,4-BD (0.275 mole, 24.75 gr), PEG (0.055 mole, 55 gr), DMT (0.22 mole, 42.68 gr), catalyst (0.1067 gr, 111 µl) and stabilising agent (0.128 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After stirring for 67 minutes at this temperature (after 40 minutes from refluxing), the temperature was set to 185 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 36 %. The reaction mixture was stirred at this temperature for 22 minutes and then the temperature was set to 260 ^{o}C when the ratio of the total volume of MeOH collected was 63% and it stayed at this temperature for 177 minutes. The reaction mixture was stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 74.32 % when it was set 280 ^{o}C. After 8 minutes, the temperature reached 280 ^{o}C and the vacuum was applied. The pressure was decreased to 2.8 mbar in 44 minutes. The reaction mixture was stirred at this temperature for 121 minutes and when the reaction was over, the ratio of the volume collected to the theoretical one was 87.74 %.

5. Synthesis of PEE/1000/ 37 wt % PBT (5)

1,4-BD (0.3 mole, 27 gr), PEG (0.06 mole, 60 gr), DMT (0.24 mole, 46.56 gr) catalyst (0.116 gr, 121 µl) and the stabilizing agent (0.139 gr, 0.3% DMT) were mixed in a 150 ml glass reaction vessel and the mixture was constantly stirred and gradually heated to 175 ^{o}C. The temperature was kept constant at 175 ^{o}C for 133 minutes and it was set to 210 ^{o}C. After stirring for 49 minutes at this temperature, the temperature was increased to 260 ^{o}C when the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 87.7%. When the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 71.8%, the vacuum was applied and the pressure was decreased to 2.4 mbar in 69 minutes. The temperature was kept constant at 260 ^{o}C for 129 minutes and when the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 75.13%, it was set to 280 ^{o}C. The reaction was stopped after stirring 49 minutes at this temperature to get the target compound with volume ratio of 75.3%.

6. Synthesis of PEE/1000/ 49 wt % PBT (1)

1,4-BD (0.0824 mole, 7.418 gr), PEG (0.0105 mole, 10.50 gr), DMT (0.0619 mole, 12.00 gr) catalyst (0.03 gr, 30 µl) and the stabilizing agent (0.00359 gr, 0.3% DMT) were mixed in a 75 ml glass reaction vessel and the mixture was constantly stirred and gradually heated to 175 ^{o}C. It stayed at 175 ^{0}C for 24 minutes and then the temperature was set to 255 ^{o}C. 50 minutes later, the vacuum was applied gradually and the pressure was decreased to 2.6 mbar in one hour. The mixture was heated to 275 ^{o}C and stayed at this temperature for 80 minutes.

7. Synthesis of PEE/1000/ 49 wt % PBT (2)

1,4-BD (0.0824 mole, 7.418 gr), PEG (0.0105 mole, 10.50 gr), DMT (0.0619 mole, 12.00 gr) catalyst (0.03 gr, 30 µl) and the stabilizing agent (0.00359 gr, 0.3% DMT) were mixed in a 75 ml glass reaction vessel and the mixture was constantly stirred and gradually heated to 175 ^{o}C. The mixture stayed at this temperature for 25 minutes and then the temperature was set to 260 ^{o}C. After one hour, vacuum was applied and the pressure was decreased to 2.6 mbar in 70 minutes. The mixture stayed at 260 ^{o}C for 123 minutes and then the temperature was set to 275 ^{o}C and stayed at this temperature for 110 minutes to get the desired compound.

8. Synthesis of PEE/1000/ 49 wt % PBT (3)

1,4-BD (0.0824 mole, 7.418 gr), PEG (0.0105 mole, 10.50 gr), DMT (0.0619 mole, 12.00 gr) catalyst (0.03 gr, 30 µl) and the stabilizing agent (0.00359 gr, 0,3% DMT) were mixed in a 75 ml glass reaction vessel and the mixture was constantly stirred and gradually heated to 175 ^{o}C. After staying 25 minutes at this temperature, the mixture was heated to 260 ^{o}C. The mixture stayed at this temperature for half an hour and then vacuum was applied. In 67 minutes, the pressure was decreased to 2.3 mbar and the heating and stirring continued. After temperature has reached 260 ^{o}C, the mixture stayed at this temperature for 95 min and then the temperature was set to 275 ^{o}C. After one hour, the reaction was stopped in order to get the polymer.

9. Synthesis of PEE/1000/ 49 wt % PBT (4)

1,4-BD (0.329 mole, 29.61 gr), PEG (0.042 mole, 42.00 gr), DMT (0.247 mole, 47.92 gr) catalyst (0.12 gr, 120 µl) and the stabilizing agent (0.1437gr, 0.3% DMT) were mixed in a 150. ml glass reaction vessel and the mixture was constantly stirred and gradually heated to 175 ^{0}C. The mixture stayed at this temperature for 25 minutes and accordingly, it was raised to 260 ^{0}C. After one hour, vacuum was applied and in 90 minutes, the pressure was decreased to 2.4 mbar. For 177 minutes, the mixture was stirred at 260 ^{0}C and then the temperature was set to 275 ^{0}C. The reaction was stopped after 43 minutes to get the desired compound.

10. Synthesis of PEE/1000/ 49 wt % PBT (5)

The reactants, 1,4 BD (0.329 mole, 29.61 gr), PEG (0.042 mole, 42 gr), DMT (0.247 mole, 47.92 gr), catalyst (120 µl) and stabilising agent (0.1437 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After stirring for 25 minutes at this temperature, the reaction mixture was heated to 260 ^{o}C and stayed at this temperature for 177 minutes. Meanwhile, after first one hour, the vacuum was applied and the pressure was decreased to 2.6 mbar in 90 minutes. The temperature was set to 275 ^{o}C and after reaching this temperature, the reaction mixture stayed at this temperature for 50 minutes to get the desired compound.

11. Synthesis of PEE/1000/ 49 wt % PBT (6)

The reactants, 1,4-BD (0.329 mole, 29.61 gr), PEG (0.042 mole, 42 gr), DMT (0.247 mole, 47.92 gr), catalyst (120 µl) and stabilising agent (0.1437 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After stirring 66 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C when 64% of the theoretical volume of MeOH was collected. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 71.6 % when it was set to 280 ^{o}C. When the temperature was 280 ^{o}C, the vaccum was applied and the pressure was decreased to 2.5 mbar in 44 minutes. The reaction was stopped after stirring the reaction mixture for 115 minutes and the ratio of the total volume of MeOH and excess 1,4-BD to the theoretical total volume of MeOH and excess 1,4-BD was 86.1%.

12. Synthesis of PEE/1000/49 wt % PBT (7)

The reactants, 1,4 BD (0.329 mole, 29.61 gr), PEG (0.042 mole, 42 gr), DMT (0.247 mole, 47.92 gr), catalyst (120 µl) and stabilising agent (0,1437 gr) were mixed in a 150 ml recation vessel and heated to 175 ^{o}C. After stirring 62 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 65.13 %. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 65.16 % when it was set to 280 ^{o}C. After 14 minutes, the temperature reached 280 ^{o}C and the vacuum was applied. The pressure was decreased to 2.9 mbar in 79 minutes. The reaction mixture was stirred at this temperature for 121 minutes and when the reaction was over, the ratio of the volume collected to the theoretical total volume of MeOH and excess 1,4-BD was 80.65 % and the pressure was 2.6 mbar.

13. Synthesis of PEE/1000/49 wt % PBT (8)

The reactants, 1,4-BD (0.329 mole, 29.61 gr), PEG (0.042 mole, 42 gr), DMT (0.247 mole, 47.92 gr), catalyst (0.121 gr, 125 µl) and stabilising agent (0.1437 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. The temperature was kept constant at 175 ^{o}C for 165 minutes and it was set to 210 ^{o}C. After stirring for 42 minutes at this temperature, the temperature was increased to 260 ^{o}C when the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 88.6%. When the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 72.2%, the vacuum was applied and the pressure was decreased to 2.3 mbar in 99 minutes. The temperature was kept constant at 260 ^{o}C for 126 minutes and when the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 76.1%, it was set to 280 ^{o}C. The reaction was stopped after stirring 52 minutes at this temperature to get the target compound with volume ratio of 77.7%.

14. Synthesis of PEE/1000/ 57 wt % PBT (1)

The reactants, 1,4 BD (0.371 mole, 33.39 gr), PEG (0.035 mole, 35 gr), DMT (0.271 mole, 52.49 gr), catalyst (0.131 gr, 135 µl) and stabilising agent (0.1574 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After the temperature has reached 175 ^{o}C, it was set to 260 ^{o}C and the reaction mixture stayed at this temperature for 188 minutes. After first one hour, the vacuum was applied and the pressure was decreased to 2.3 mbar in 101 minutes. The temperature of the reaction mixture was increased to 275 ^{o}C and after 43 minutes, the reaction was stopped.

15. The synthesis of PEE/1000/ 57 wt % PBT (2)

The reactants, 1,4-BD (0.371 mole, 33.39 gr), PEG (0.035 mole, 35 gr), DMT (0.2706 mole, 52.49 gr), catalyst (0.131 gr, 135 µl) and stabilising agent (0.1574 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After stirring 60 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 64%. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 74.4 % when it was set to 280 ^{o}C. After 19 minutes, the temperature increased to 280 ^{o}C and the vacuum was applied. The pressure was decreased to 2.6 mbar in 44 minutes. The reaction mixture was stirred at this temperature for 116 minutes and when the reaction was over, the ratio of the volume collected to the theoretical total volume of MeOH and excess 1,4-BD was 90.9%.

16. The synthesis of PEE/1000/ 57 wt % PBT (3)

The reactants, 1,4-BD (0.371 mole, 33.39 gr), PEG (0.035 mole, 35 gr), DMT (0.2706 mole, 52.49 gr), catalyst (0.131 gr, 135 µl) and stabilising agent (0.1574 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. The temperature was kept constant at 175 ^{o}C for 87 minutes and it was set to 210 ^{o}C. After stirring for 17 minutes at this temperature, the temperature was increased to 260 ^{o}C when the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 91.6%. When the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 76.7%, the vacuum was applied and the pressure was decreased to 2.6 mbar in 69 minutes. The temperature was kept constant at 260 ^{o}C for 131 minutes and when the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 83.2%, it was set to 280 ^{o}C. The reaction was stopped after stirring 52 minutes at this temperature to get the target compound with volume ratio of 85.6%.

17. Synthesis of PEE/1000/ 75 wt % PBT (1)

The reactants, 1,4-BD (0.478 mole, 43.02 gr), PEG (0.02 mole, 20 gr), DMT (0.332 mole, 64.408 gr), catalyst (0.161 gr, 170 µl) and stabilising agent (0.19 gr) were mixed in a 150

ml reaction vessel and heated to 175 ^{o}C. After 109 minutes, when the 75% of the total volume of MeOH was collected, the temperature was set to 220 ^{o}C. The reaction mixture was stirred for 31 minutes at this temperature, when the 58% of the total volume of MeOH and excess 1,4-BD were collected, the temperature was set to 260 ^{o}C. 58 minutes later, 72% of the total volume of MeOH and excess 1,4-BD were collected and the temperature was set to 270 ^{o}C. When the temperature was reached this value and the ratio increased to 75%, the vacuum was applied and the pressure was decreased to 2.8 mbar in 50 minutes. After 50 minutes, the temperature was set to 275 ^{o}C and accordingly, after 15 minutes the temperature was set to 280 ^{o}C. When the reaction mixture was reached this temperature, shearing was observed. The reaction was stopped after one hour, when the ratio of the total volume of MeOH and excess 1,4-BD to the theoretical total volume of MeOH and excess 1,4-BD was 88.9%.

18. Synthesis of PEE/1000/ 75 wt % PBT (2)

The reactants, 1,4-BD (0.478 mole, 43.02 gr), PEG (0.02 mole, 20 gr), DMT (0.332 mole, 64.408 gr), catalyst (0.161 gr, 170 µl) and stabilising agent (0.19 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After 51 minutes, when the 71% of the total volume of MeOH was collected, the temperature was set to 260 ^{o}C. After one hour at this temperature, when the ratio of the total volume of MeOH and excess 1,4-BD to the theoretical total volume of MeOH and excess 1,4-BD was 71.6%, the vacuum was applied and the pressure was decreased to 2.1 mbar in one hour. The reaction mixture stayed at 260 ^{o}C for 136 minutes and then the temperature was set to 280 ^{o}C. After 25 minutes, the temperature reached this value and shearing was observed. In the end of 30 minutes, when the ratio of the total volume of MeOH and excess 1,4-BD to the theoretical total volume of MeOH and excess 1,4-BD was 85%, the reaction was stopped to get the target compund.

19. Synthesis of PEE/1000/ 75 wt % PBT (3)

The reactants, 1,4-BD (0.478 mole, 43.02 gr), PEG (0.02 mole, 20 gr), DMT (0.332 mole, 64.408 gr), catalyst (0.161 gr, 170 µl) and stabilising agent (0.19 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After stirring 58 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to the theretical MeOH volume was 72.30%. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected the theoretical total volume of MeOH and excess 1,4-BD was 76.88 % when it was set to 280 ^{o}C. After 19 minutes, the temperature reached 280 ^{0}C and the vacuum was applied. The pressure was decreased to 2.3 mbar in 49 minutes. The reaction mixture was stirred at this temperature for 116 minutes and when the reaction was over, the ratio of the volume collected to the theoretical total volume of MeOH and excess 1,4-BD was 93.22 %.

20. Synthesis of PEE/1000/ 75 wt % PBT (5)

The reactants, 1,4-BD (0.478 mole, 43.02 gr), PEG (0.02 mole, 20 gr), DMT (0.332 mole, 64.408 gr), catalyst (0.161 gr, 170 µl) and stabilising agent (0.19 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. The temperature was kept constant at 175 ^{o}C for 73 minutes and it was set to 210 ^{o}C. After stirring for 38 minutes at this temperature, the temperature was increased to 260 ^{o}C when the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 88.3%. When the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 74.2%, the vacuum was applied and the pressure was decreased to 3.5 mbar in 69 minutes. The temperature was kept constant at 260 ^{o}C for 130 minutes and when the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 81.3%, it was set to 280 ^{o}C. The reaction was stopped after stirring 65 minutes at this temperature to get the target compound with volume ratio of 83.5%.

21. Synthesis of PEE/600/57 wt % PBT (1)

The reactants, 1,4 BD (0.375 mole, 33.75 gr), PEG (0.054 mole, 32.4 gr), DMT (0.286 mole, 55.48 gr), catalyst (0.139 gr, 144 µl) and stabilising agent (0.166 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After stirring 56 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical MeOH volume was 66 %. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 64.15 % when it was set to 280 ^{o}C. After 14 minutes, the temperature reached 280 ^{o}C and the vacuum was applied. The pressure was decreased to 2.4 mbar in 48 minutes. The reaction mixture was stirred at this temperature for 106 minutes and when the reaction was over, the ratio of the volume collected to the theoretical total volume of MeOH and excess 1,4-BD was 74.64 %.

22. Synthesis of PEE/600/ 57 wt % PBT (2)

The reactants, 1,4 BD (0.375 mole, 33.75 gr), PEG (0.054 mole, 32.4 gr), DMT (0.286 mole, 55.48 gr), catalyst (0.139 gr, 144 µl) and stabilising agent (0.166 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After stirring 62 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to theoretical volume MeOH was 38.94 %. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 49.1 % when it was set to 280 ^{o}C. After 13 minutes, the temperature reached 280 ^{o}C and the vacuum was applied. The pressure was decreased to 2.6 mbar in 69 minutes. The reaction mixture was stirred at this temperature for 122 minutes and when the reaction was over, the ratio of the volume collected to the theoretical total volume of MeOH and excess 1,4-BD was 61.92 % and the pressure was 1.4 mbar.

23. Synthesis of PEE/600/67 wt % PBT (1)

Firstly, 1,4-BD (0.0847 mole, 7.623 gr), PEG (0.008 mole, 4.8 gr), DMT (0.0618 mole, 11.989 gr) catalyst (0.0299 gr, 30 µl) and the stabilizing agent (0.00359 gr, 0.3% DMT) were mixed in a 75 ml glass reaction vessel and the mixture was constantly stirred and gradually heated to 170 ^{o}C. After staying at 170 ^{o}C for 37 minutes, the temperature was set to 255 ^{o}C and during the temperature elevation (23 minutes), transesterification step occured. After the first 30 minutes, the vacuum was applied and the pressure was gradually decreased. Through the reaction, pressure was in a range between 2.4-2.8 mbar. Heating and stirring were continued for 165 minutes during the polycondensation step to yield the desired compound.

24. Synthesis of PEE/600/67 wt % PBT (2)

The reactants, 1,4 BD (0.4236 mole, 38.12 gr), PEG (0.04 mole, 24 gr), DMT (0.309 mole, 59.946 gr), catalyst (0.150 gr, 156 µl) and stabilising agent (0.179 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After stirring 79 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 56 %.The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 74.34 % when it was set to 280 ^{o}C. After 10 minutes, the temperature reached 280 ^{o}C and the vacuum was applied. The pressure was decreased to 3,6 mbar in 44 minutes. The reaction mixture was stirred at this temperature for 103 minutes and when the reaction was over, the ratio of the volume collected was 89.31 %.

25. Synthesis of PEE/600/67 wt % PBT (3)

The reactants, 1,4 BD (0.4236 mole, 38.12 gr), PEG (0.04 mole, 24 gr), DMT (0.309 mole, 59.946 gr), catalyst (0.150 gr, 156 µl) and stabilising agent (0.179 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After stirring 66 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 60.87 %. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 69.7 % when it was set to 280 ^{0}C. After 22 minutes, the temperature reached 280 ^{o}C and the vacuum was applied. The pressure was decreased to 3.2 mbar in 70 minutes. The reaction mixture was stirred at this temperature for 113 minutes and when the reaction was over, the ratio of the volume collected was 83.72 % and the pressure was 1.7 mbar.

26. Synthesis of PEE/2000/41 wt % PBT (1)

The reactants, 1,4 BD (0.2965 mole, 26.69 gr), PEG (0.028 mole, 56 gr), DMT (0.216 mole, 41.90 gr), catalyst (0.1048 gr, 109 µl) and stabilising agent (0.125 gr) were mixed

in a 150 ml reaction vessel and heated to 175 ^{o}C. After stirring 79 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 185 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 35.5 %. The reaction mixture was stirred at this temperature for 20 minutes and then the temperature was set to 260 ^{o}C when the ratio of the total volume of MeOH collected was 57.3%. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 72.3 % when it was set to 280 ^{o}C. After 11 minutes, the temperature became 280 ^{0}C and the vacuum was applied. The pressure was decreased to 4.5 mbar in 52 minutes. The reaction mixture was stirred at this temperature for 100 minutes and when the reaction was over, the ratio of the volume collected was 88.53 %.

27. Synthesis of PEE/2000/41 wt % PBT (2)

The reactants, 1,4 BD (0.2965 mole, 26.69 gr), PEG (0.028 mole, 56 gr), DMT (0.216 mole, 41.90 gr), catalyst (0.1048 gr, 109 µl) and stabilising agent (0.125 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After stirring 91 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 26.36 %. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 64.90 % when it was set to 280 ^{o}C. After 12 minutes, the temperature reached 280 ^{o}C and the vacuum was applied. The pressure was decreased to 3.3 mbar in 51 minutes. The reaction mixture was stirred at this temperature for 108 minutes and when the reaction was over, the ratio of the volume collected was 81.15 %.

28. Synthesis of PEE/2000/57 wt % PBT (1)

The reactants, 1,4 BD (0.39 mole, 35.1 gr), PEG (0.0195 mole, 39 gr), DMT (0.273 mole, 52.96 gr), catalyst (138 µl) and stabilising agent (0.158 gr) were mixed in a150 ml reaction vessel and heated to 175 ^{o}C. After stirring 79 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 57 %. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 90.81 % when it was set to 280 ^{o}C. After 15 minutes, the temperature reached 280 ^{o}C and the vacuum was applied. The pressure was decreased to 3.5 mbar in 65 minutes. The reaction mixture was stirred at this temperature for 120 minutes and when the reaction was over, the ratio of the volume collected was more than 96 % and the pressure was 1.5 mbar.

29. Synthesis of PEE/2000/75 wt % PBT (1)

The reactants, 1,4 BD (0.396 mole, 35.64 gr), PEG (0.009 mole, 18 gr), DMT (0.27 mole, 52.38 gr), catalyst (0.131 gr, 136 μl) and stabilising agent (0.157 gr) were mixed in a 150 ml reaction vessel and heated to 175 ^{o}C. After stirring 84 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 82.5 %. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 22.46 % when it was set to 280 ^{o}C. After 14 minutes, the temperature reached 280 ^{o}C and the vacuum was applied. The pressure was decreased to 2,4 mbar in 67 minutes. The reaction mixture was stirred at this temperature for 121 minutes and when the reaction was over, the ratio of the volume collected was 31.32 % and the pressure was 1.0 mbar.

30. Synthesis of PEE/1000/49 wt % PBT-0.5% (1)

Firstly, PEG (0.042 mole, 42 gr) and 0.5% MC (0.4625 gr) were mixed in a 150 ml reaction vessel and stirred for 3 hours in ultrasonic bath at 60 ^{o}C. Then, the other reactants, 1,4 BD (0.329 mole, 29.61 gr), DMT (0.247 mole, 47.92 gr), catalyst (gr, 120 μl) and stabilising agent (0.1437 gr) were added and heated to 175 ^{o}C. After stirring 65 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 5 %. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 17,42 % when it was set to 280 ^{o}C. After 21 minutes, the temperature reached 280 ^{o}C and the vacuum was applied. The pressure was decreased to 3.2 mbar in 74 minutes. The reaction mixture was stirred at this temperature for 114 minutes and when the reaction was over, the ratio of the volume collected was 30.97 % and the pressure was 2.2 mbar.

31. Synthesis of PEE/1000/ 49 wt % PBT-1% (1)

1,4-BD (0.0824 mole, 7.418 gr), PEG (0.0105 mole, 10.50 gr), DMT (0.0619 mole, 12.00 gr) catalyst (0.03 gr, 30 μl), Cloisite 30B (0.299 gr, 1% of the total amount of starting compounds) and the stabilizing agent (0.00359 gr, 0.3% DMT) were mixed in a 75 ml glass reaction vessel and the mixture was constantly stirred and gradually heated to 175 ^{o}C. The reaction mixture stayed at this temperature for 25 minutes and then it was heated to 260 ^{o}C. After 30 minutes, the vacuum was applied and the pressure was decreased to 2,3 mbar in 70 minutes. The mixture stayed at 260 ^{o}C for 127 minutes and then the temperature was set to 275 ^{o}C and stayed at this temperature for 33 minutes to get the desired compound.

32. Synthesis of PEE/1000/ 49 wt % PBT-1% (2)

1,4-BD (0.0824 mole, 7.418 gr), PEG (0.0105 mole, 10.50 gr), DMT (0.0619 mole, 12.00 gr) catalyst (0.03 gr, 30 µl), Cloisite 30 (0.299 gr, 1% of the total amount of starting compound) and the stabilizing agent (0.00359 gr, 0.3% DMT) were mixed in a 75 ml glass reaction vessel and the mixture was constantly stirred and gradually heated to 175 ^{o}C. After 25 minutes, the reaction mixture was heated to 260 ^{o}C and stayed at this temperature for 130 minutes. The vacuum was applied after staying half an hour at this temperature and the pressure was decreased to 2.2 mbar in 70 minutes. Heating and stirring continued for 130 minutes at this temperature and then it was set to 275 ^{o}C. The reaction was stopped after 95 minutes to get the target compound.

33. Synthesis of PEE/1000/49 wt % PBT-1% (3)

1,4-BD (0.329 mole, 29.61 gr), PEG (0.042 mole, 42.00 gr), DMT (0.247 mole, 47.92 gr) catalyst (0.12 gr, 120 µl) the stabilizing agent (0.1437gr, 0.3% DMT) and Cloisite 30B (1.195 gr, 1% of the total amount of starting compounds) were mixed in a 150. ml glass reaction vessel and the mixture was constantly stirred and gradually heated to 175 ^{o}C. After stirring 33 minutes at this temperature, the temperature was set to 260 ^{o}C when 52.61% of the total volume of MeOH was collected. The reaction mixture stirred at this temperature for one hour and then the vacuum was applied. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 75.80%. The pressure was decreased to 2.7 mbar in 30 minutes. The temperature was increased to 275 ^{o}C after stirring the reaction mixture for 180 minutes. The reaction mixture stayed at this temperature for 54 minutes and then the reaction was stopped to get the desired compound.

34. Synthesis of PEE/1000/49 wt % PBT-1% (4)

Firstly, PEG (0.042 mole, 42 gr) and 1% MC (0.925 gr) were mixed in a 150 ml reaction vessel and stirred for 3 hours in ultrasonic bath at 60 ^{o}C. Then, the other reactants, 1,4 BD (0.329 mole, 29.61 gr), DMT (0.247 mole, 47.92 gr), catalyst (120 µl) and stabilising agent (0.1437 gr) were added and heated to 175 ^{o}C. After stirring 60 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 46.09 %. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 41.94 % when it was set to 280 ^{o}C. After 21 minutes, the temperature reached 280 ^{o}C and the vacuum was applied. The pressure was decreased to 0.8 mbar in 72 minutes. The reaction mixture was stirred at this temperature for 114 minutes and when the reaction was over, the ratio of the volume collected was 73 % and the pressure was 0.7 mbar.

35. Synthesis of PEE/1000/49 wt % PBT-1% (5)

Firstly, PEG (0.042 mole, 42 gr) and 1% MC (0.925 gr) were mixed in a 150 ml reaction vessel and stirred for 3 hours in ultrasonic bath at 60 ^{o}C. Then, the other reactants, 1,4 BD (0.329 mole, 29.61 gr), DMT (0.247 mole, 47.92 gr), catalyst (0.4792 gr, 500 µl) and stabilising agent (0.1437 gr) were added and heated to 175 ^{o}C. After stirring 72 minutes at this temperature (after 45 minutes from refluxing), the temperature was set to 260 ^{o}C and the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 57 %. The reaction mixture stirred at this temperature for one hour and then the temperature was set to 280 ^{o}C. The ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 67.74 % when it was set to 280 ^{o}C. After 18 minutes, the temperature reached 280 ^{o}C and the vacuum was applied. The pressure was decreased to 3.3 mbar in 83 minutes. The reaction mixture was stirred at this temperature for 117 minutes and when the reaction was over, the ratio of the volume collected was 85.81 % and the pressure was 2.2 mbar.

36. Synthesis of Synthesis of PEE/1000/57 wt % PBT-0.1% (1)

To begin, 1,4 BD (0.371 mole, 33.39 gr) and 0.1% MC (0.09469 gr) were mixed in a 150 ml reaction vessel and stirred for 30 minutes in ultrasonic bath at 30 ^{o}C. Then, the other reactants, PEG (0.035 mole, 35 gr), DMT (0.2706 mole, 52.49 gr), catalyst (0.131 gr, 135µl) and stabilising agent (0.1574 gr) were added and heated to 175 ^{o}C. The temperature was kept constant at 175 ^{o}C for 74 minutes and it was set to 210 ^{o}C. After 30 minutes, the temperature was set to 260 ^{o}C when the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 91.7 %. After 60 minutes, the vacuum was applied and the pressure was decreased to 3 mbar in 66 minutes. The temperature was kept constant at 260 ^{o}C for 126 minutes and when the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 85%, it was set to 280 ^{o}C. The reaction was stopped after stirring 46 minutes at this temperature to get the target compound with ratio of 87.4%.

37. Synthesis of Synthesis of PEE/1000/57 wt % PBT-0.3% (1)

1,4 BD (0.371 mole, 33.39 gr) and 0.3% MC (0.284 gr) were mixed in a 150 ml reaction vessel and stirred for 30 minutes in ultrasonic bath at 30 ^{o}C. Then, the other reactants, PEG (0.035 mole, 35 gr), DMT (0.2706 mole, 52.49 gr), catalyst (0.131 gr, 135µl) and stabilising agent (0.1574 gr) were added and heated to 175 ^{o}C. The temperature was kept constant at 175 ^{o}C for 69 minutes and it was set to 210 ^{o}C. After stirring 23 minutes at this temperature, when the ratio of total volume of MeOH collected to the theoretical volume of MeOH was 90.7%, it was set to 260 ^{o}C. After 60 minutes, the vacuum was applied and the pressure was decreased to 3 mbar in 66 minutes. The temperature was kept constant at 260 ^{o}C for 126 minutes and when the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 79.1%, it was set to 280 ^{o}C. The reaction was stopped after stirring 47 minutes at this temperature to get the target compound with volume ratio of 80.9 %.

38. Synthesis of Synthesis of PEE/1000/57 wt % PBT-0.5% (1)

First, 1,4 BD (0.371 mole, 33.39 gr) and 0.5% MC (0.473 gr) were mixed in a 150 ml reaction vessel and stirred for 30 minutes in ultrasonic bath at 30 ^{o}C. Then, the other reactants, PEG (0.035 mole, 35 gr), DMT (0.2706 mole, 52.49 gr), catalyst (0.131 gr, 135µl) and stabilising agent (0.1574 gr) were added and heated to 175 ^{o}C. The temperature was kept constant at 175 ^{o}C for 128 minutes and it was set to 210 ^{o}C. After stirring 39 minutes at this temperature, when the ratio of total volume of MeOH collected to the theoretical volume of MeOH was 90.7%, it was set to 260 ^{o}C. After 60 minutes, the vacuum was applied and the pressure was decreased to 3 mbar in 64 minutes. The temperature was kept constant at 260 ^{o}C for 124 minutes and when the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 80.6.%, it was set to 280 ^{o}C. The reaction was stopped after stirring 47 minutes at this temperature to get the target compound with volume ratio of 84.7 %.

39. Synthesis of Synthesis of PEE/1000/75 wt % PBT-0.1% (1)

1,4 BD (0.478 mole, 43.02 gr) and 0.1% MC (0.09 gr) were mixed in a 150 ml reaction vessel and stirred for 30 minutes in ultrasonic bath at 30 ^{o}C. Then, the other reactants, PEG (0.02 mole, 20 gr), DMT (0.332 mole, 64.408 gr), catalyst (0.161 gr, 167.7 µl) and stabilising agent (0.1437 gr) were added and heated to 175 ^{o}C. The temperature was kept constant at 175 ^{o}C for 79 minutes and it was set to 210 ^{o}C. After stirring 41 minutes at this temperature, when the ratio of total volume of MeOH collected to the theoretical volume of MeOH was 85%, it was set to 260 ^{o}C. After 35 minutes, the vacuum was applied and the pressure was decreased to 3.2 mbar in 64 minutes. The temperature was kept constant at 260 ^{o}C for 134 minutes and when the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 76.4%, it was set to 280 ^{o}C. The reaction was stopped after stirring 47 minutes at this temperature to get the target compound with volume ratio of 79.2%.

40. Synthesis of Synthesis of PEE/1000/75 wt % PBT-0.3% (1)

To begin, 1,4 BD (0.478 mole, 43.02 gr) and 0.3% MC (0.2697 gr) were mixed in a 150 ml reaction vessel and stirred for 30 minutes in ultrasonic bath at 30 ^{o}C. Then, the other reactants, PEG (0.02 mole, 20 gr), DMT (0.332 mole, 64.408 gr), catalyst (0.161 gr, 167.7 µl) and stabilising agent (0.1437 gr) were added and heated to 175 ^{o}C. The temperature was kept constant at 175 ^{o}C for 75 minutes and it was set to 210 ^{o}C. After 24 minutes, since the volume of collected methanol in the graduated cylinder did not change significantly, the temperature was increased to 220 ^{o}C. It was set to 260 ^{o}C when the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was 85%. After 35 minutes, the vacuum was applied and the pressure was decreased to 2.5 mbar in 61 minutes. The temperature was kept constant at 260 ^{o}C for 100 minutes and when the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 84%, it was set to 280 ^{o}C. The reaction was

stopped after stirring 62 minutes at this temperature to get the target compound with ratio of 86.5%.

41. Synthesis of Synthesis of PEE/1000/75 wt % PBT-0.5% (1)

1,4 BD (0.478 mole, 43.02 gr) and 0.5% MC (0.4496 gr) were mixed in a 150 ml reaction vessel and stirred for 30 minutes in ultrasonic bath at 30 ^{o}C. Then, the other reactants, PEG (0.02 mole, 20 gr), DMT (0.332 mole, 64.408 gr), catalyst (0.161 gr, 167.7 µl) and stabilising agent (0.1437 gr) were added and heated to 175 ^{o}C. The temperature was kept constant at 175 ^{o}C for 88 minutes and it was set to 210 ^{o}C. After stirring for 15 minutes at this temperature, the temperature was increased to 260 ^{o}C when the ratio of the total volume of MeOH collected to the theoretical volume of MeOH was
88.7%. After 60 minutes, the vacuum was applied and the pressure was decreased to 2.8 mbar in 59 minutes. The temperature was kept constant at 260 ^{o}C for 119 minutes and when the ratio of the total volume of MeOH and excess 1,4-BD collected to the theoretical total volume of MeOH and excess 1,4-BD was 87%, it was set to 280 ^{o}C. The reaction was stopped after stirring 44 minutes at this temperature to get the target compound with ratio of 90.8%.

APPENDIX B

FTIR-ATR ANALYSIS

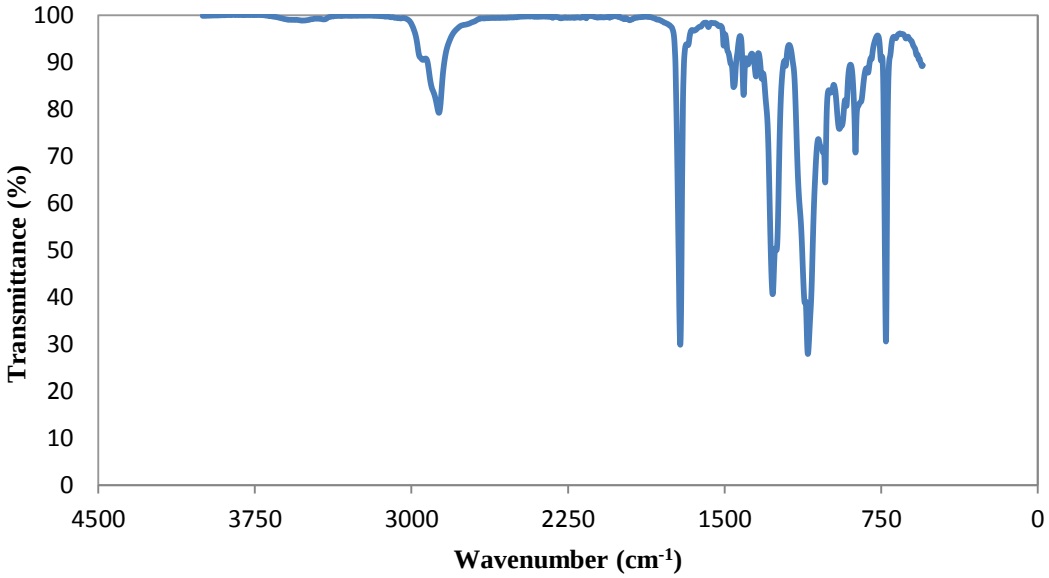

Figure B.1 PEE/1000/37 wt%PBT (5)

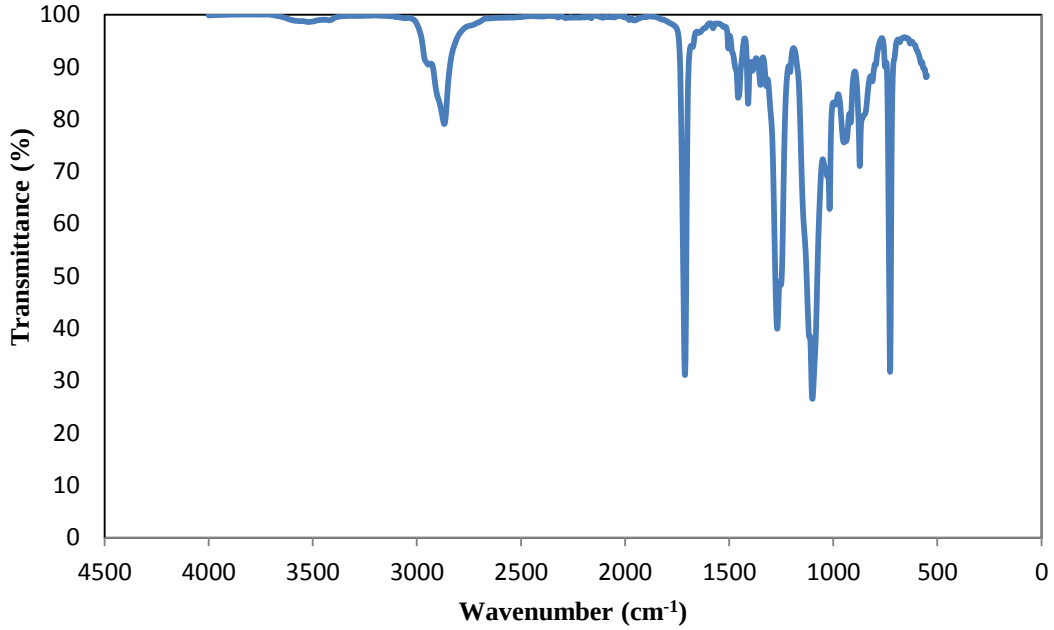

Figure B.2 PEE/1000/37 wt%PBT (5) + 0,1% TBHDP-MMT

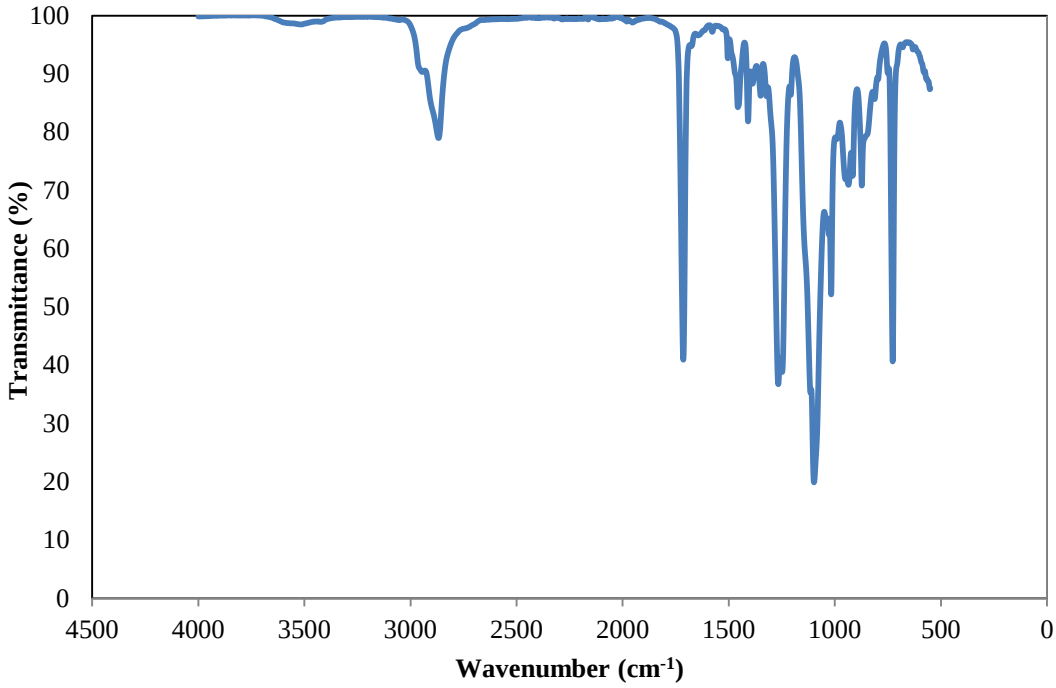

Figure B.3 PEE/1000/37 wt%PBT (5) + 0.3% TBHDP-MMT

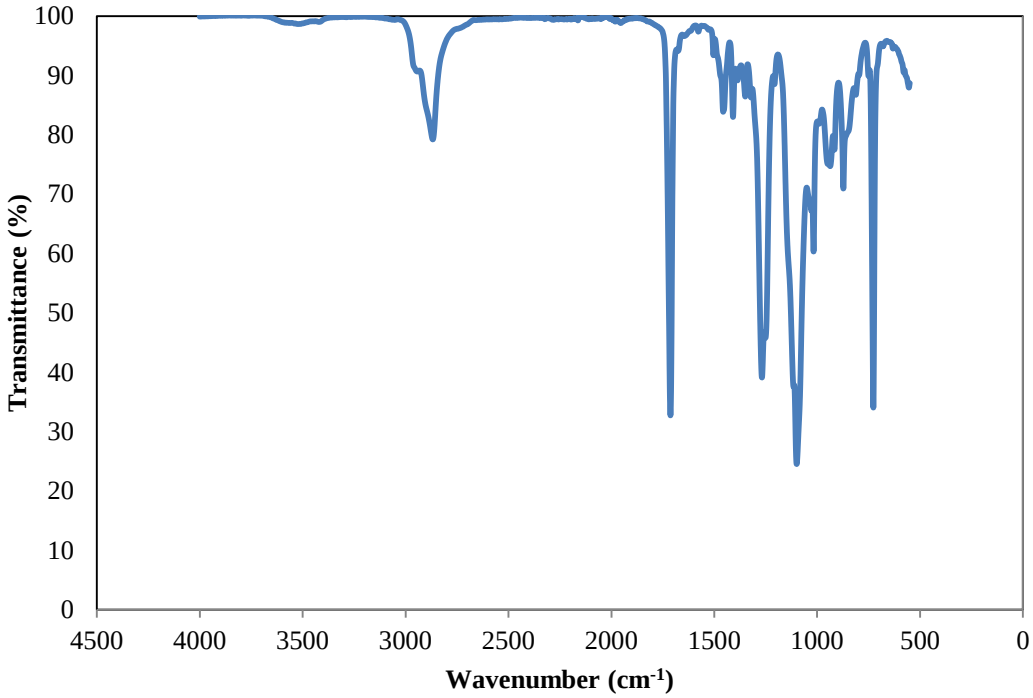

Figure B.4 PEE/1000/37 wt%PBT (5) + 0.5% TBHDP-MMT

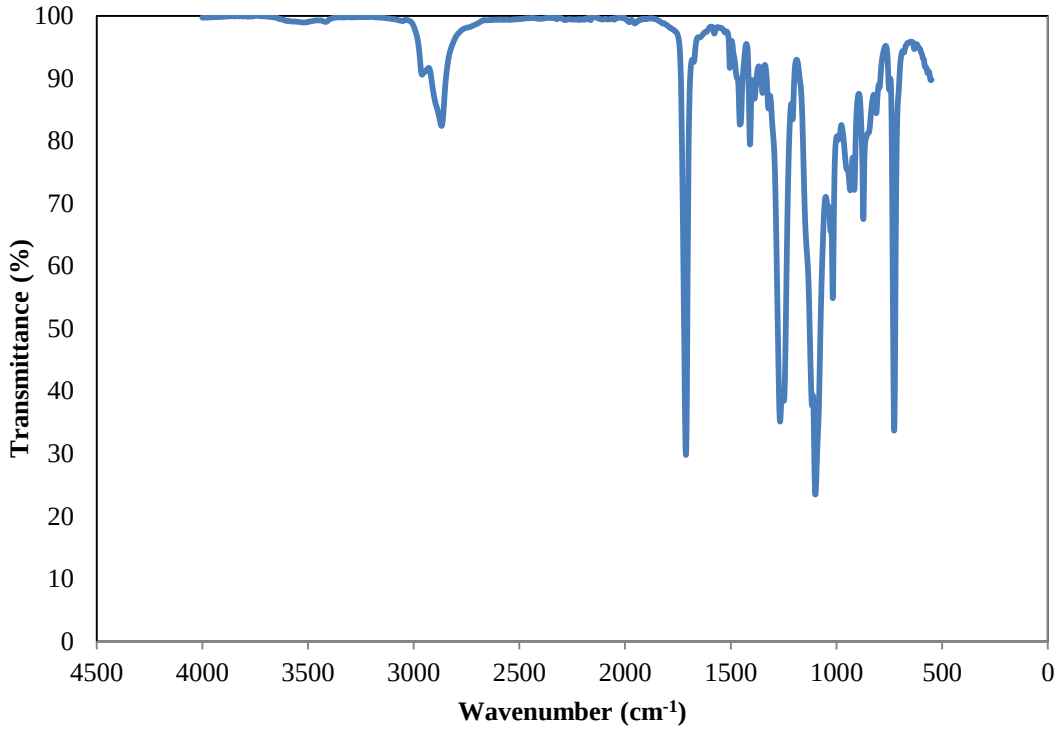

Figure B.5 PEE/1000/49 wt% PBT (8)

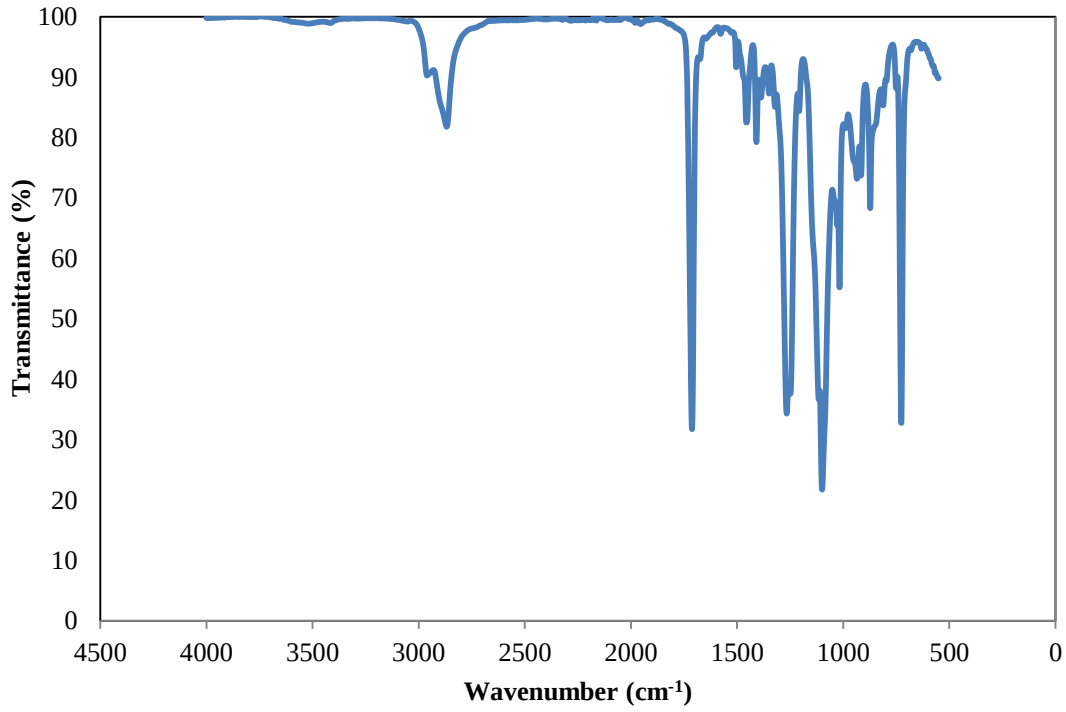

Figure B.6 PEE/1000/49 wt% PBT (8) + 0.1% TBHDP-MMT

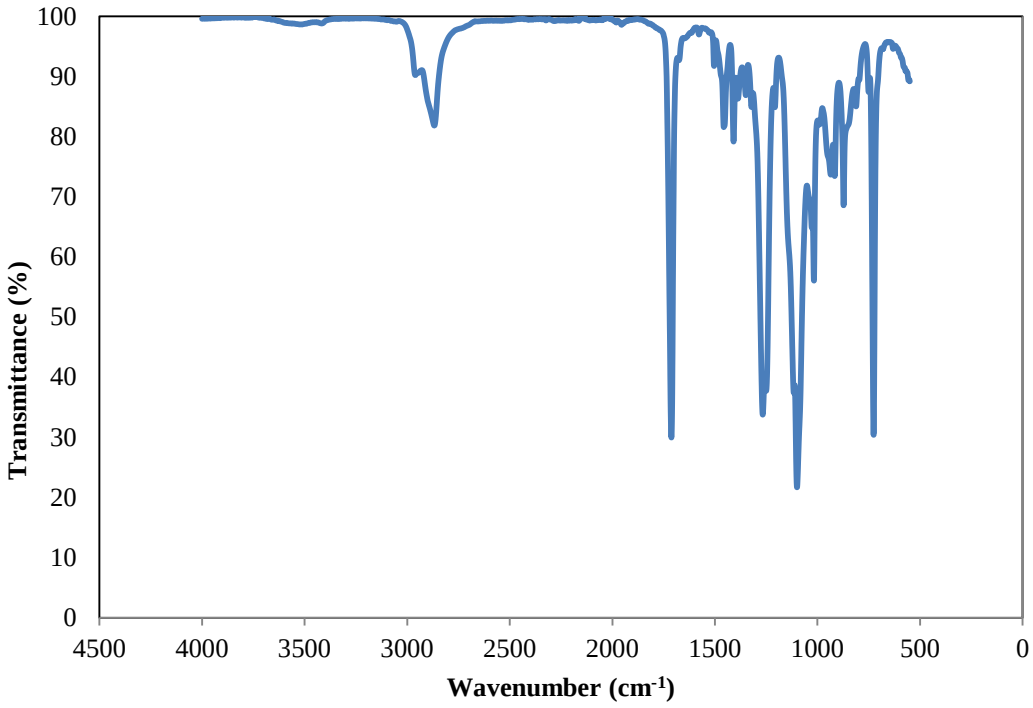

Figure B.7 PEE/1000/49 wt% PBT (8) + 0.3% TBHDP-MMT

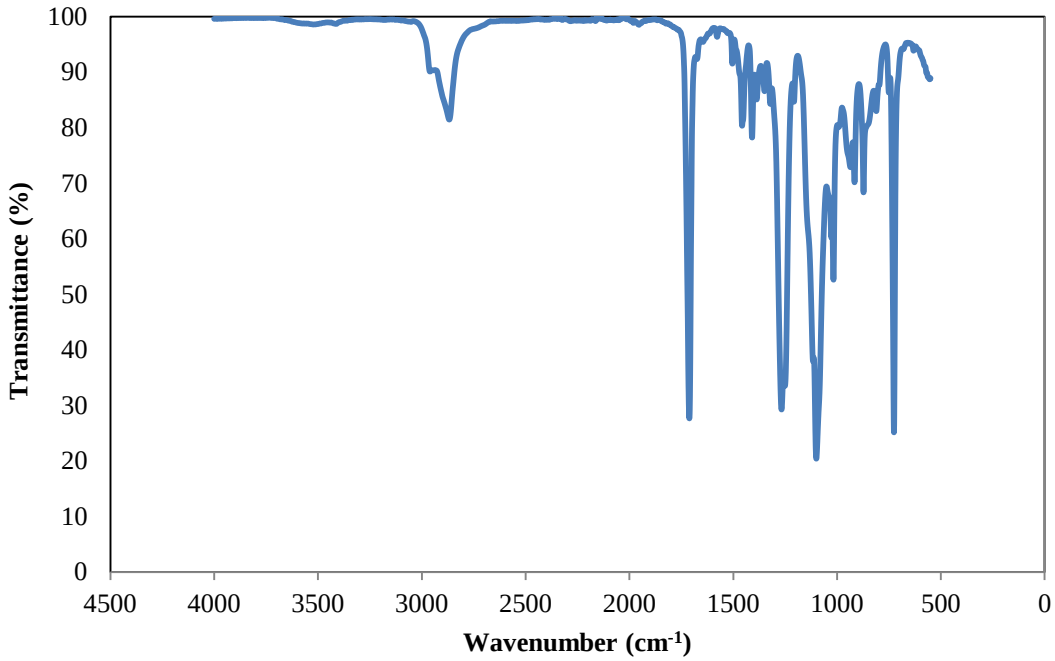

Figure B.8 PEE/1000/49 wt% PBT (8) + 0.5% TBHDP-MMT

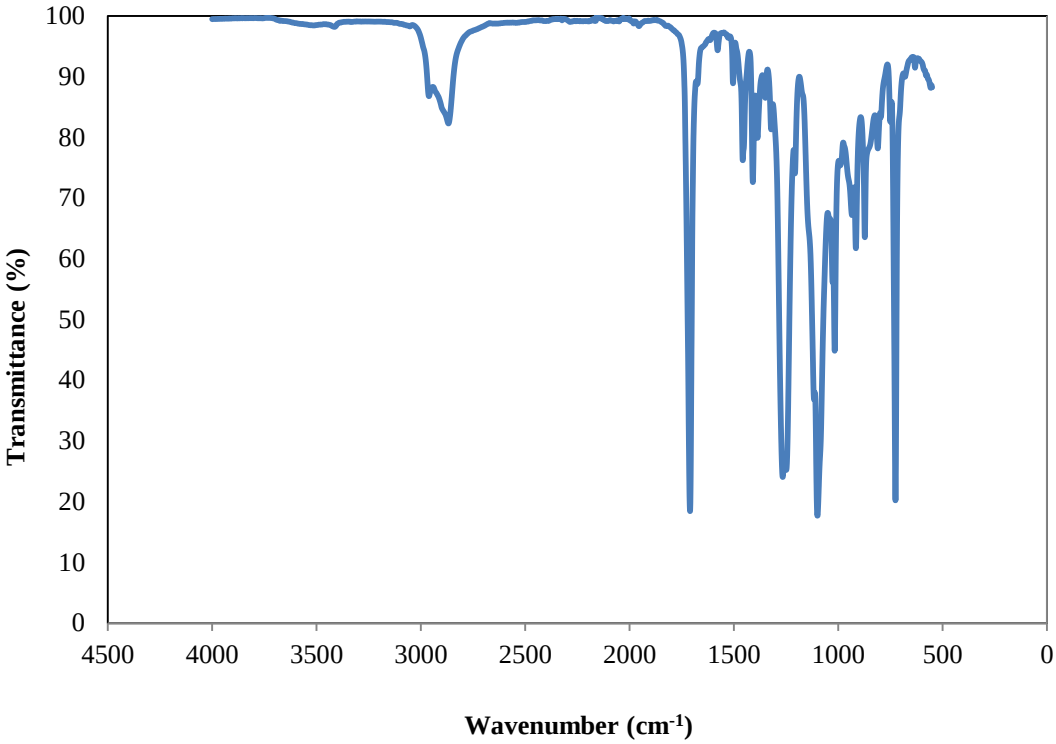

Figure B.9 PEE/1000/57 wt%PBT (3)

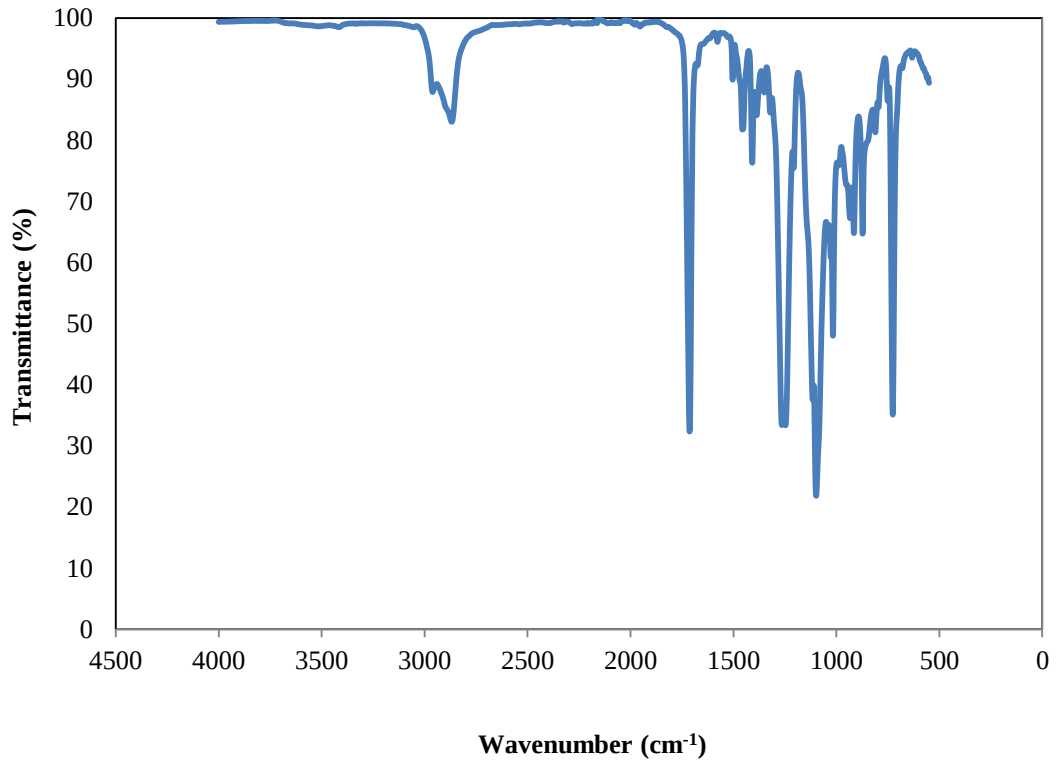

Figure B.10 PEE/1000/57 wt%PBT (3) + 0.1% TBHDP-MMT

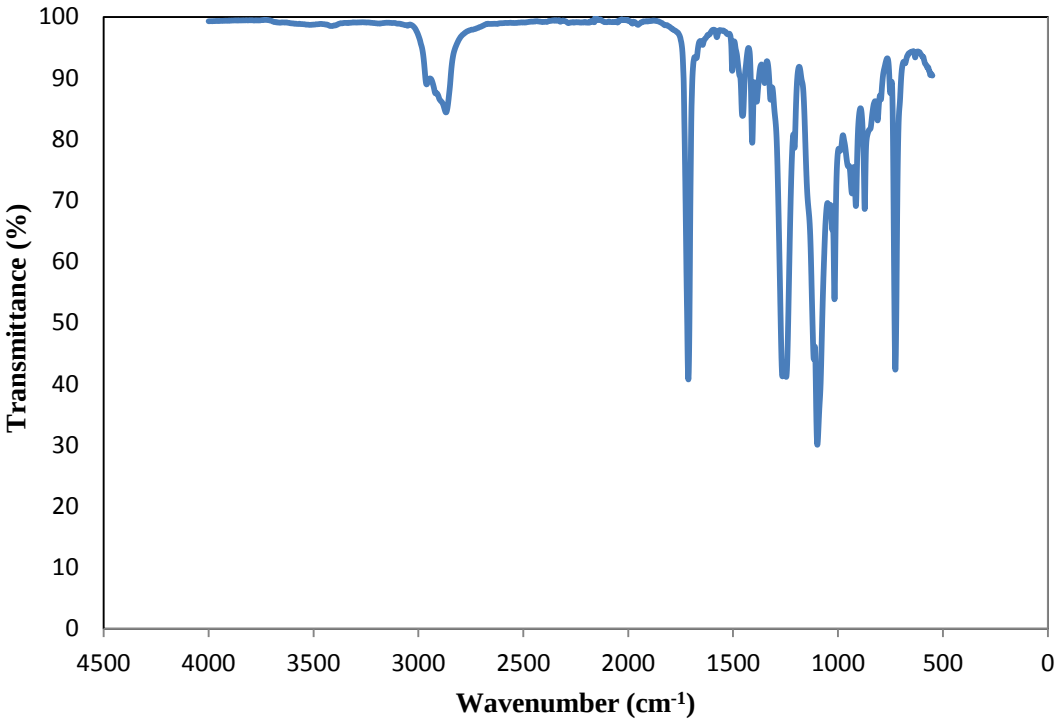

Figure B.11 PEE/1000/57 wt%PBT (3) + 0.3% TBHDP-MMT

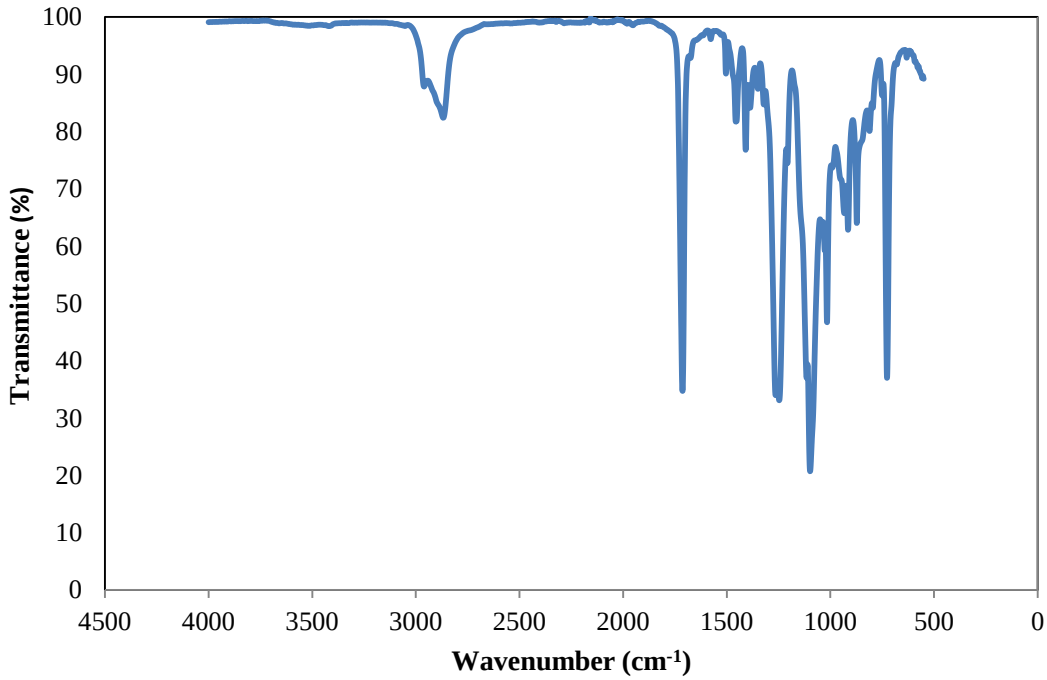

Figure B.12 PEE/1000/57 wt%PBT (3) + 0.5% TBHDP-MMT

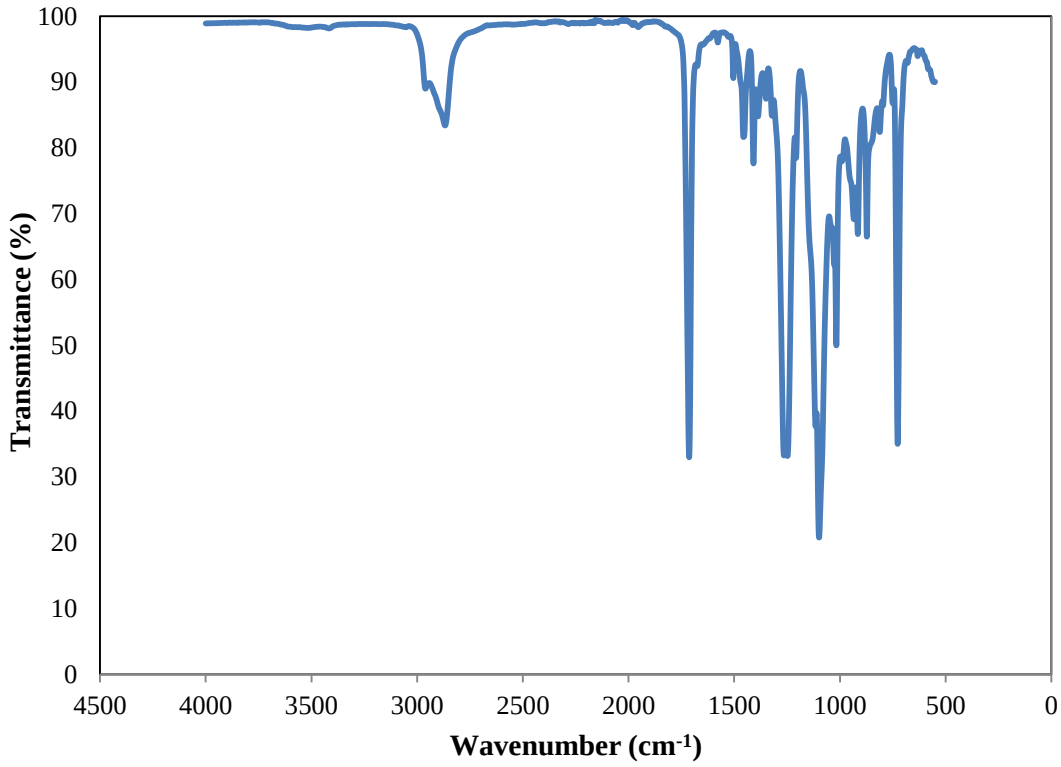

Figure B.13 PEE/1000/57 wt%PBT-0.1% TBHDP-MMT

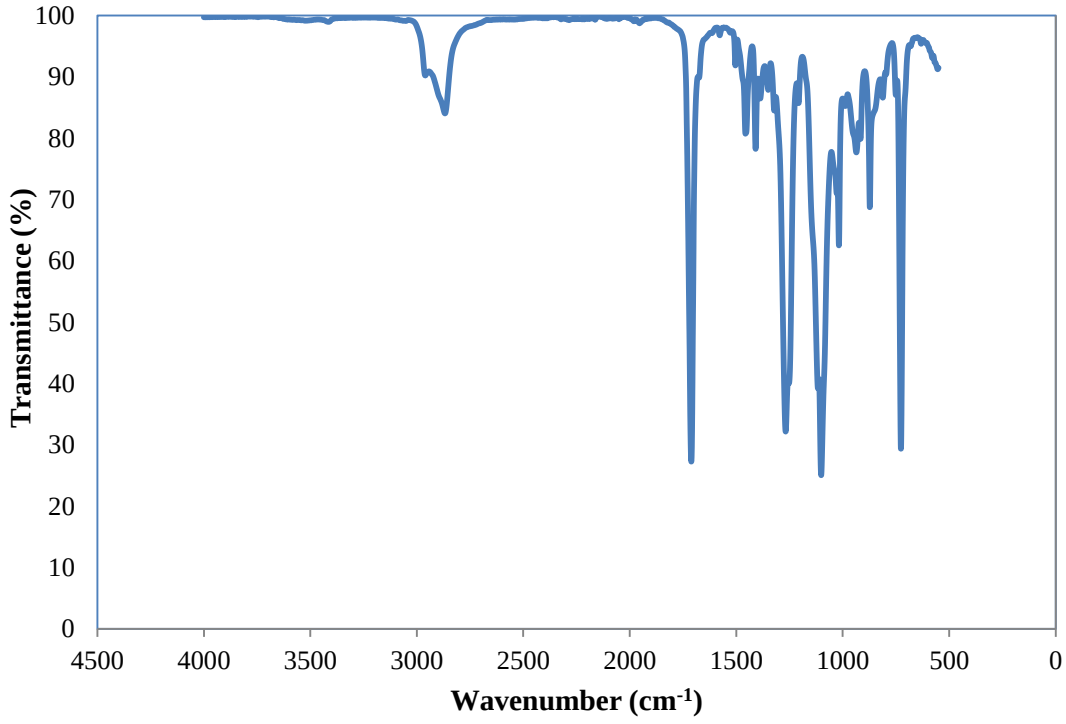

Figure B.14 PEE/1000/57 wt%PBT-0.3% TBHDP-MMT

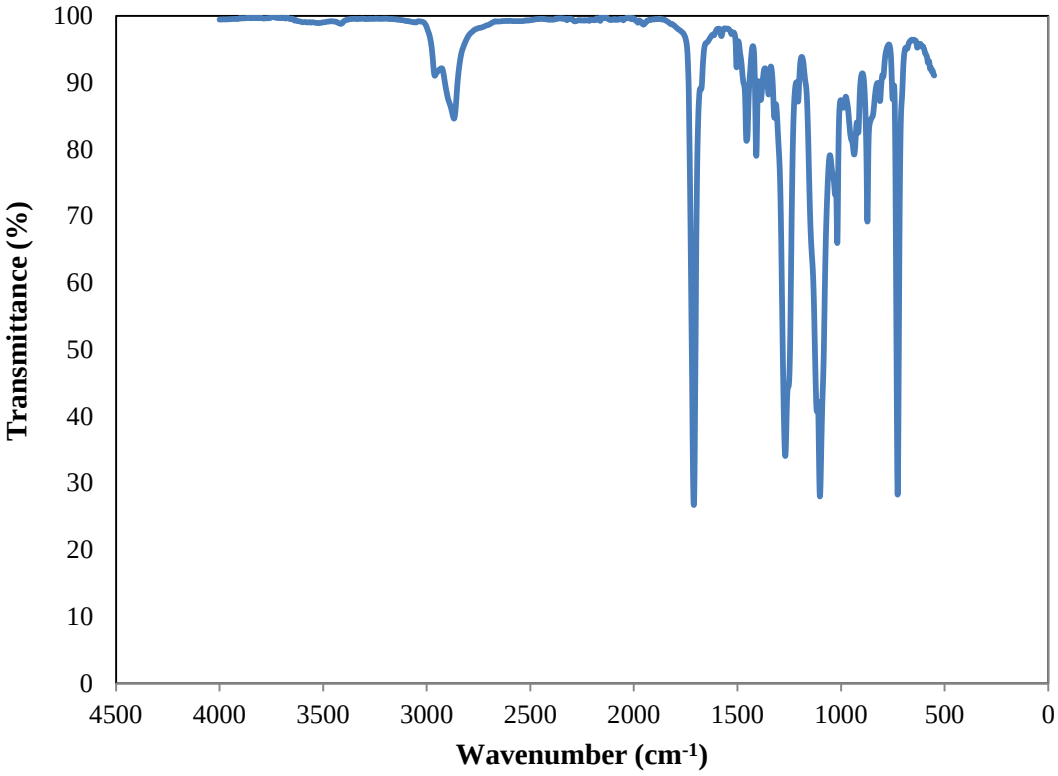

Figure B.15 PEE/1000/57 wt%PBT-0.5% TBHDP-MMT

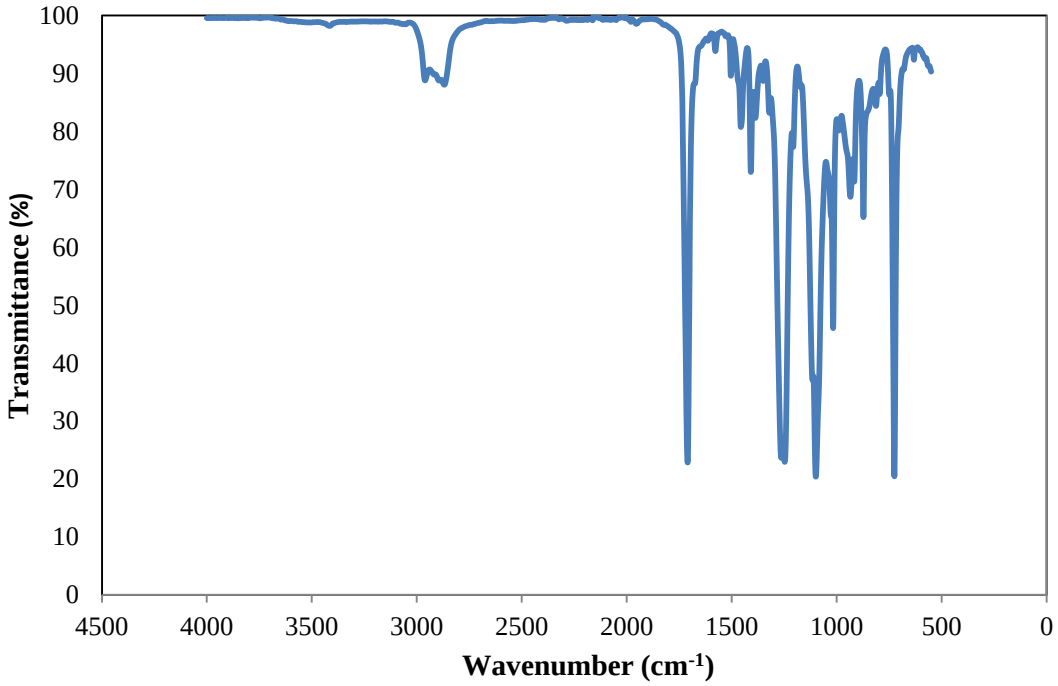

Figure B.16 PEE/1000/75 wt%PBT (5)

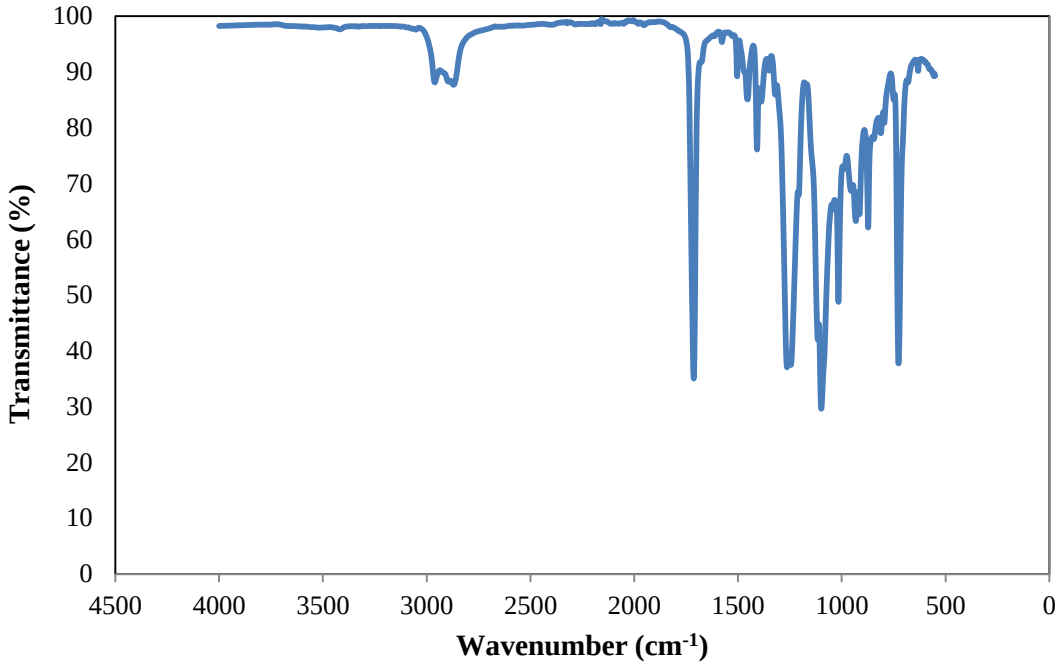

Figure B.17 PEE/1000/75 wt%PBT (5) + 0.1% TBHDP-MMT

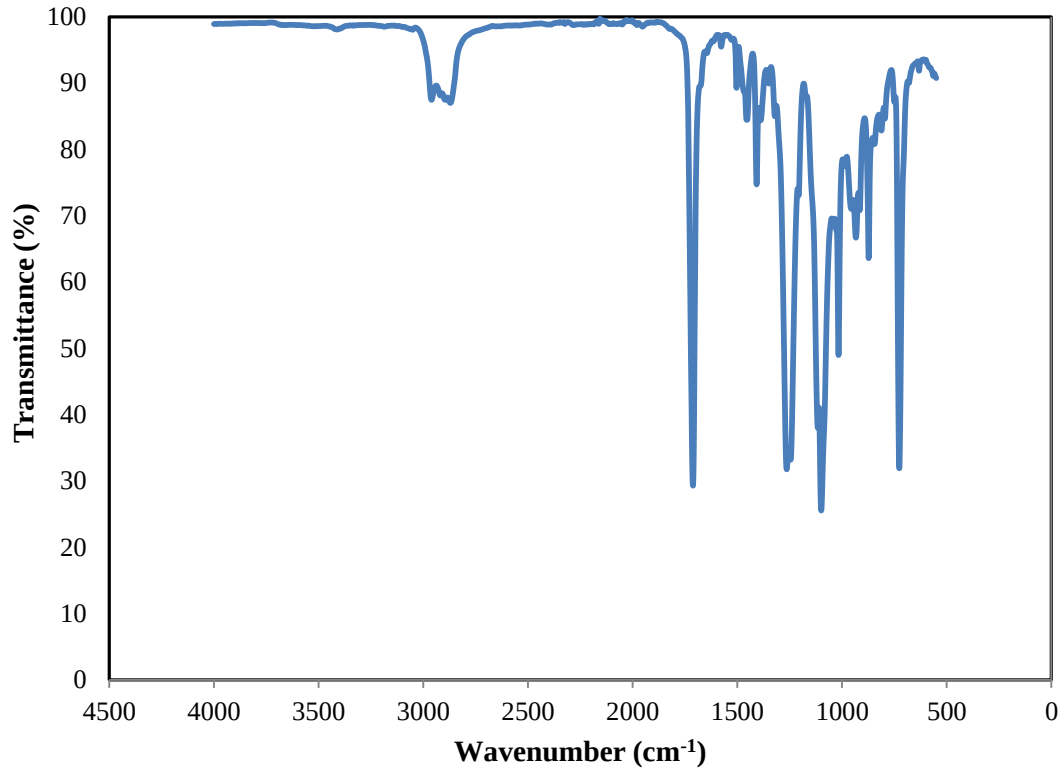

Figure B.18 PEE/1000/75 wt%PBT (5) + 0.3% TBHDP-MMT

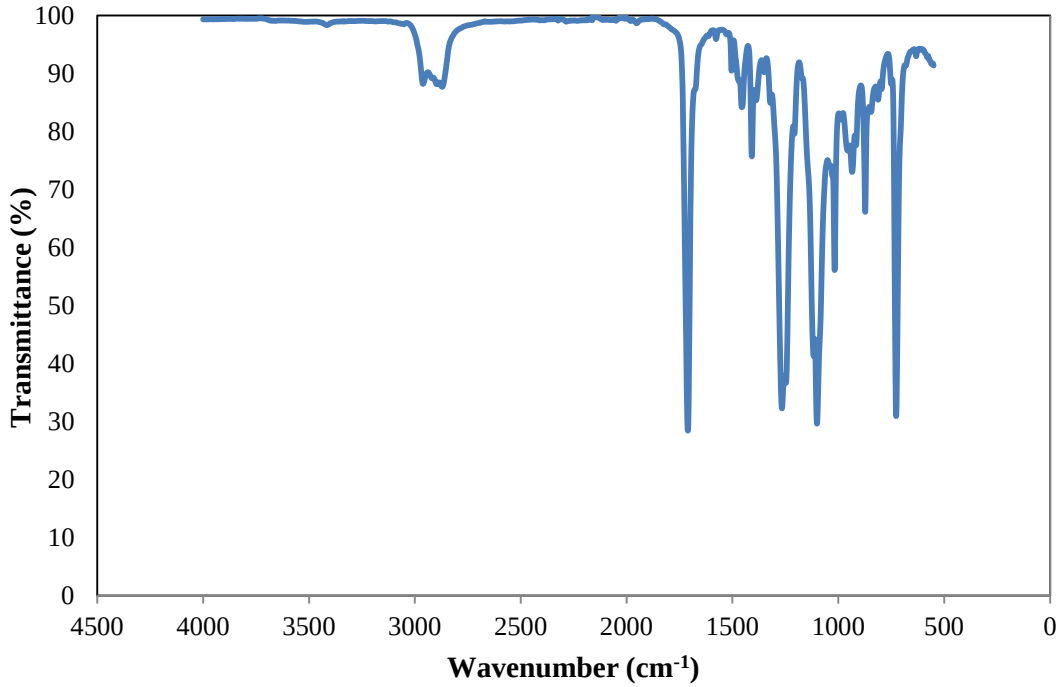

Figure B.19 PEE/1000/75 wt%PBT (5) + 0.5% TBHDP-MMT

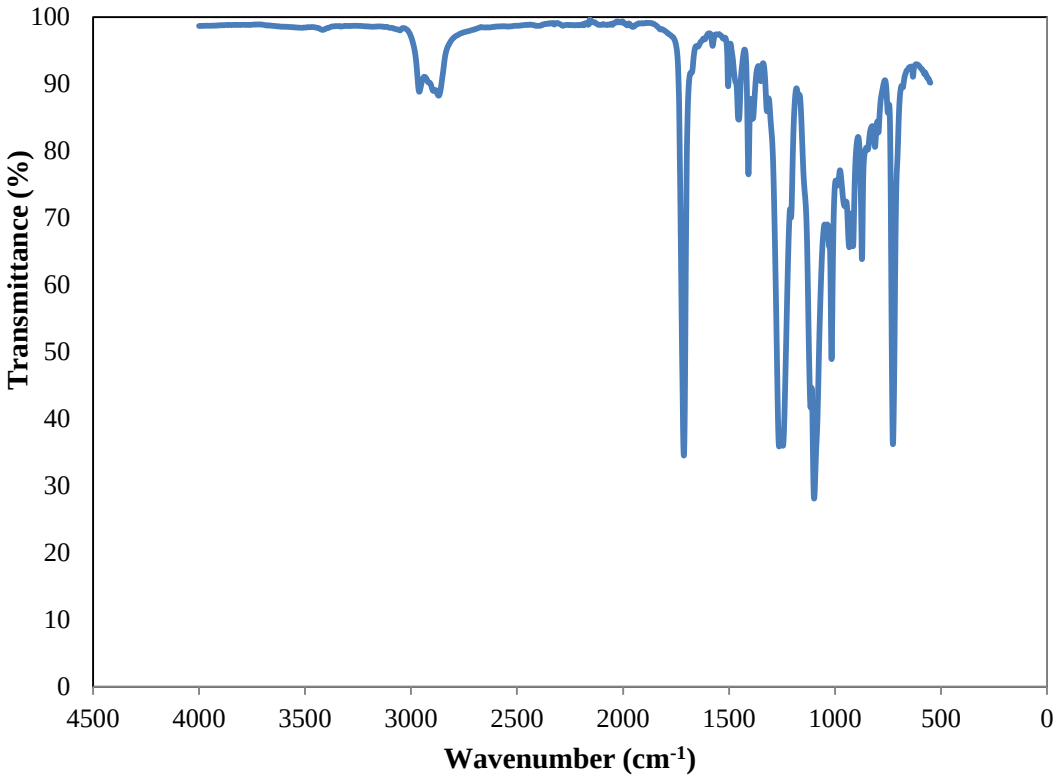

Figure B.20 PEE/1000/75 wt%PBT-0.1% TBHDP-MMT

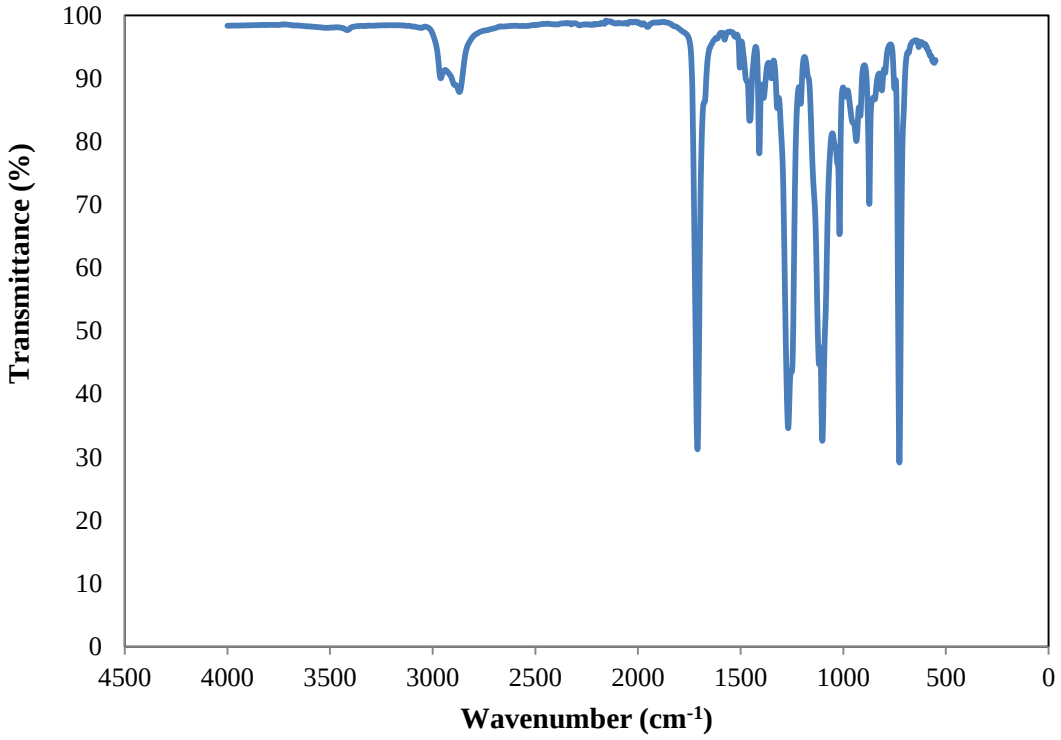

Figure B.21 PEE/1000/75 wt%PBT-0.3% TBHDP-MMT

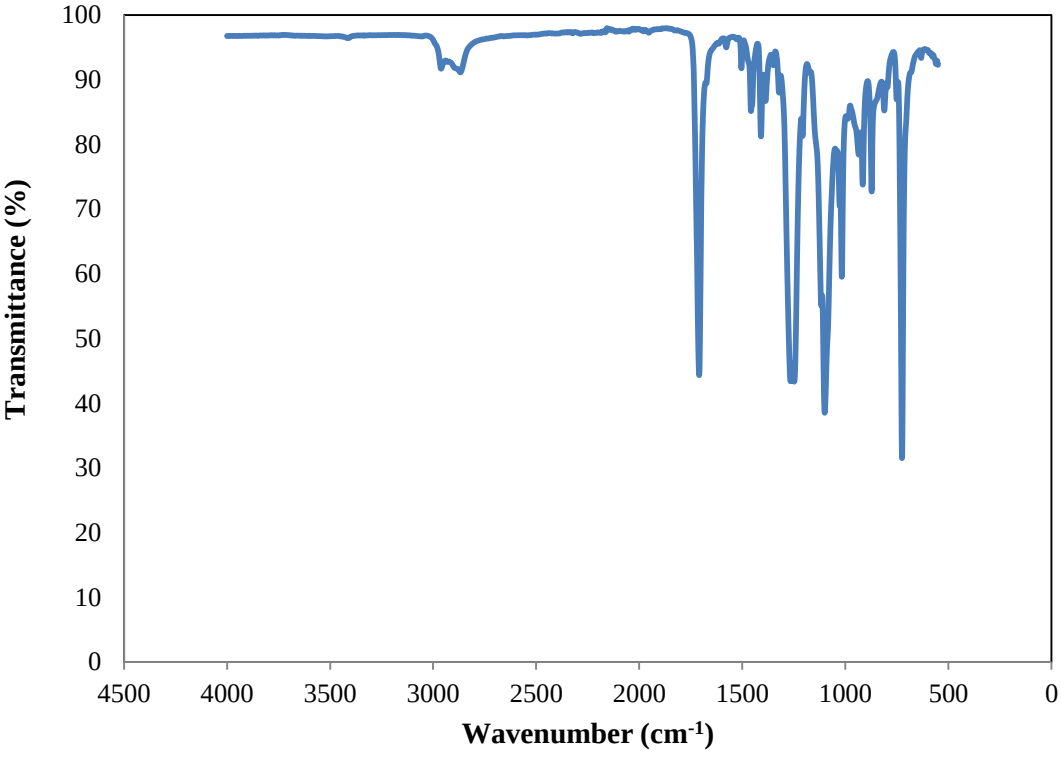

Figure B.22 PEE/1000/75 wt%PBT-0.5% TBHDP-MMT

APPENDIX C

GPC RESULTS

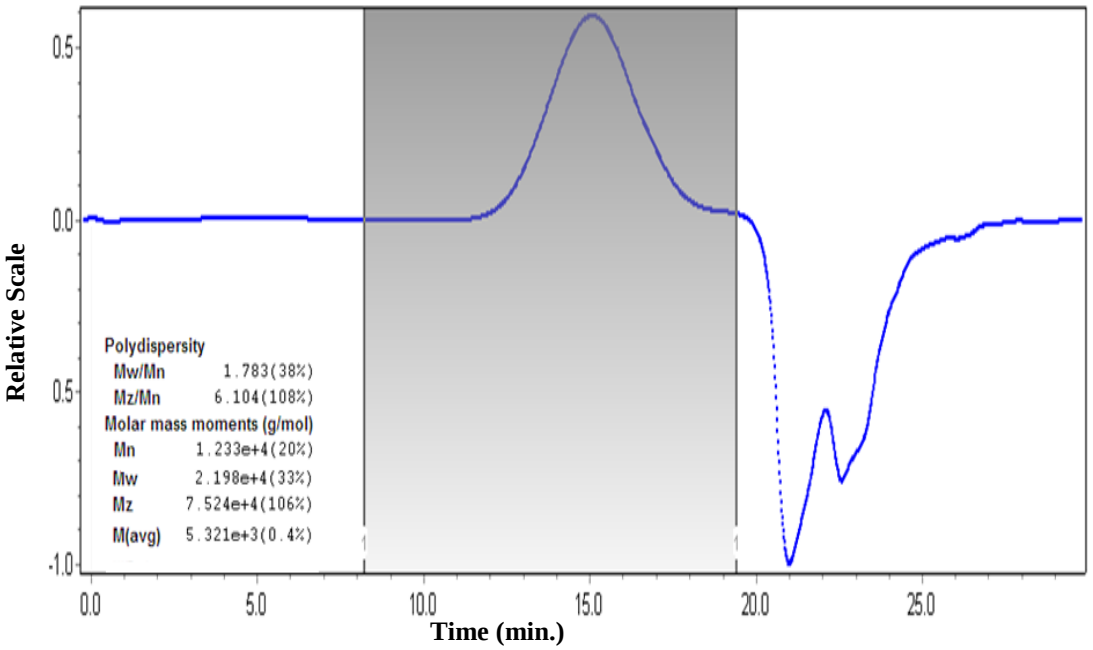

Figure C.1 GPC Analysis of PEE/1000/37 wt % PBT (1)

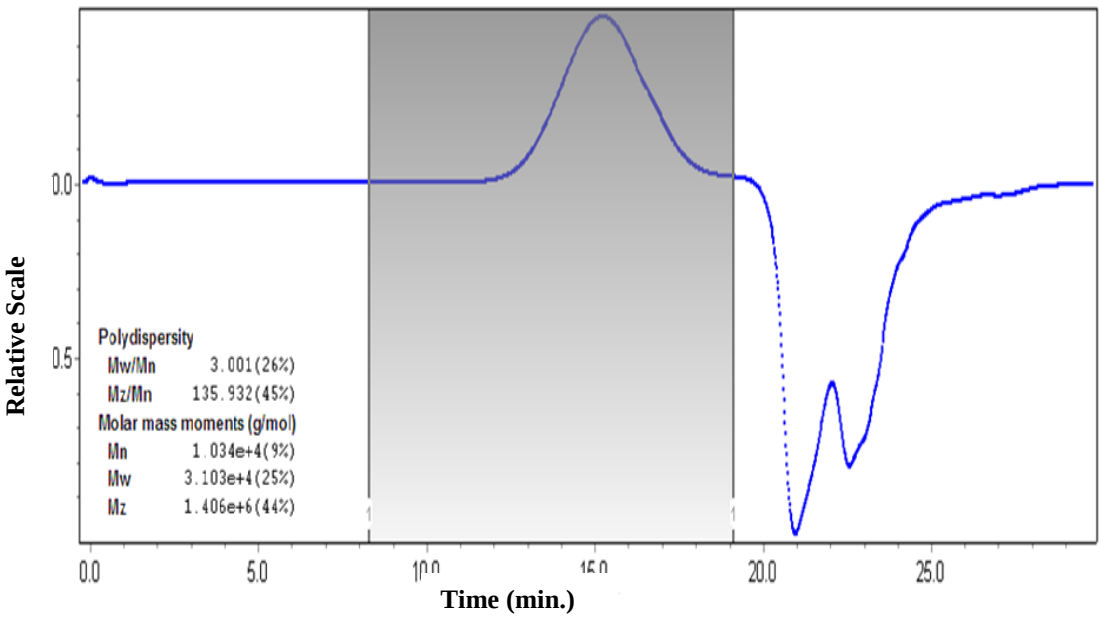

Figure C.2 GPC Analysis of PEE/1000/ 37 wt % PBT (2)

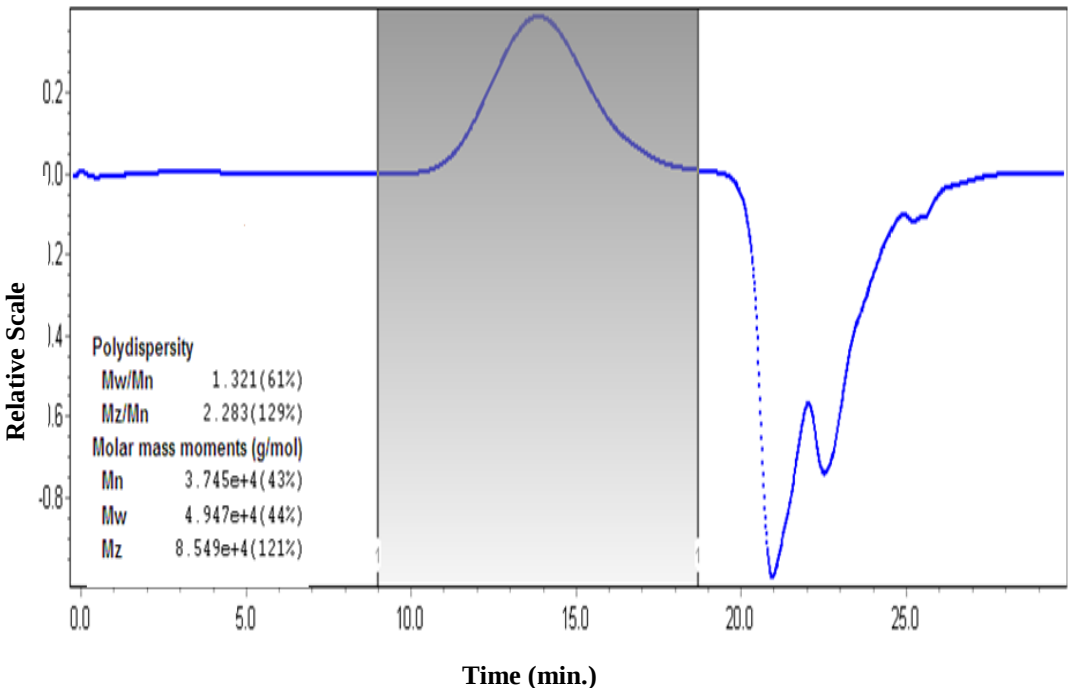

Figure C.3 GPC Analysis of PEE/1000/ 37 wt % PBT (3)

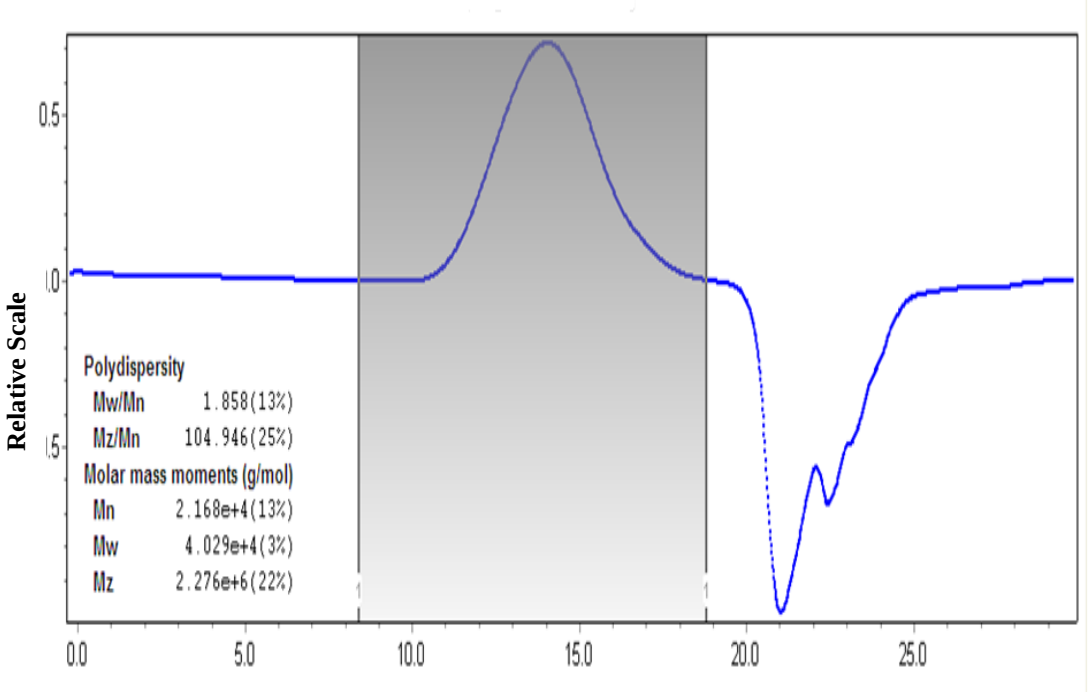

Figure C.4 GPC Analysis of PEE/1000/ 37 wt % PBT (4)

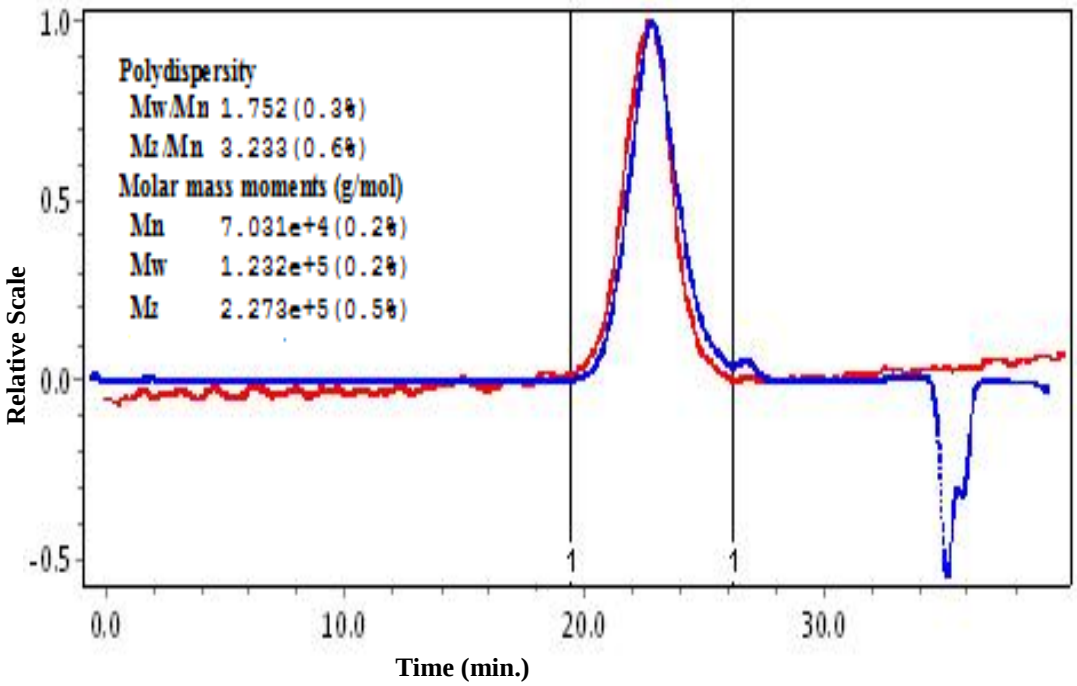

Figure C.5 GPC Analysis of PEE/1000/ 37 wt % PBT (5)

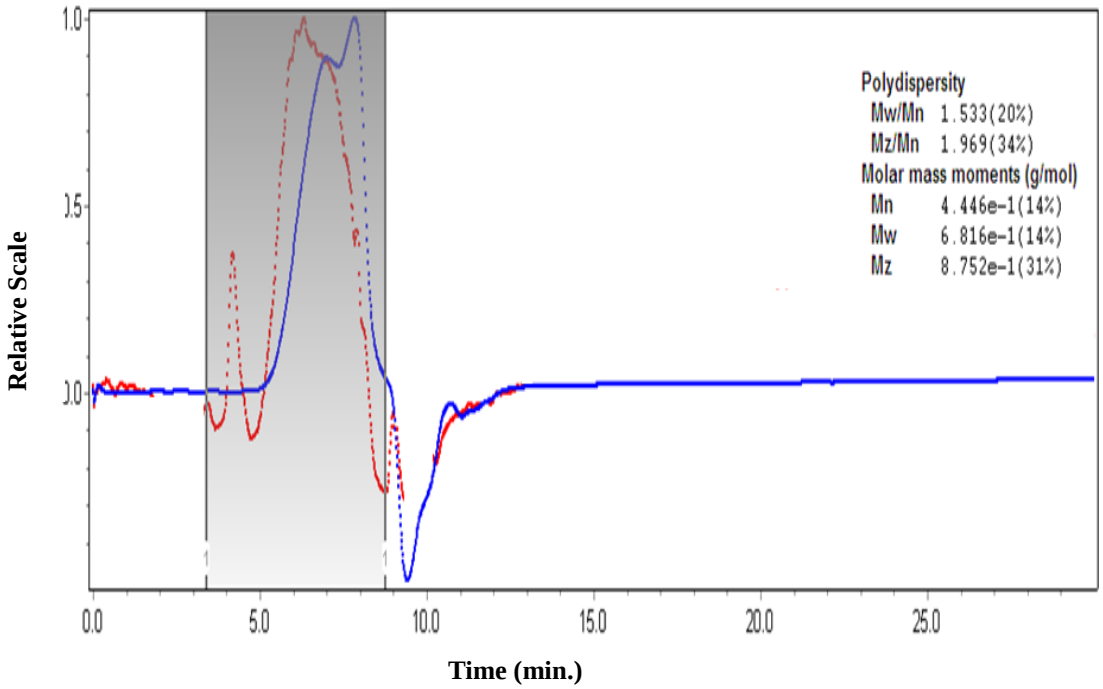

Figure C.6 GPC Analysis of PEE/1000/ 49 wt % PBT (1)

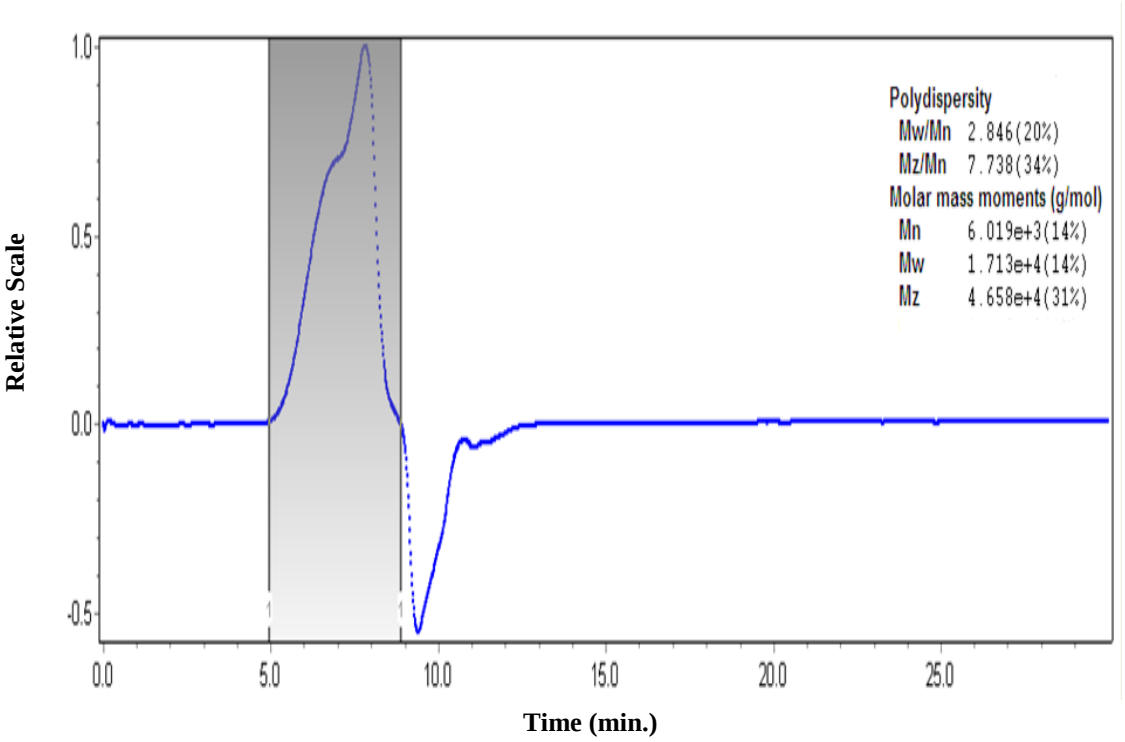

Figure C.7 GPC Analysis of PEE/1000/ 49 wt % PBT (2)

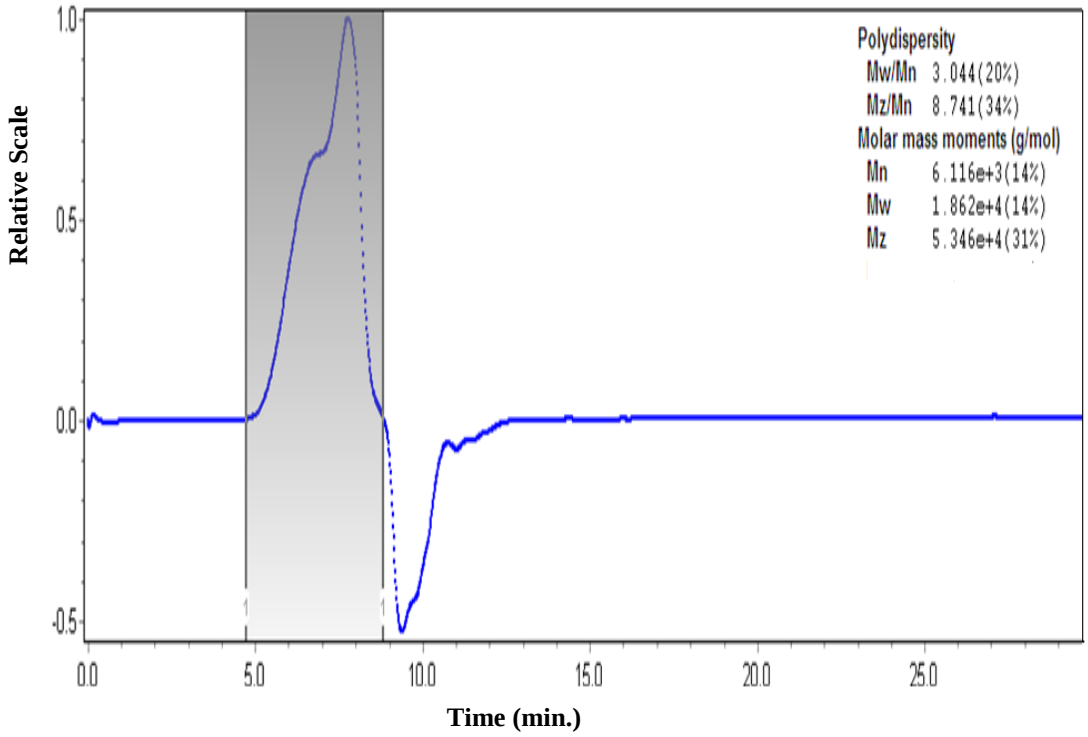

Figure C.8 GPC Analysis of PEE/1000/ 49 wt % PBT (3)

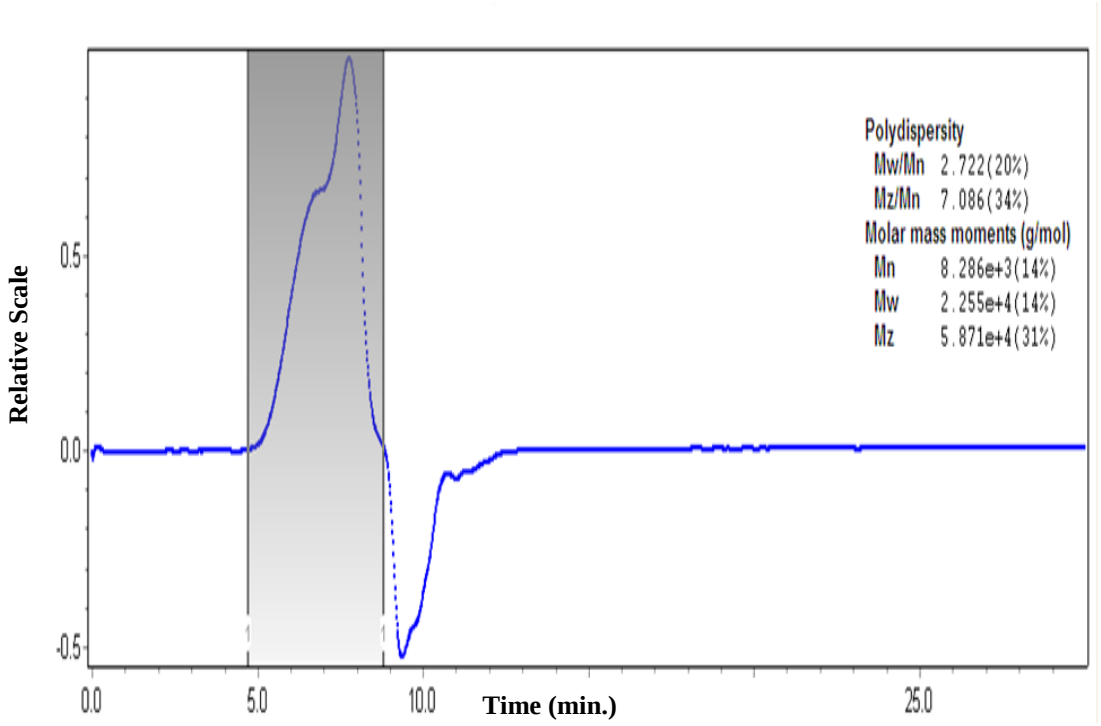

Figure C.9 GPC Analysis of PEE/1000/ 49 wt % PBT (4)

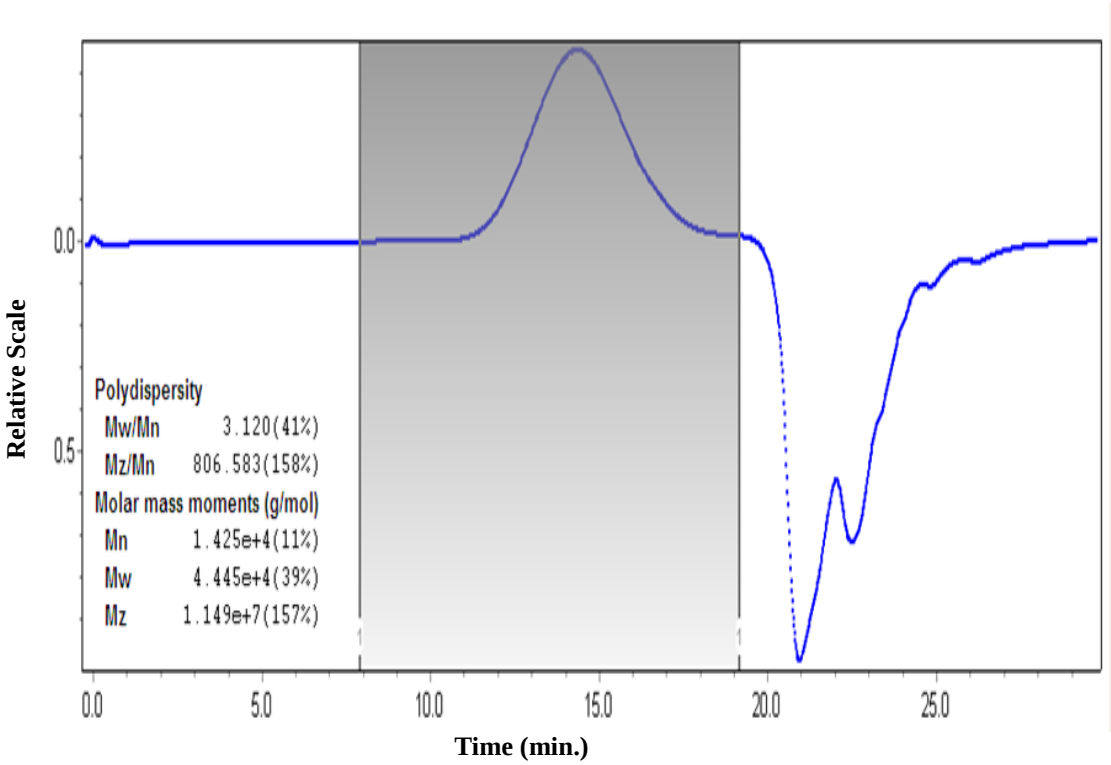

Figure C.10 GPC Analysis of PEE/1000/ 49 wt % PBT (5)

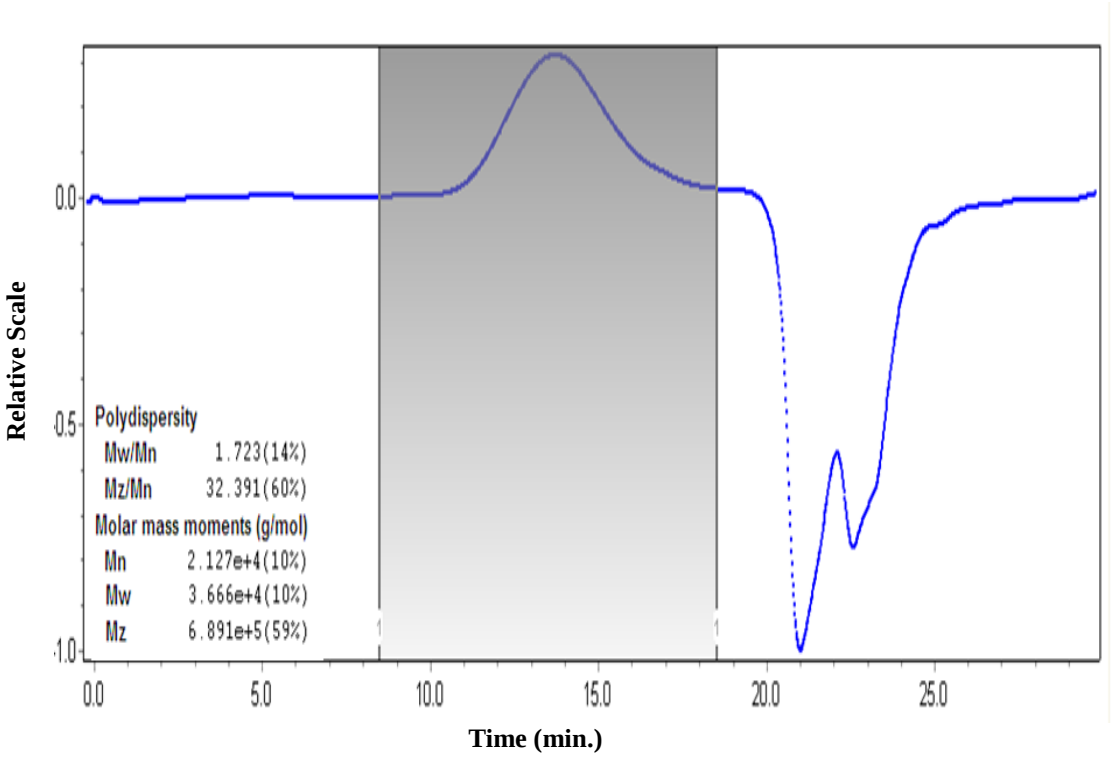

Figure C.11 GPC Analysis of PEE/1000/ 49 wt % PBT (6)

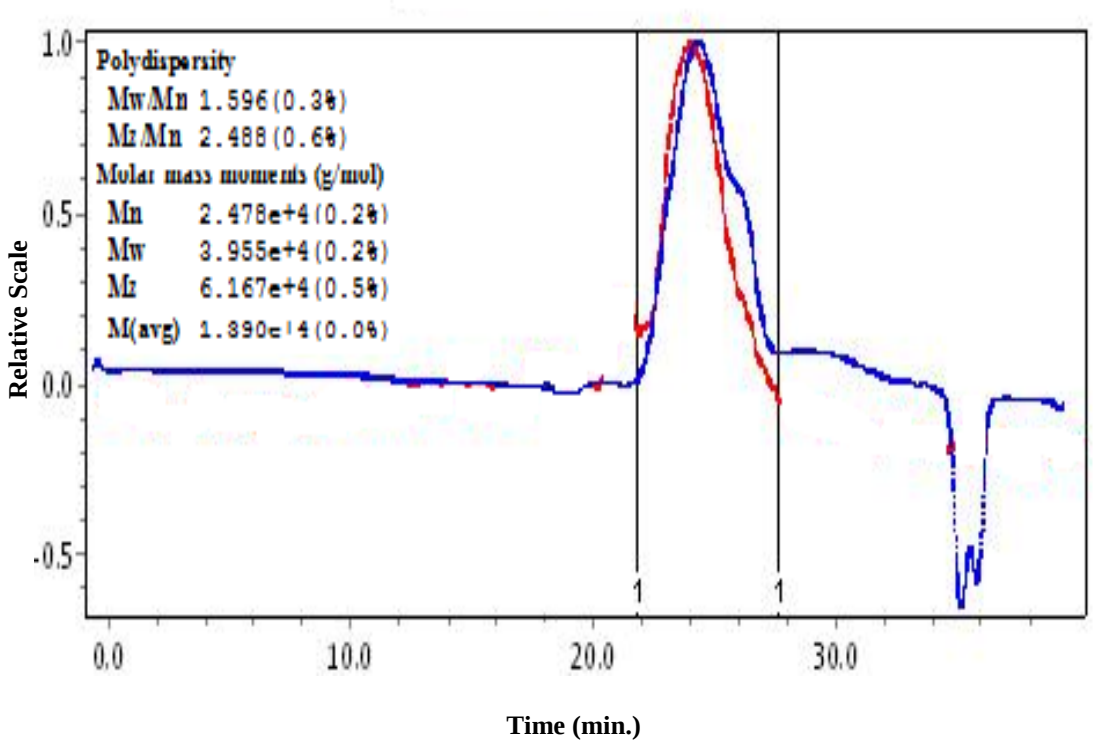

Figure C.12 GPC Analysis of PEE/1000/ 49 wt % PBT (8)

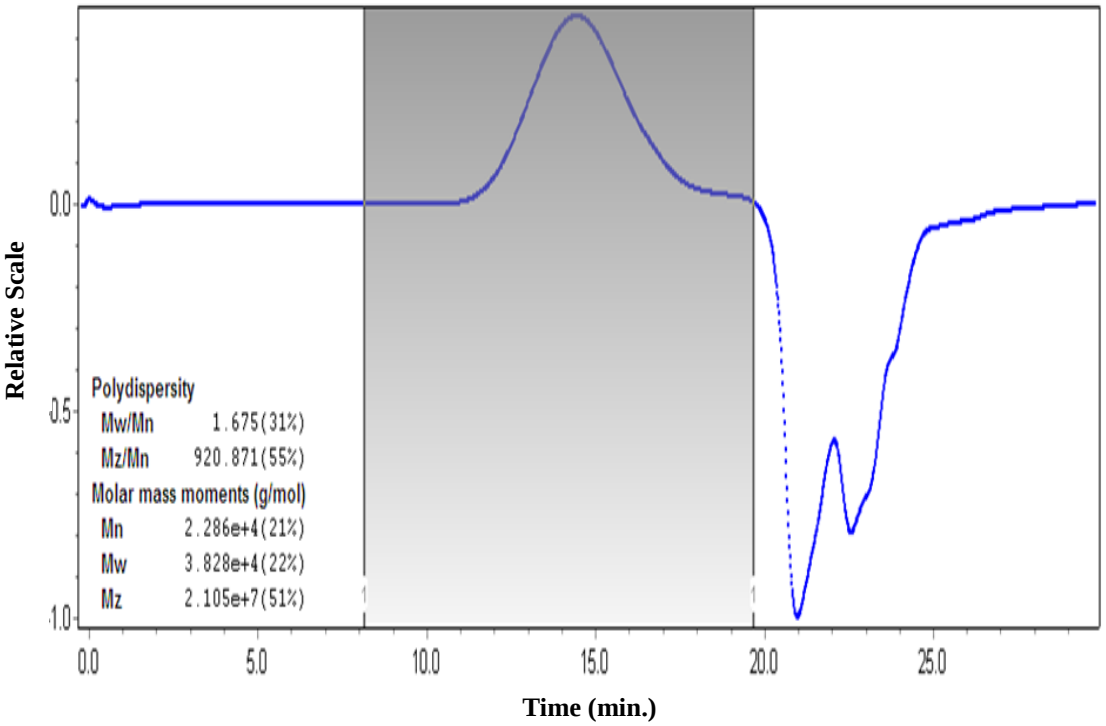

Figure C.13 GPC Analysis of PEE/1000/ 57 wt % PBT (1)

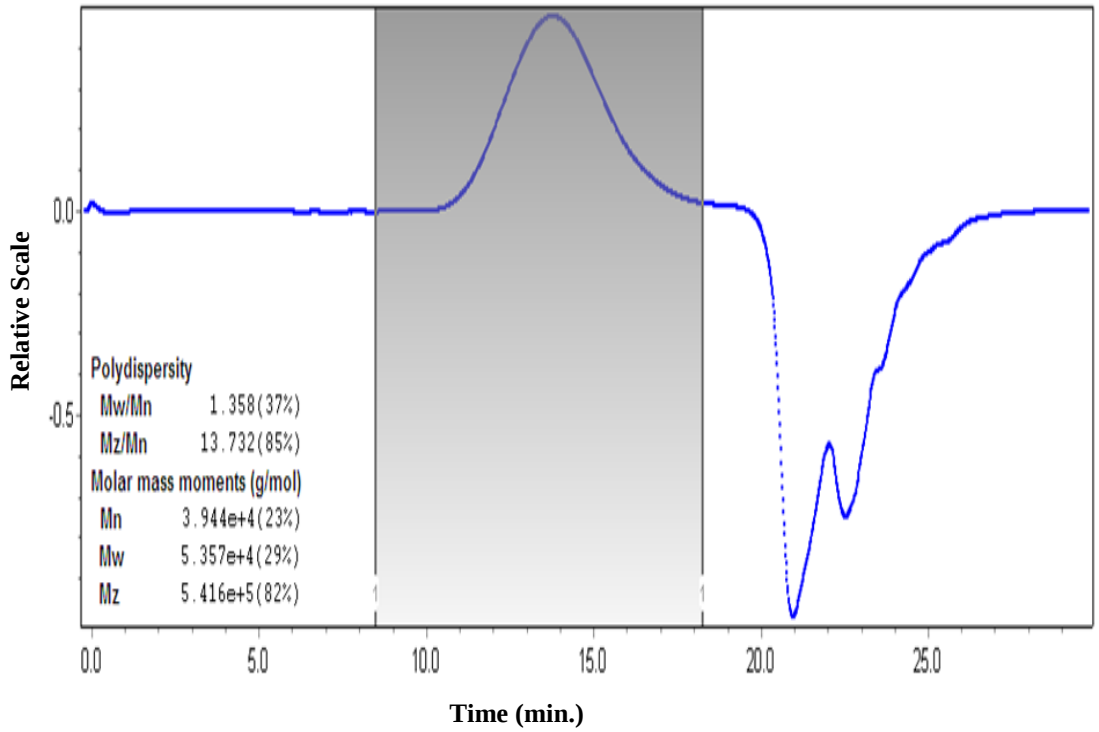

Figure C.14 GPC Analysis of PEE/1000/ 57 wt % PBT (2)

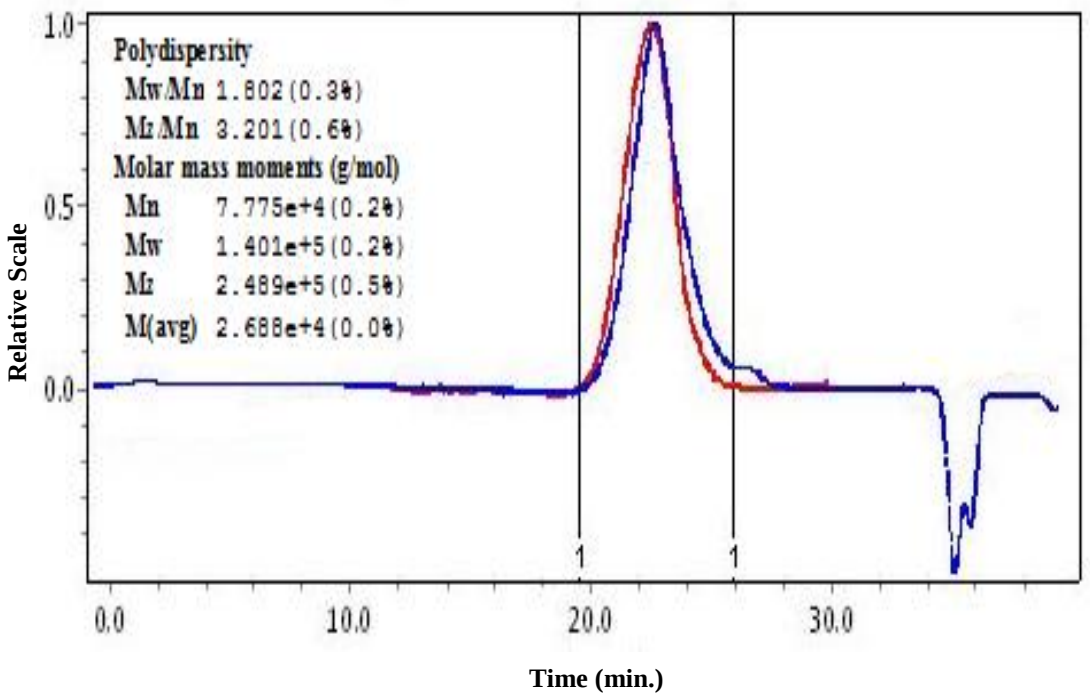

Figure C.15 GPC Analysis of PEE/1000/ 57 wt % PBT (3)

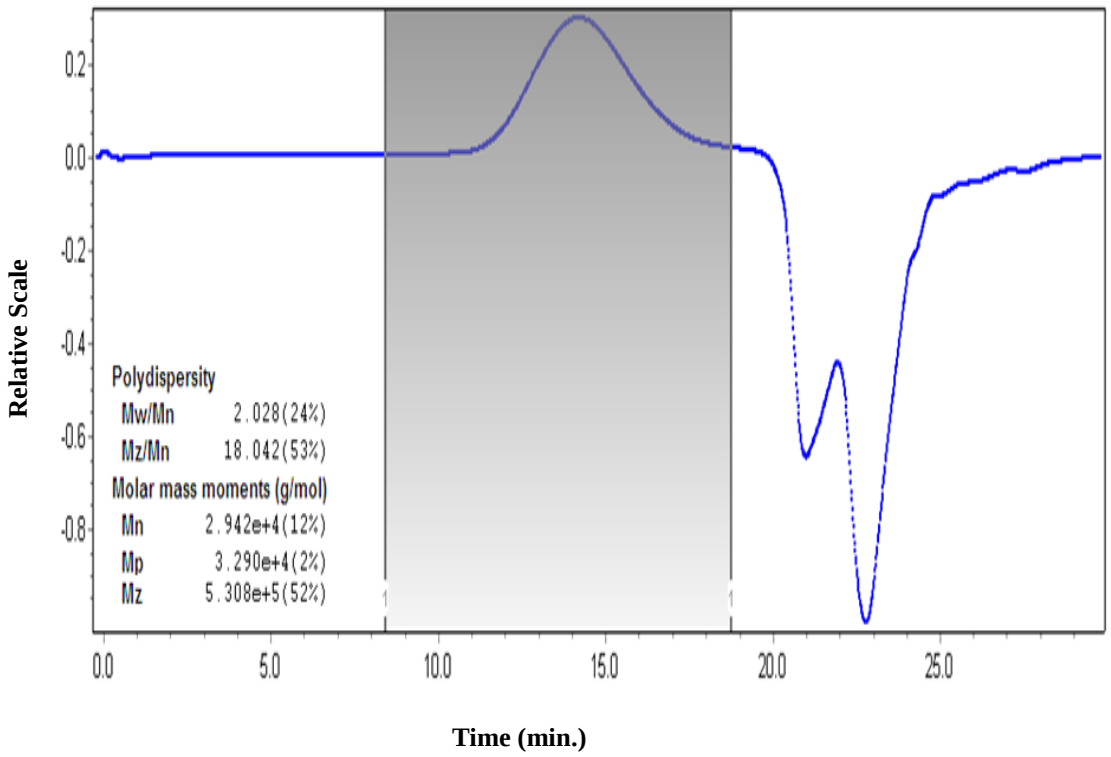

Figure C.16 GPC Analysis of PEE/1000/ 75 wt % PBT (1)

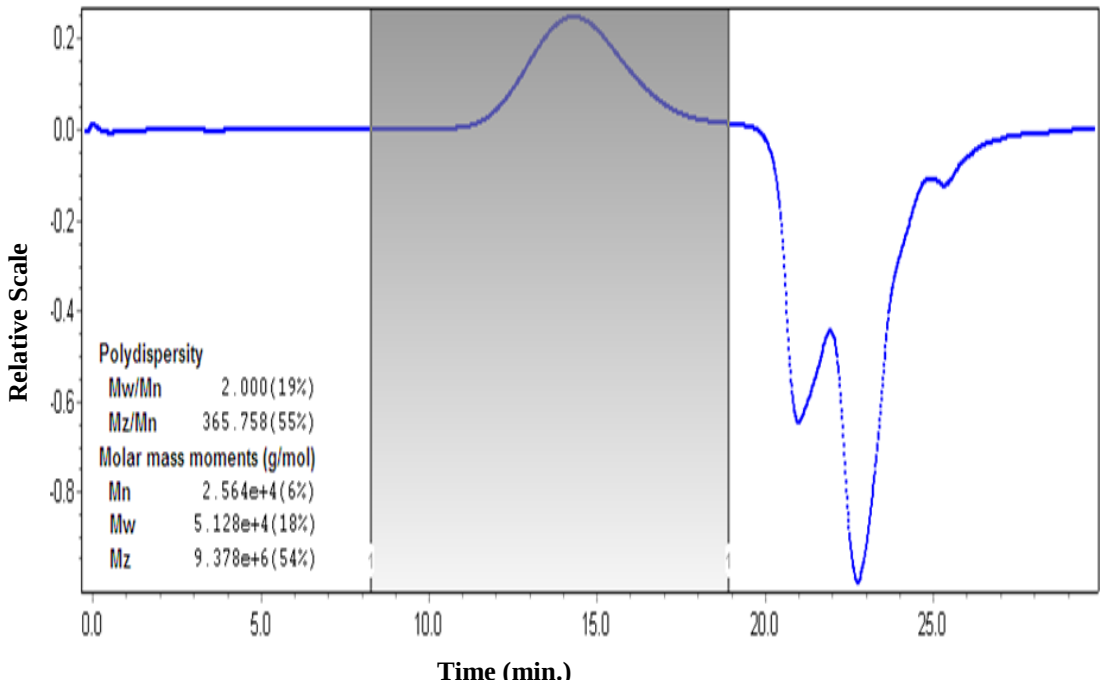

Figure C.17 GPC Analysis of PEE/1000/ 75 wt % PBT (2)

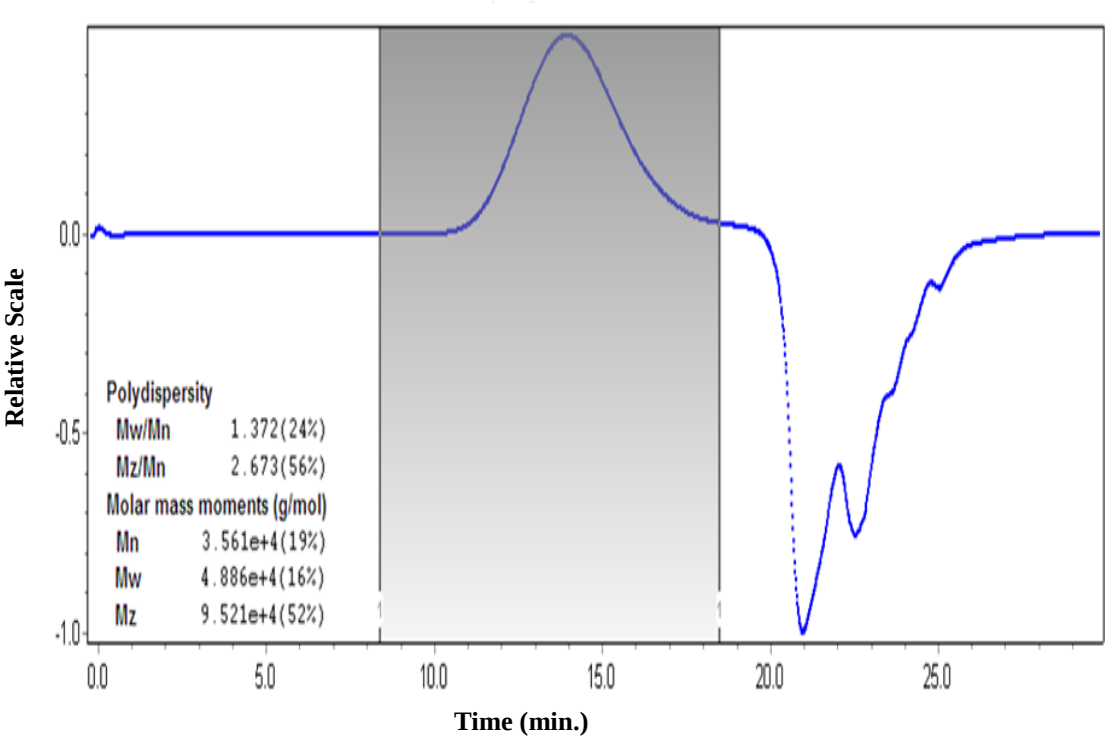

Figure C.18 GPC Analysis of PEE/1000/ 75 wt % PBT (3)

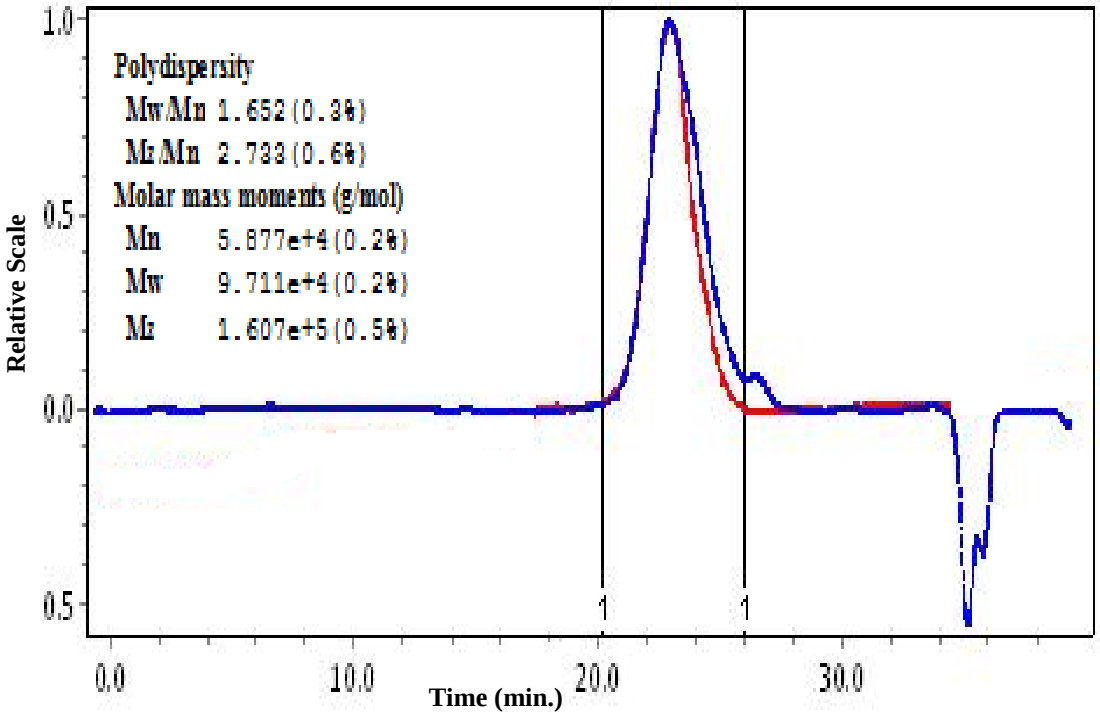

Figure C.19 GPC Analysis of PEE/1000/ 75 wt % PBT (4)

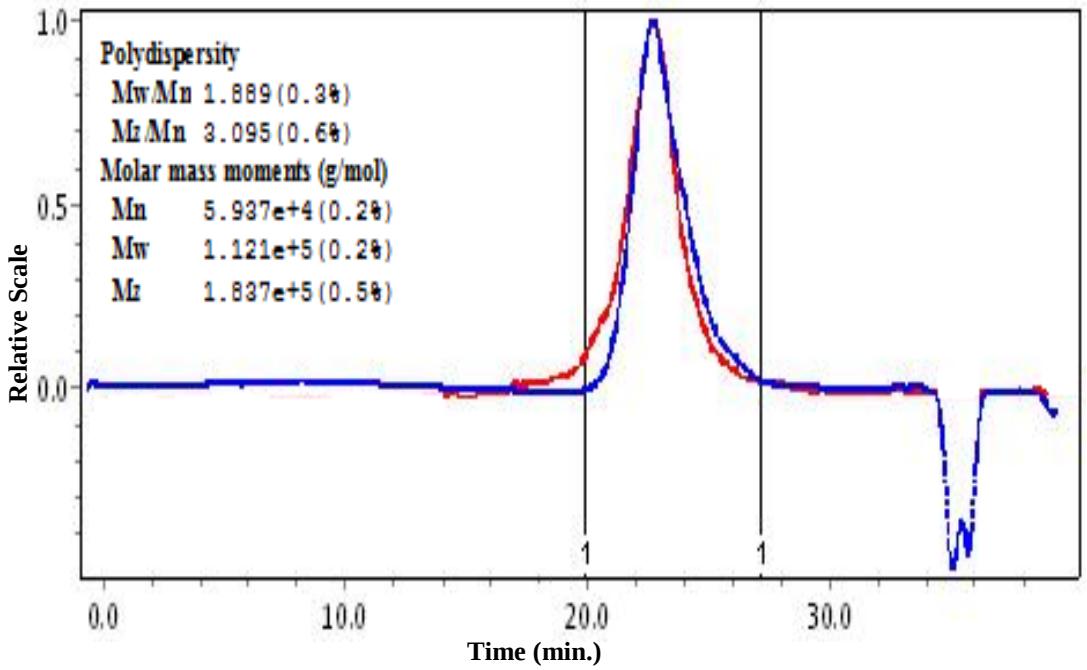

Figure C.20 GPC Analysis of PEE/1000/ 75 wt % PBT (5)

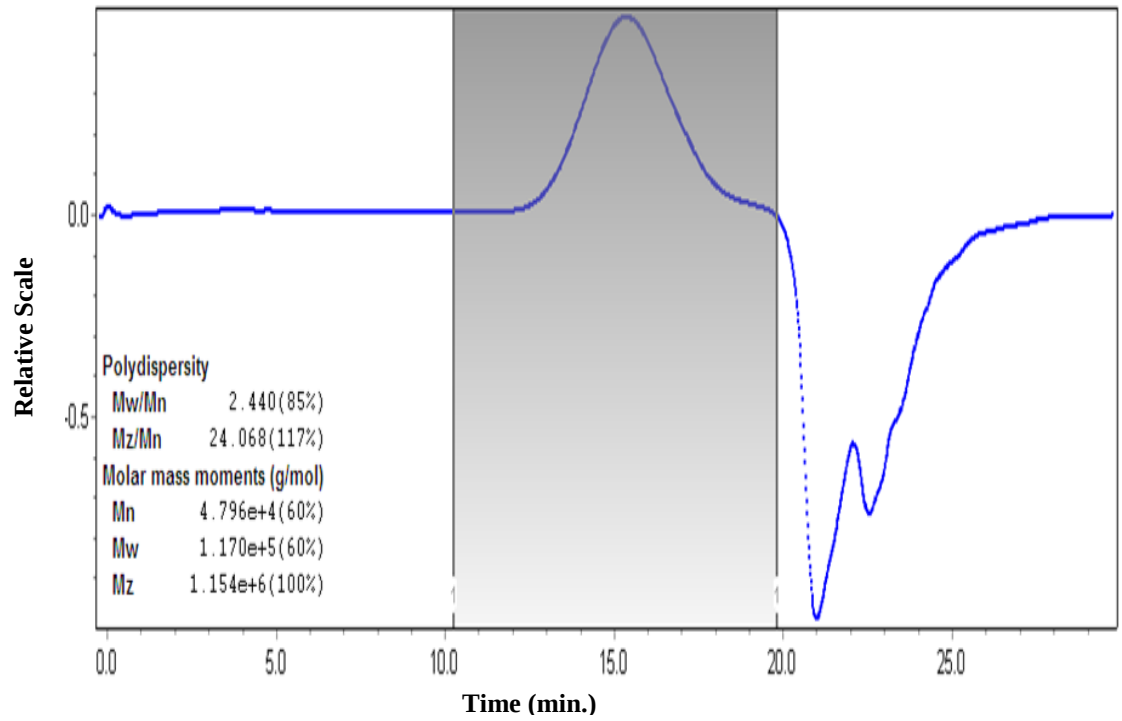

Figure C.21 GPC Analysis of PEE/600/ 57 wt % PBT (1)

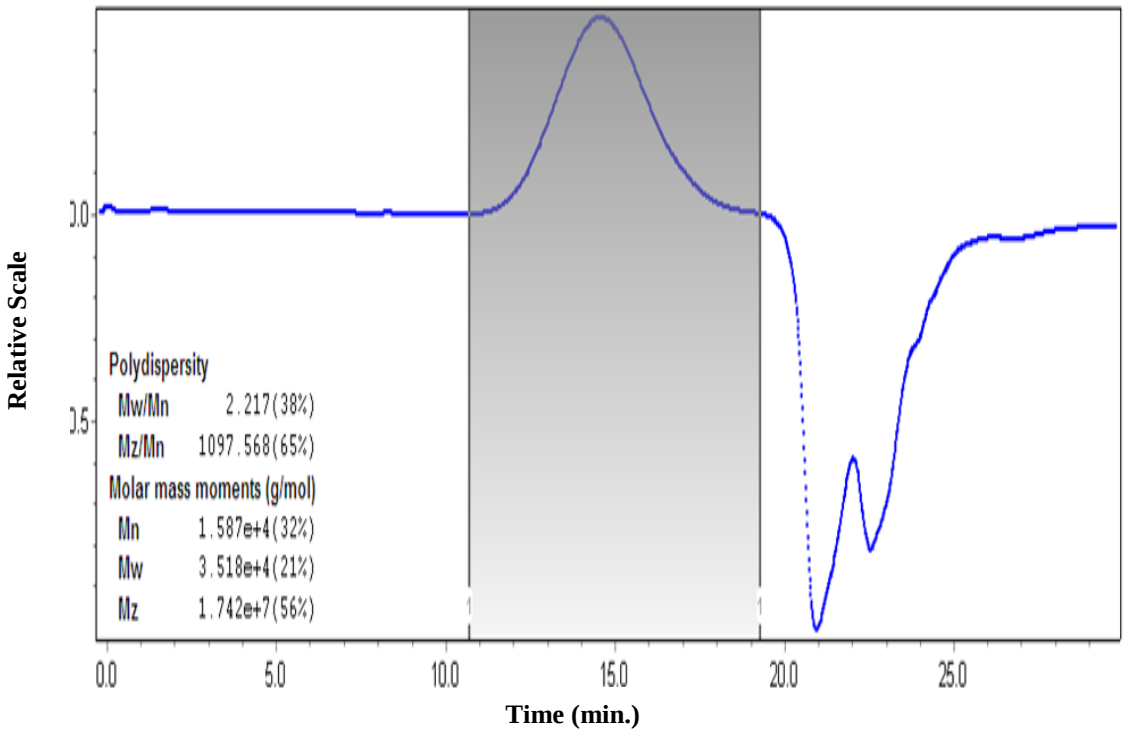

Figure C.22 GPC Analysis of PEE/600/ 57 wt % PBT (2)

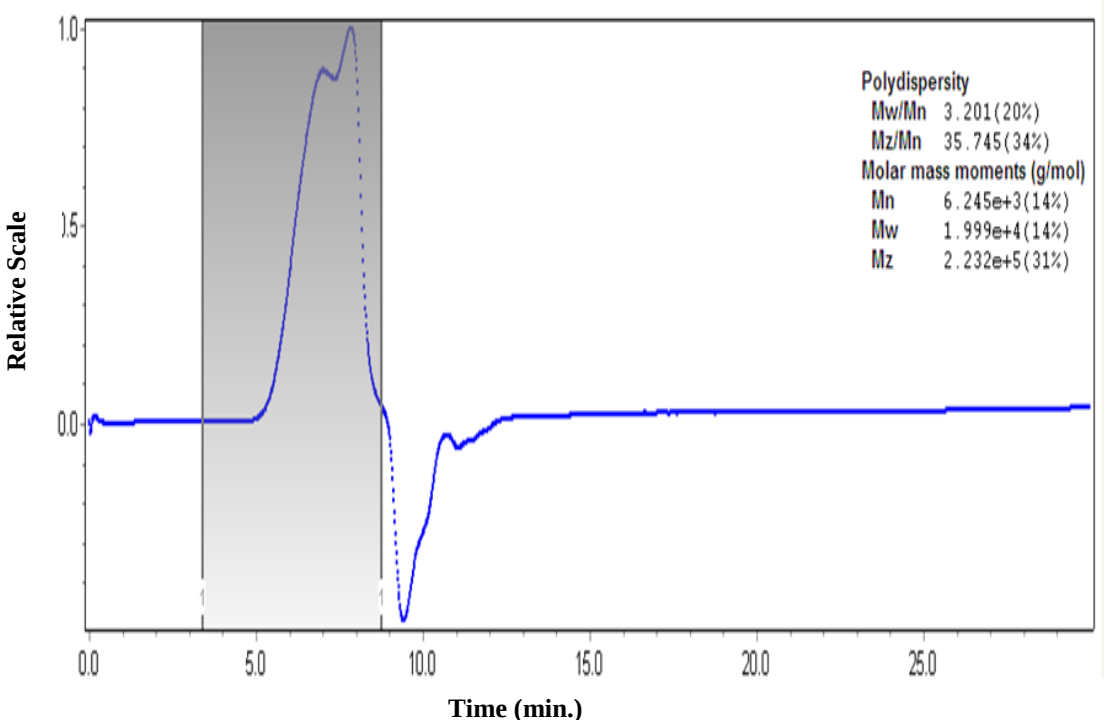

Figure C.23 GPC Analysis of PEE/600/ 67 wt % PBT (1)

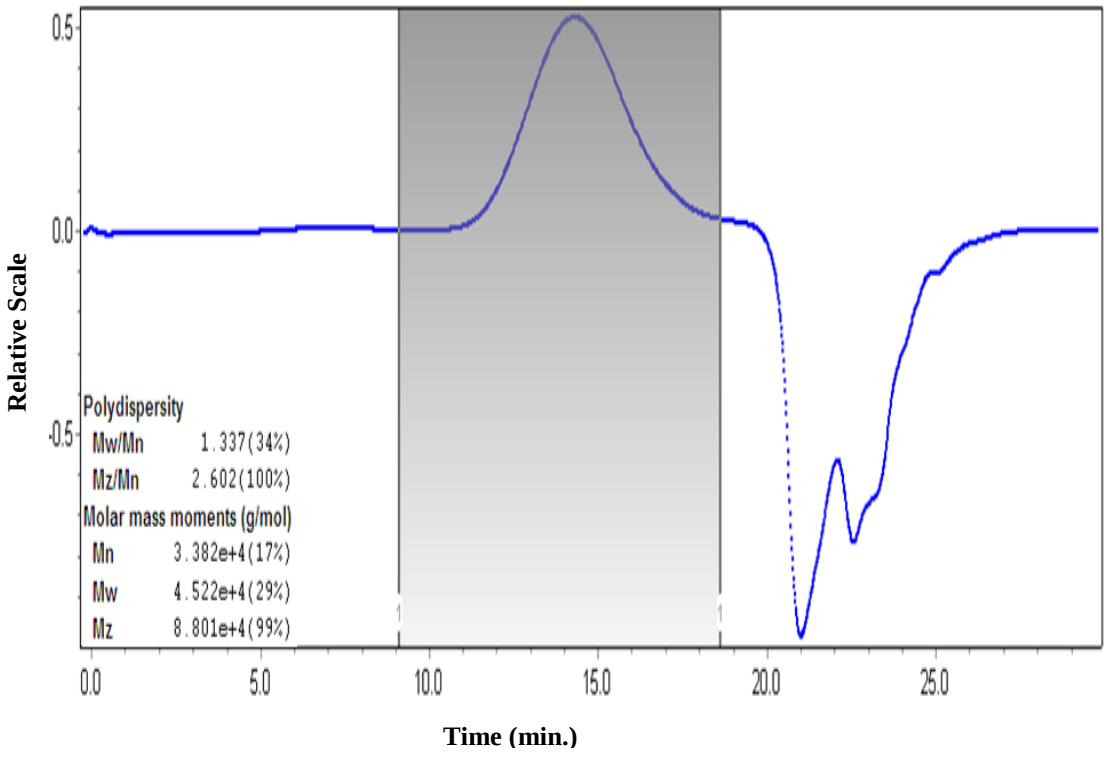

Figure C.24 GPC Analysis of PEE/600/ 67 wt % PBT (2)

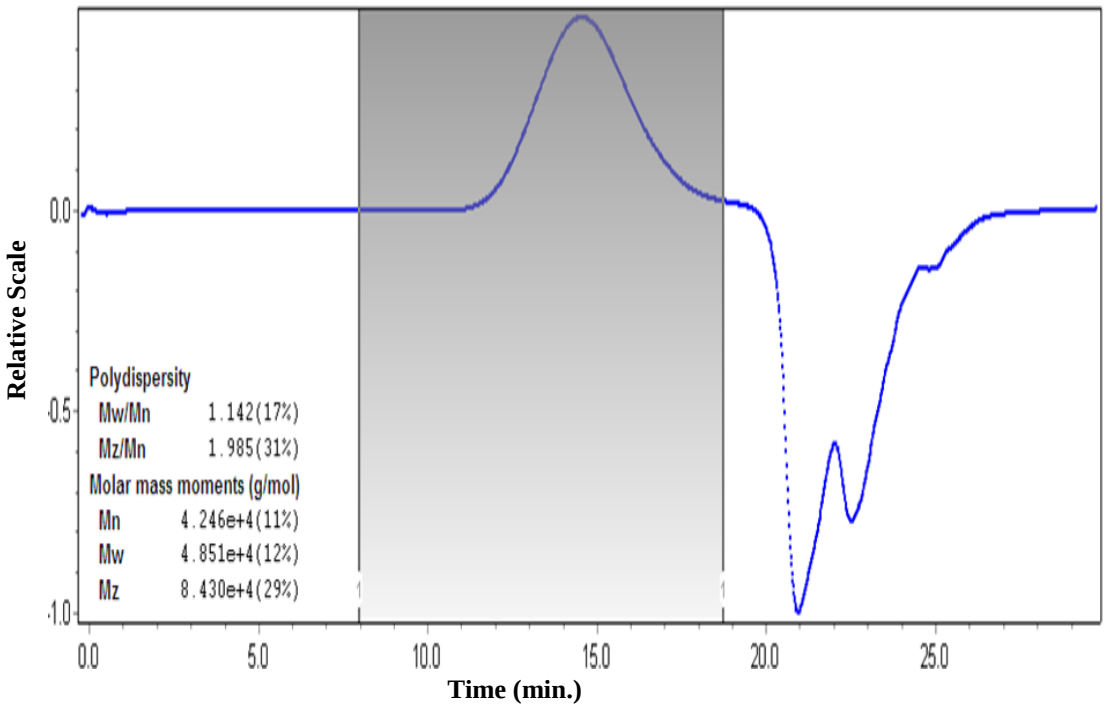

Figure C.25 GPC Analysis of PEE/600/67 wt % PBT (3)

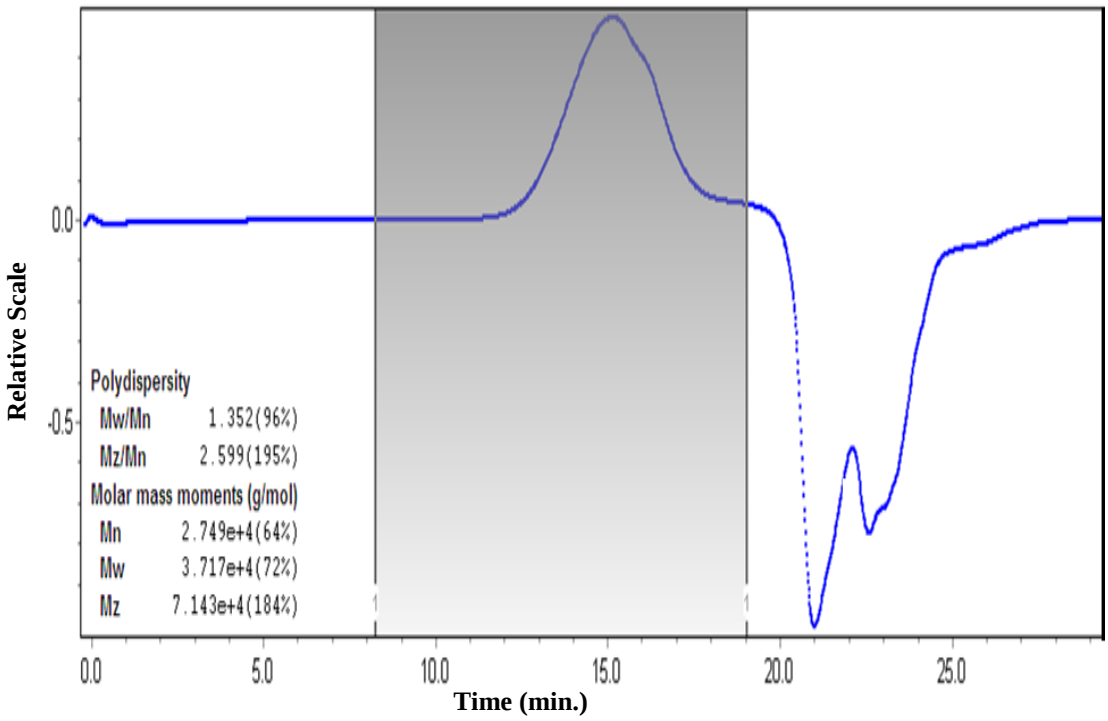

Figure C.26 GPC Analysis of PEE/2000/41 wt % PBT (1)

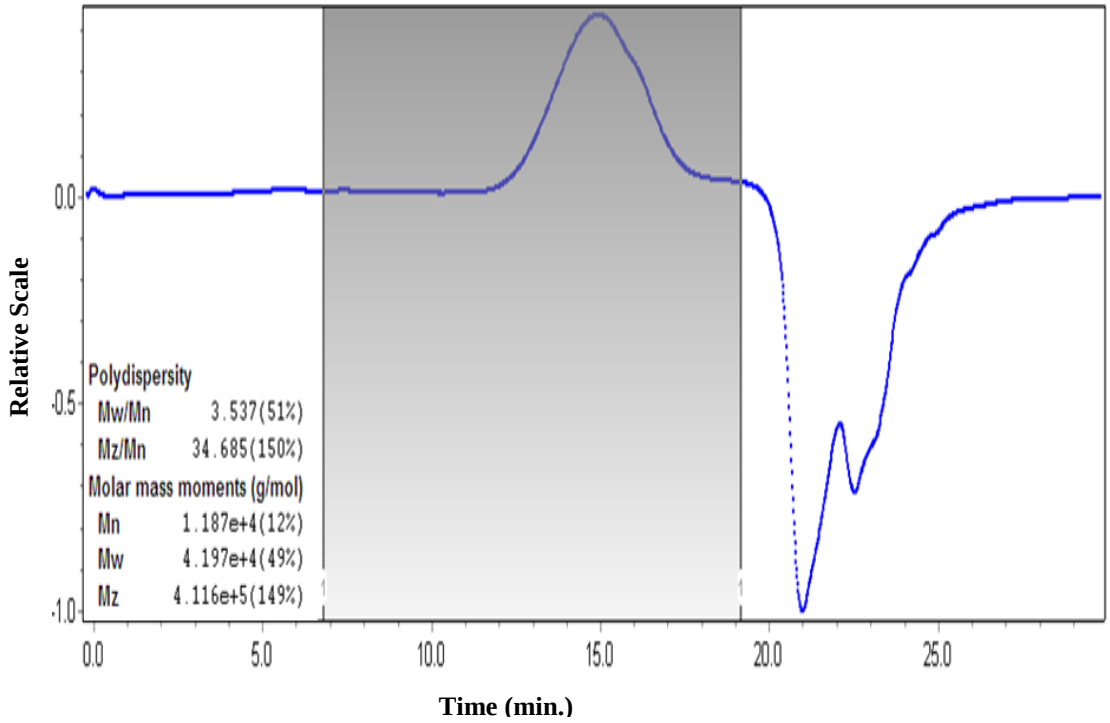

Figure C.27 GPC Analysis of PEE/2000/41 wt % PBT (2)

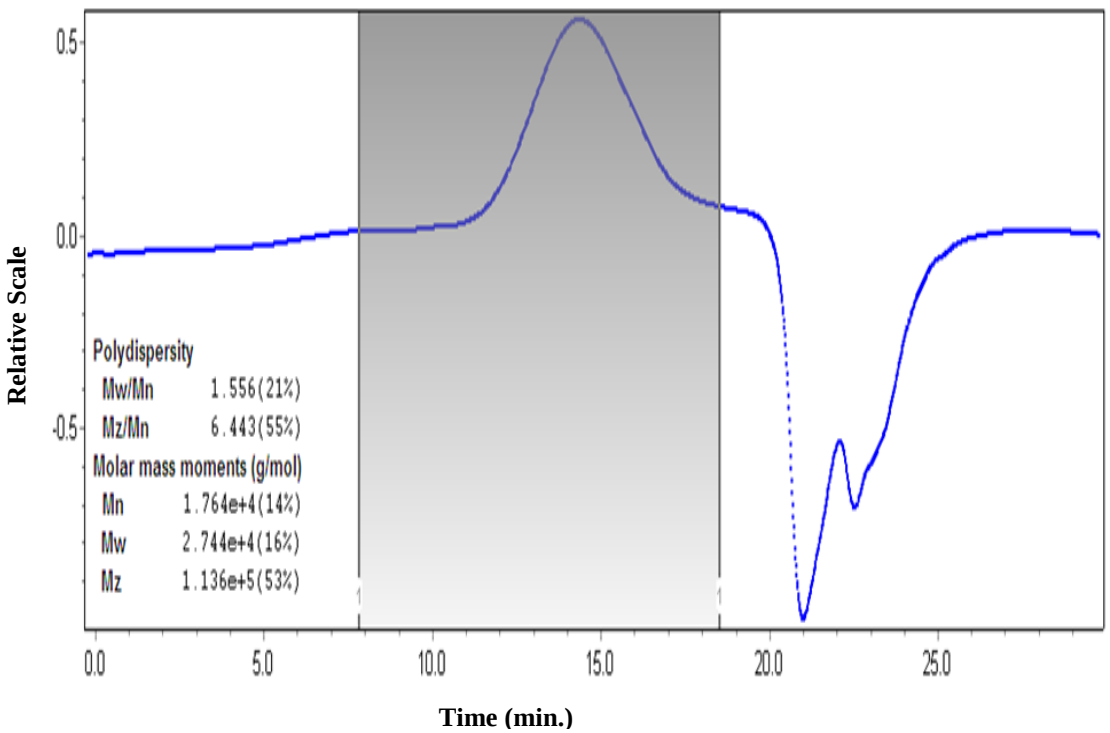

Figure C.28 GPC Analysis of PEE/2000/57 wt % PBT (1)

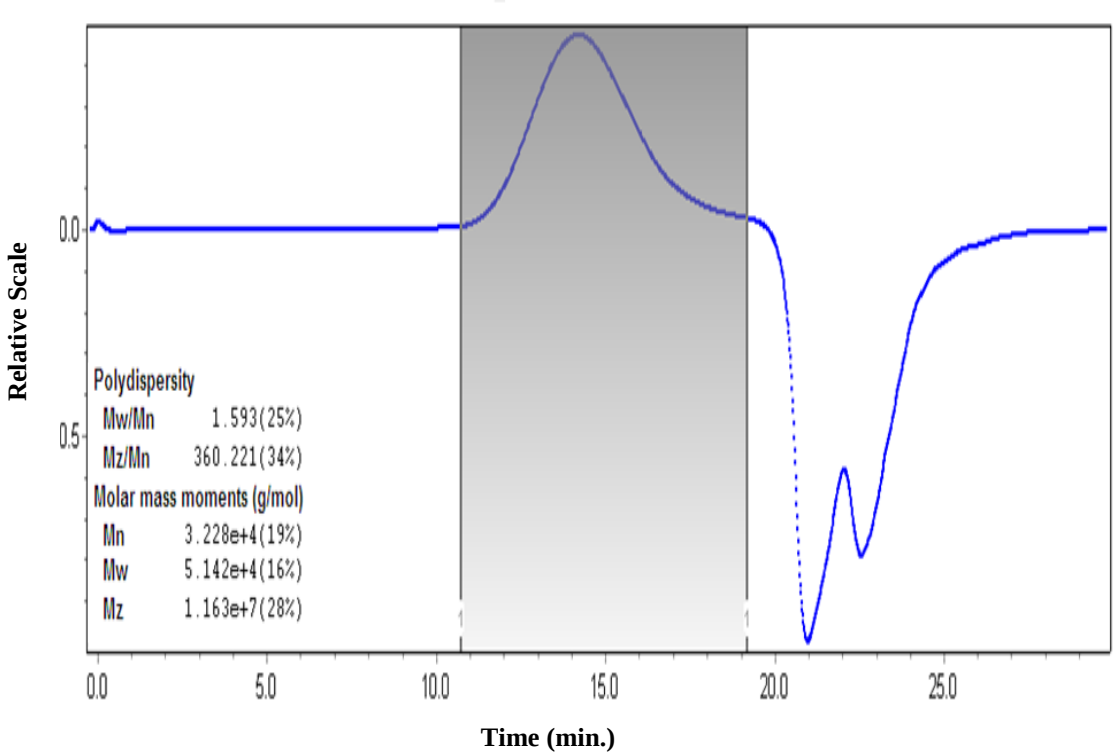

Figure C.29 GPC Analysis of PEE/2000/75 wt % PBT(1)

APPENDIX D

DSC RESULTS

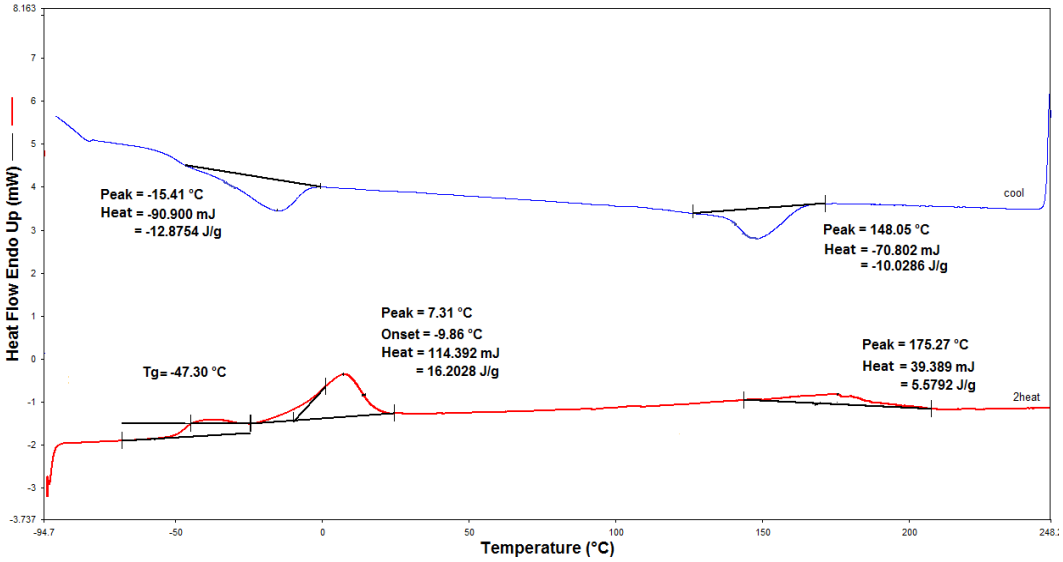

Figure D.1 DSC Analysis of PEE/1000/37 wt%PBT (5)

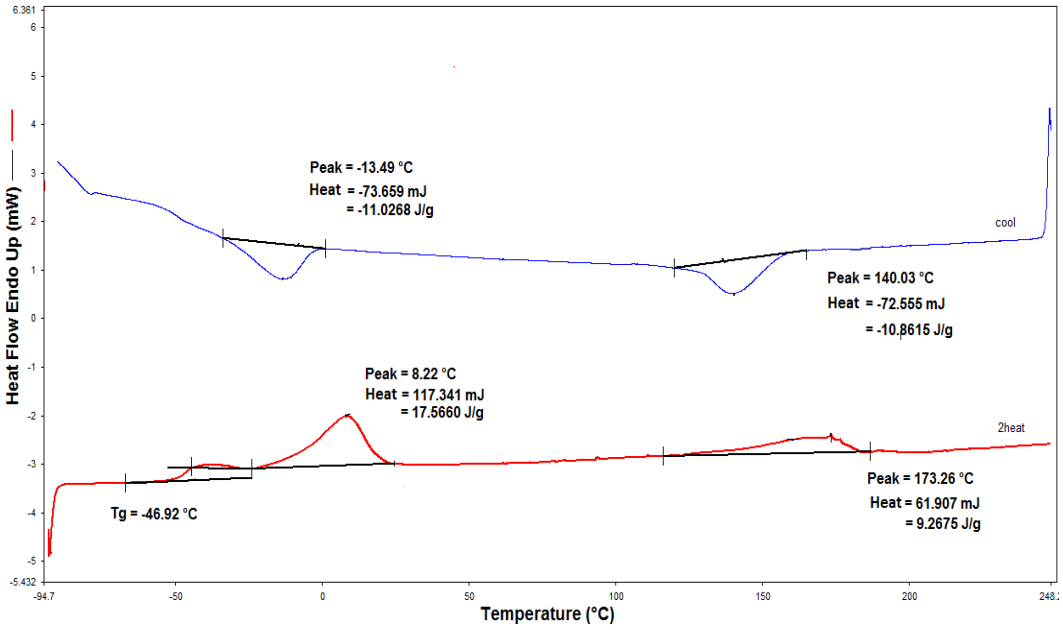

Figure D.2 DSC Analysis of PEE/1000/37 wt%PBT (5) + 0.1% TBHDP-MMT

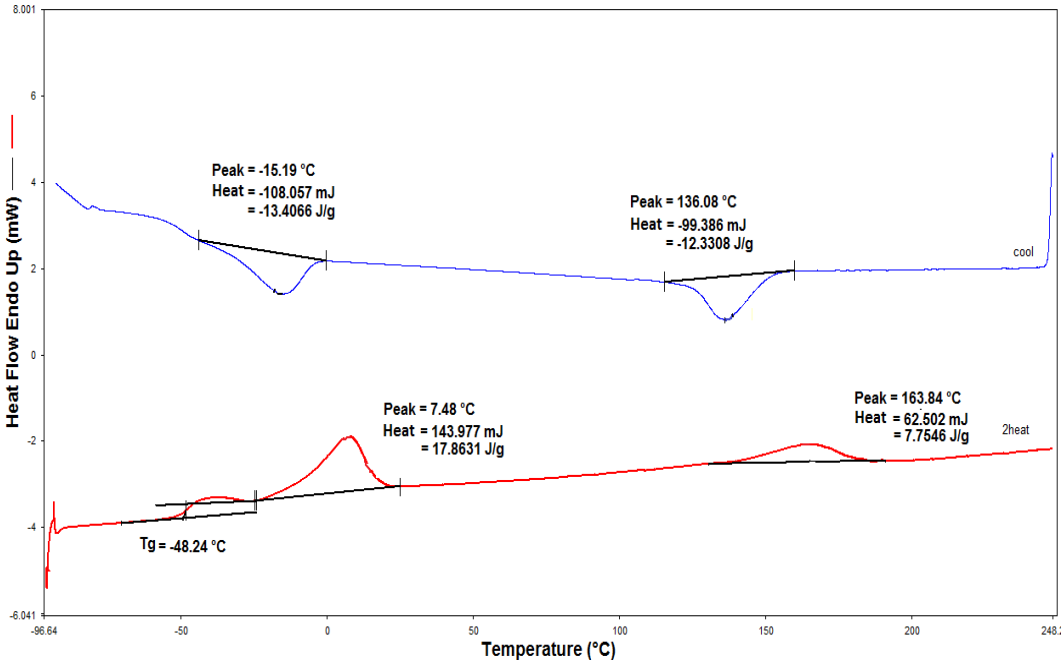

Figure D.3 DSC Analysis of PEE/1000/37 wt%PBT (5) + 0.3% TBHDP-MMT

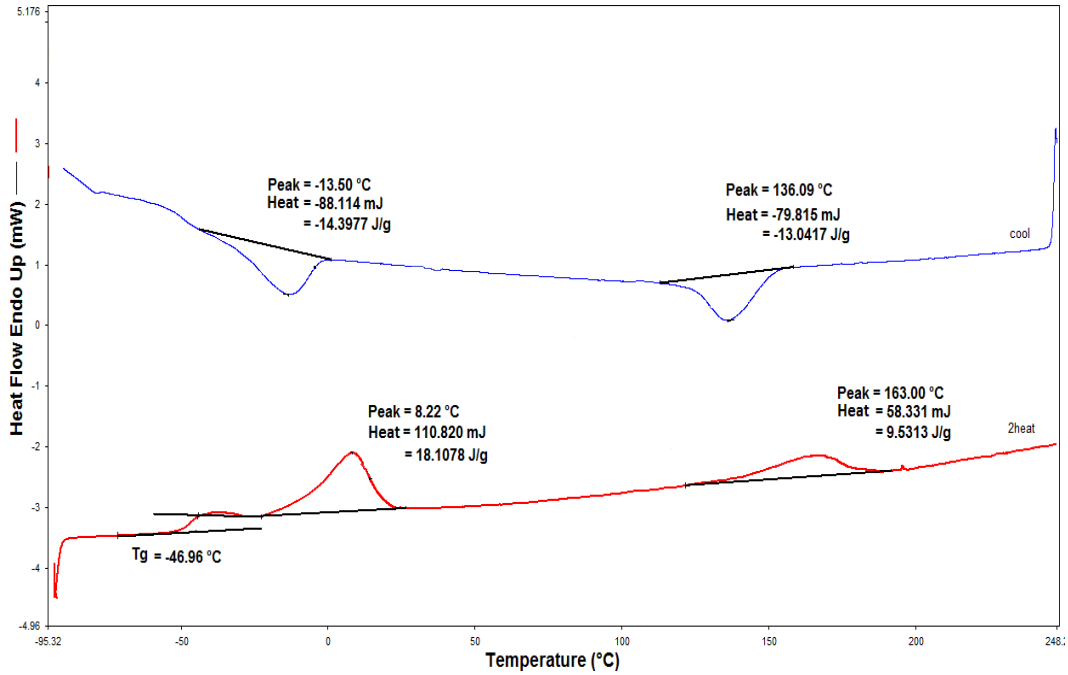

Figure D.4 DSC Analysis of PEE/1000/37 wt%PBT (5) + 0.5% TBHDP-MMT

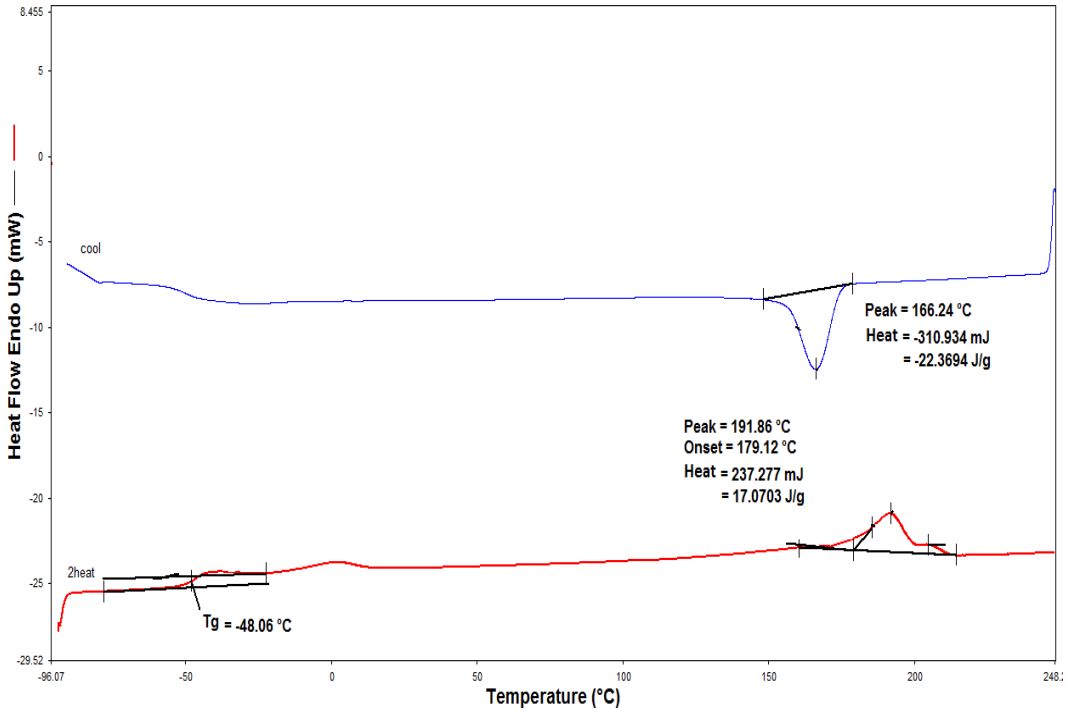

Figure D.5 DSC Analysis of PEE/1000/49 wt% PBT (8)

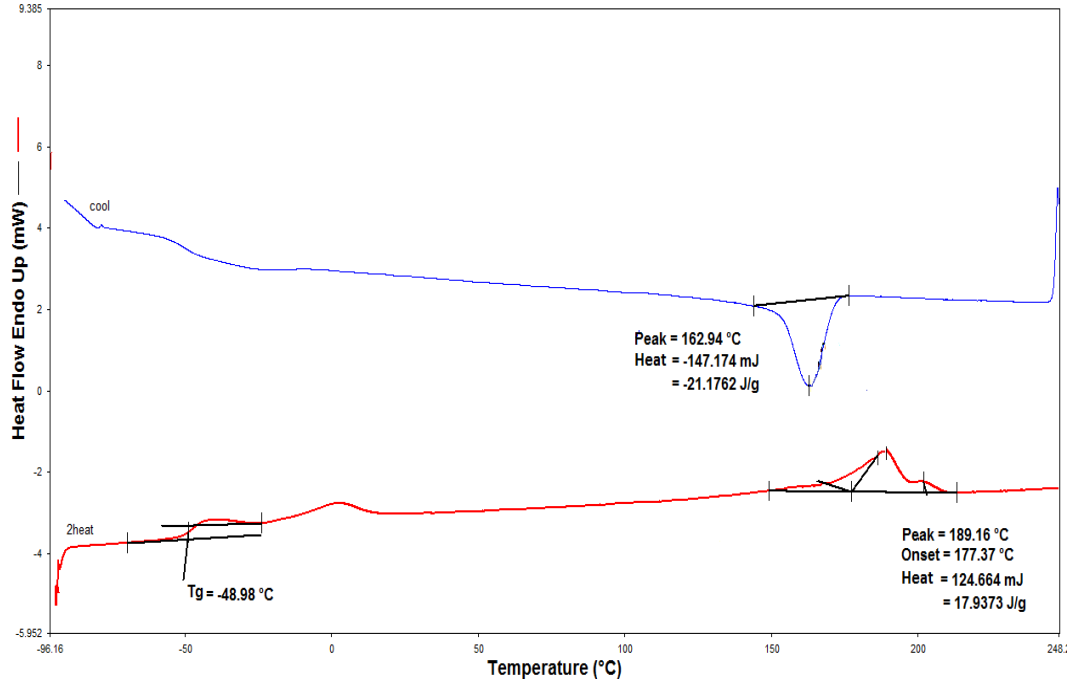

Figure D.6 DSC Analysis of PEE/1000/49 wt% PBT (8) + 0.1% TBHDP-MMT

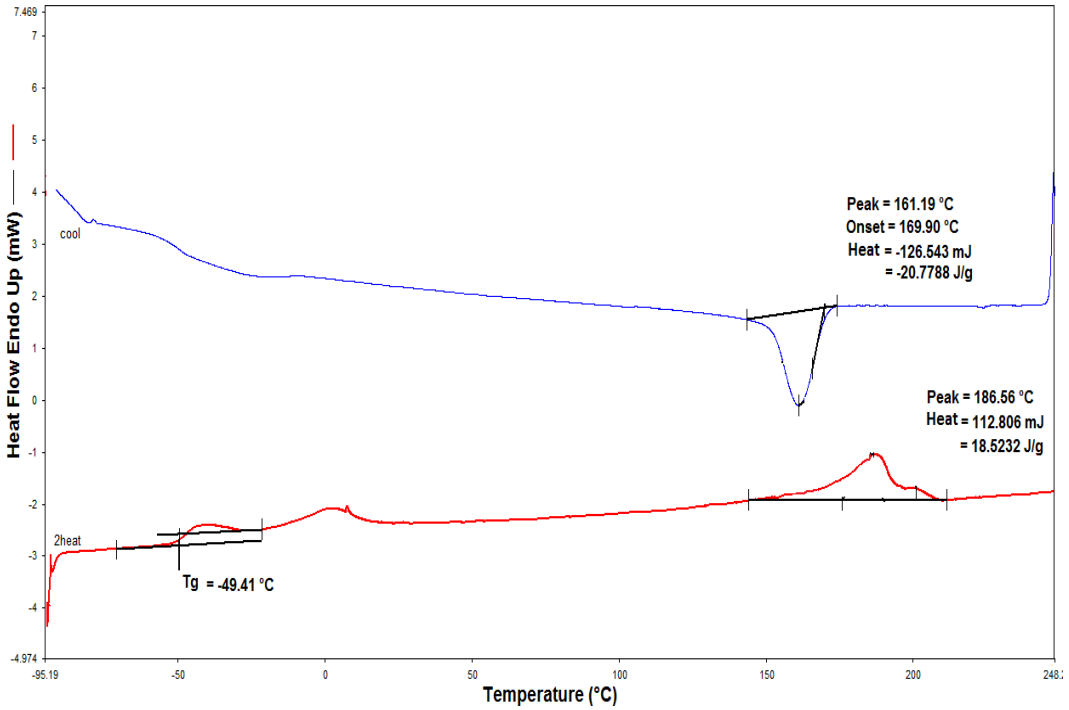

Figure D.7 DSC Analysis of PEE/1000/49 wt% PBT (8) + 0.3% TBHDP-MMT

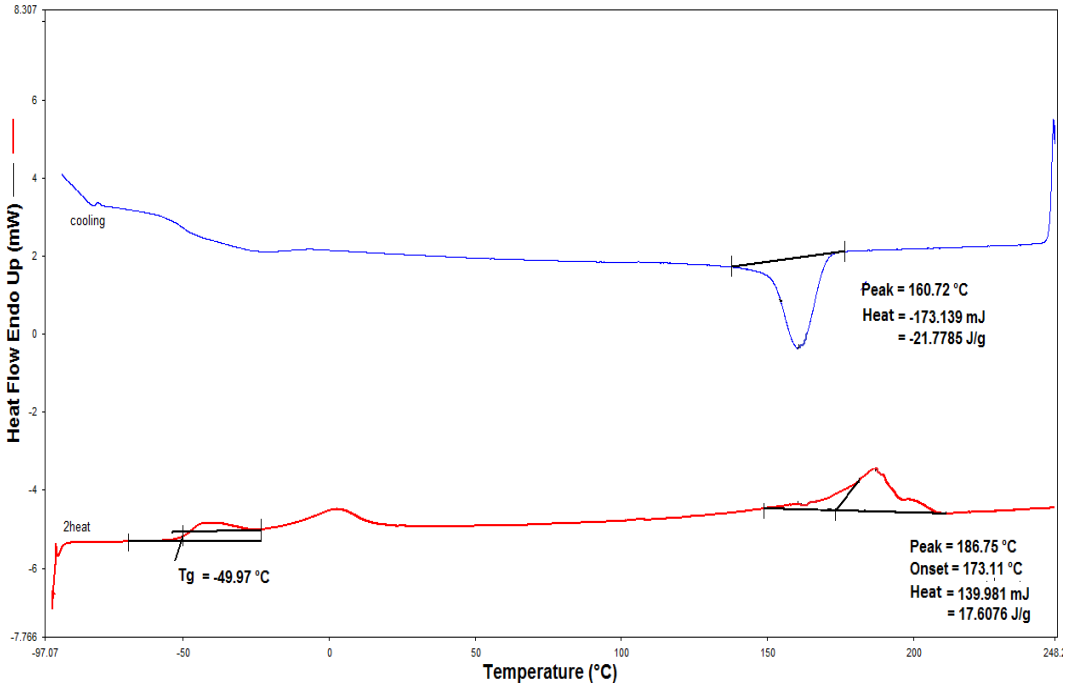

Figure D.8 DSC Analysis of PEE/1000/49 wt% PBT (8) + 0.5% TBHDP-MMT

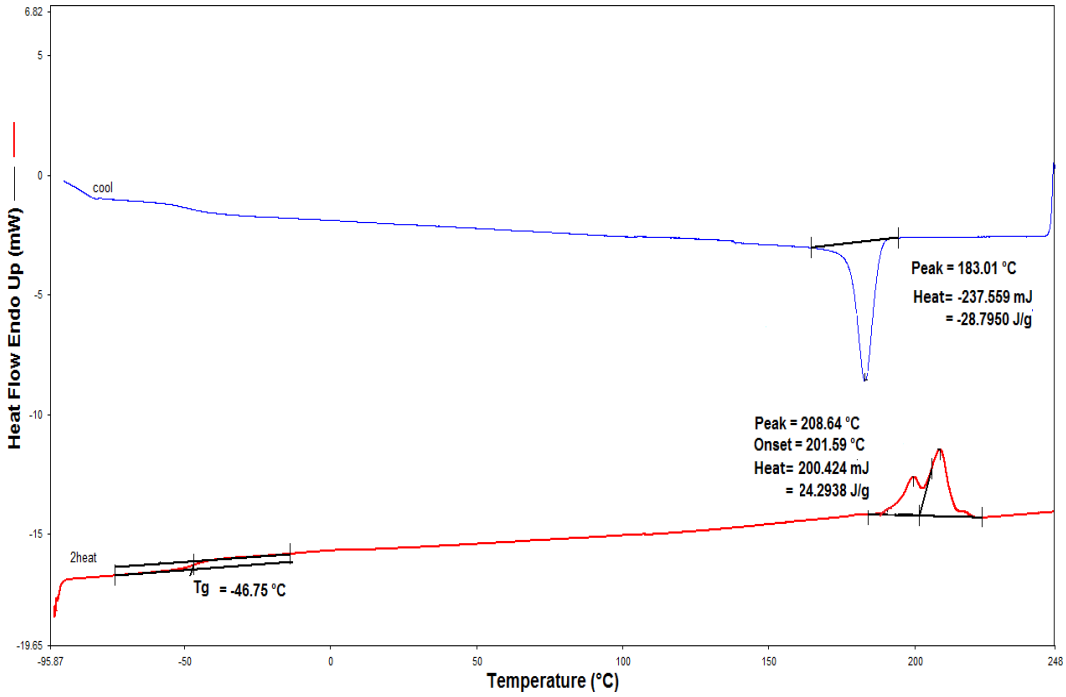

Figure D.9 DSC Analysis of PEE/1000/57 wt%PBT (3)

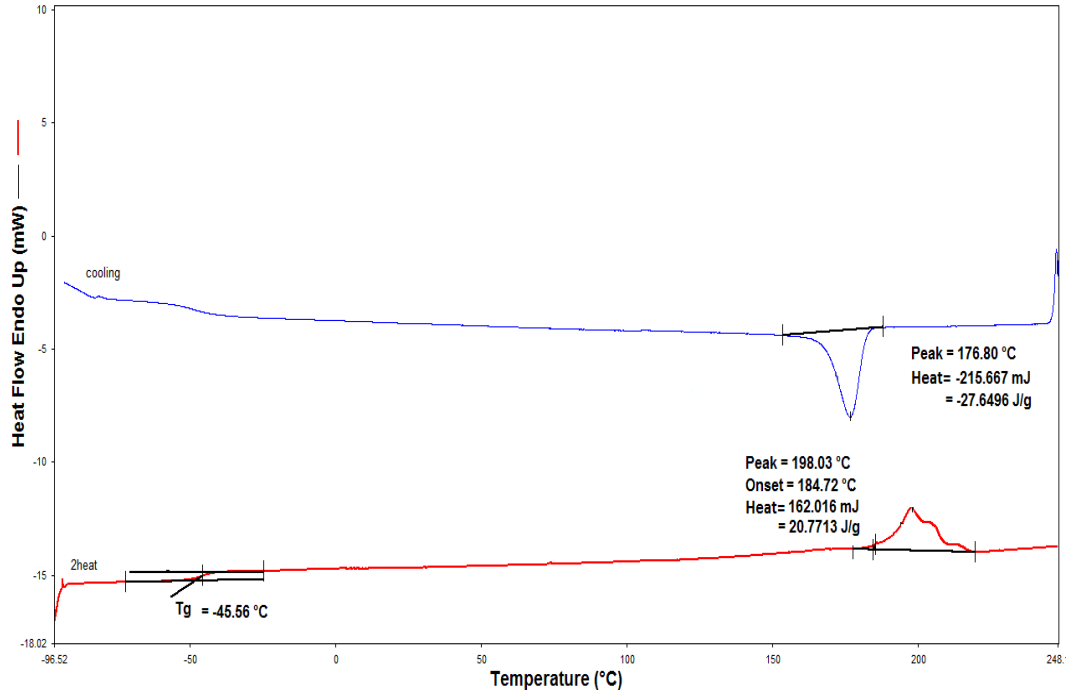

Figure D.10 DSC Analysis of PEE/1000/57 wt%PBT (3) + 0.1% TBHDP-MMT

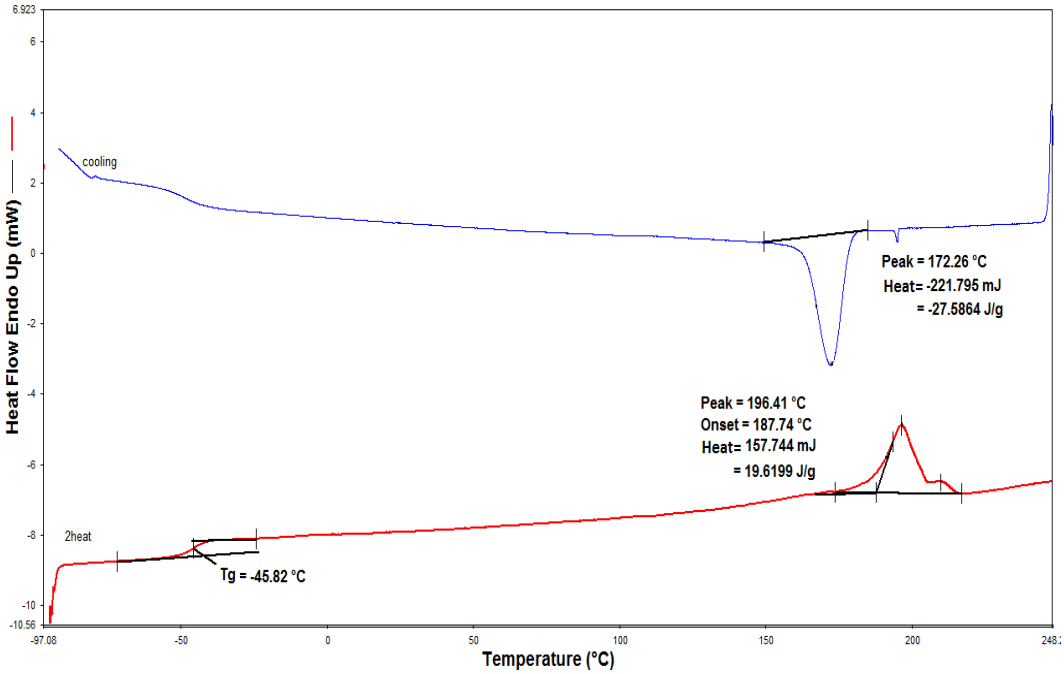

Figure D.11 DSC Analysis of PEE/1000/57 wt%PBT (3) + 0.3% TBHDP-MMT

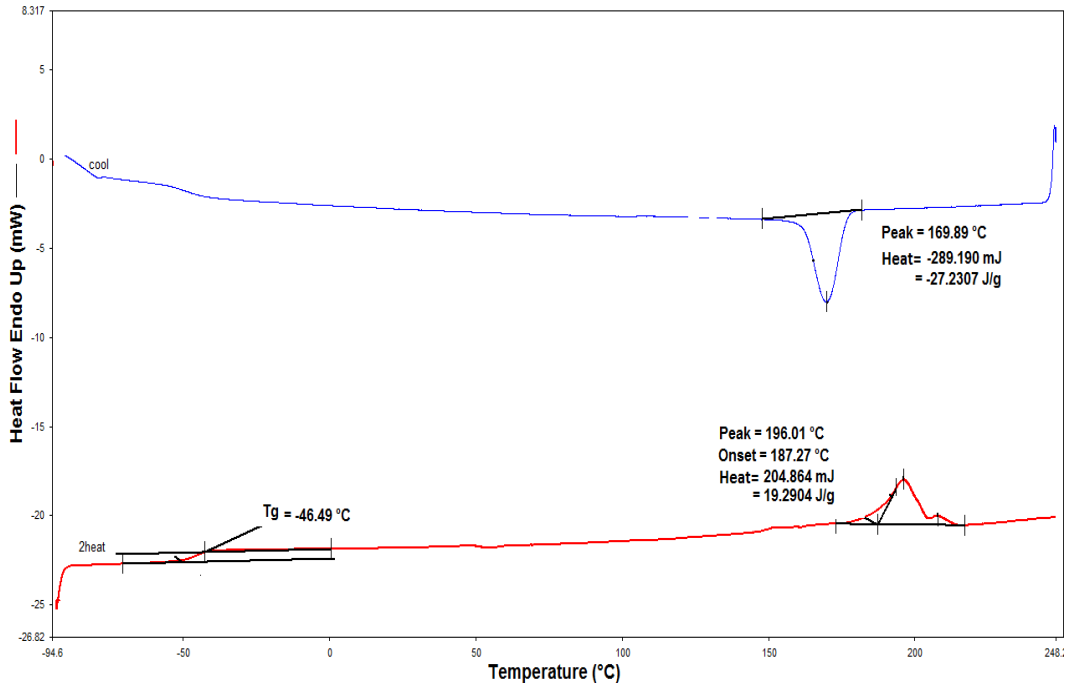

Figure D.12 DSC Analysis of PEE/1000/57 wt%PBT (3) + 0.5% TBHDP-MMT

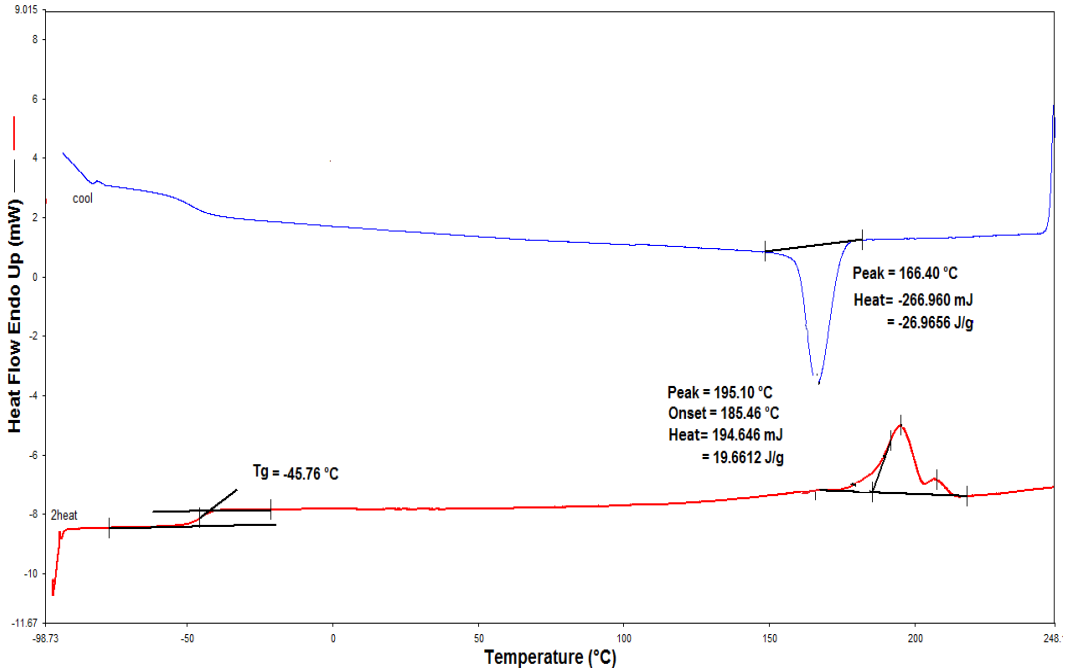

Figure D.13 DSC Analysis of PEE/1000/57 wt%PBT-0.1% TBHDP-MMT

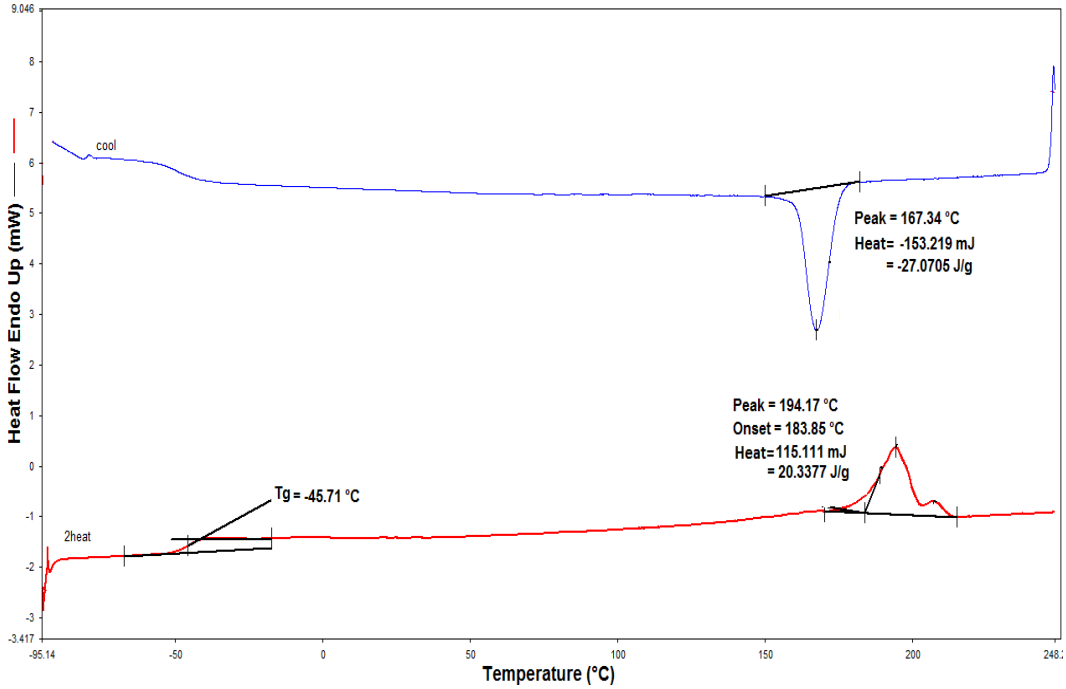

Figure D.14 DSC Analysis of PEE/1000/57 wt%PBT-0.3% TBHDP-MMT

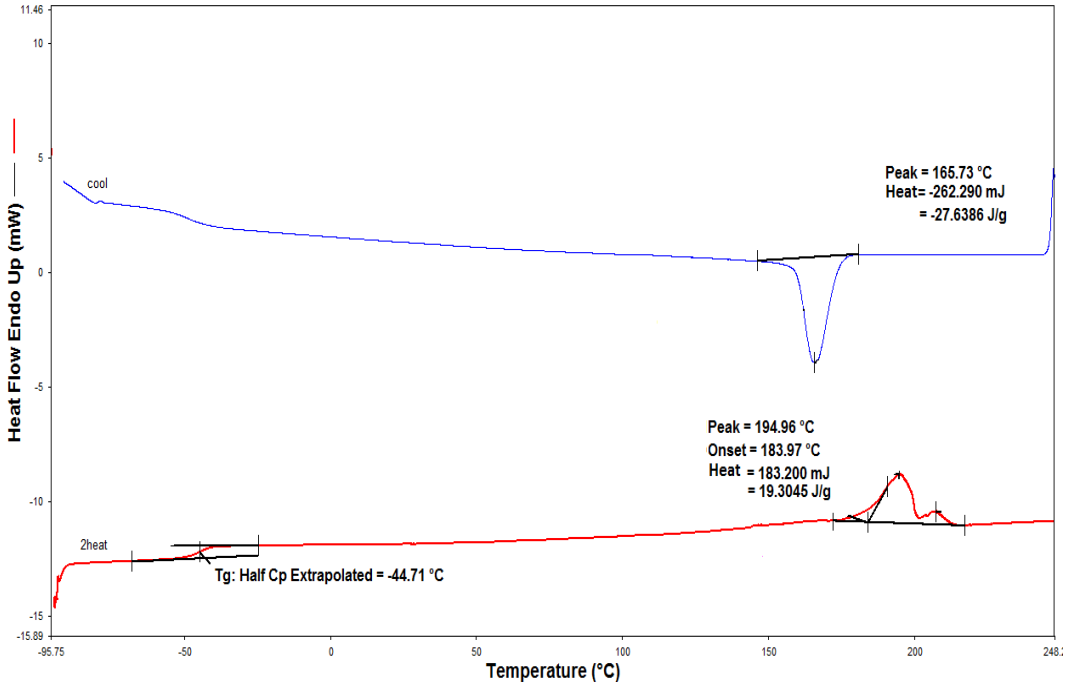

Figure D.15 DSC Analysis of PEE/1000/57 wt%PBT-0.5% TBHDP-MMT

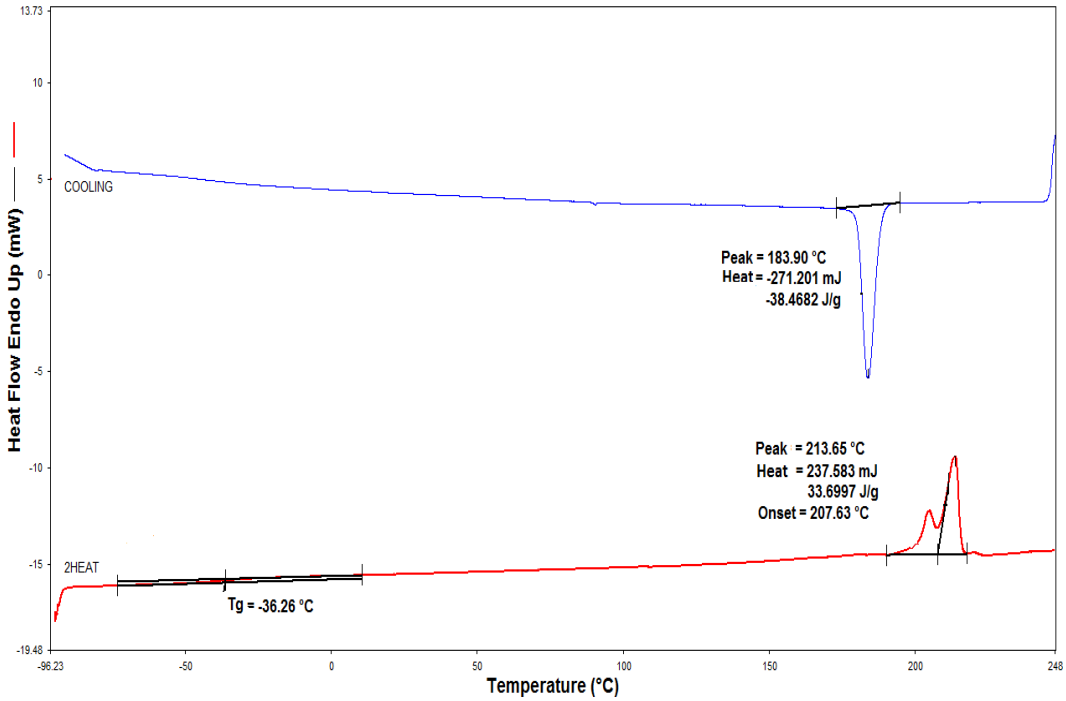

Figure D.16 DSC Analysis of PEE/1000/75 wt %PBT (5)

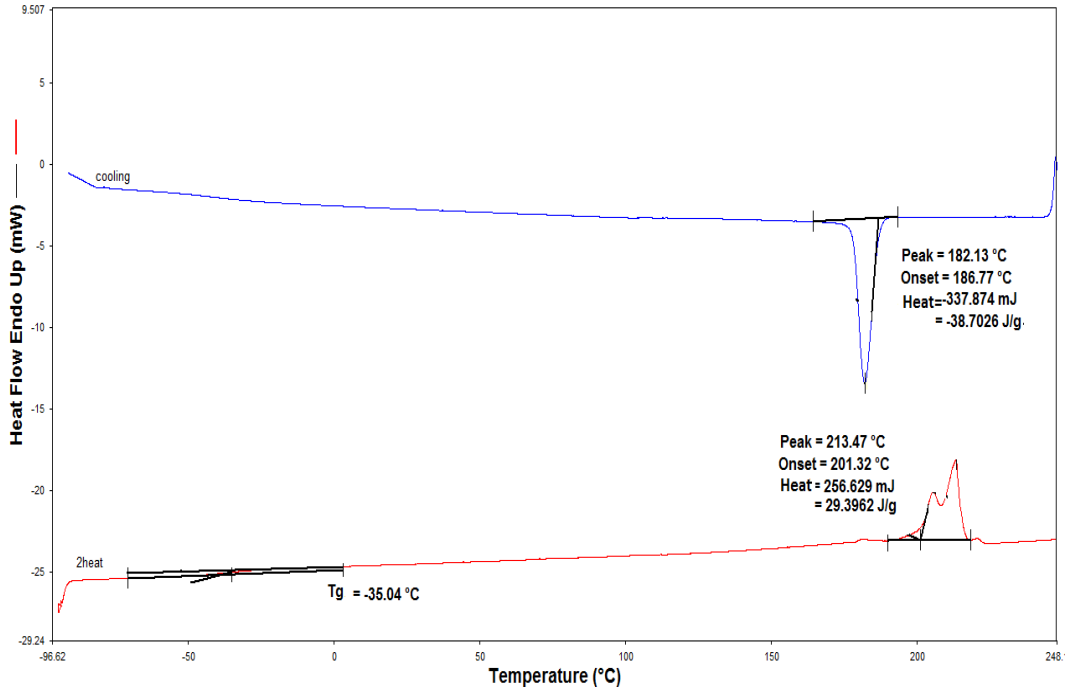

Figure D.17 DSC Analysis of PEE/1000/75 wt%PBT-0.1% TBHDP-MMT

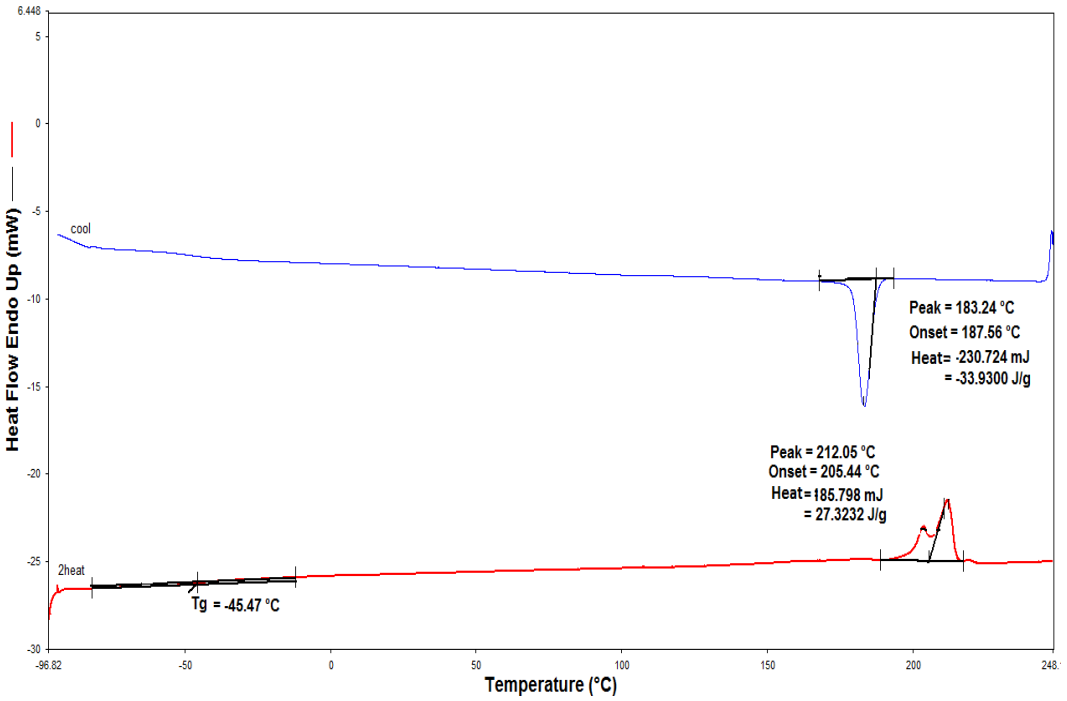

Figure D.18 DSC Analysis of PEE/1000/75 wt%PBT-0.3% TBHDP-MMT

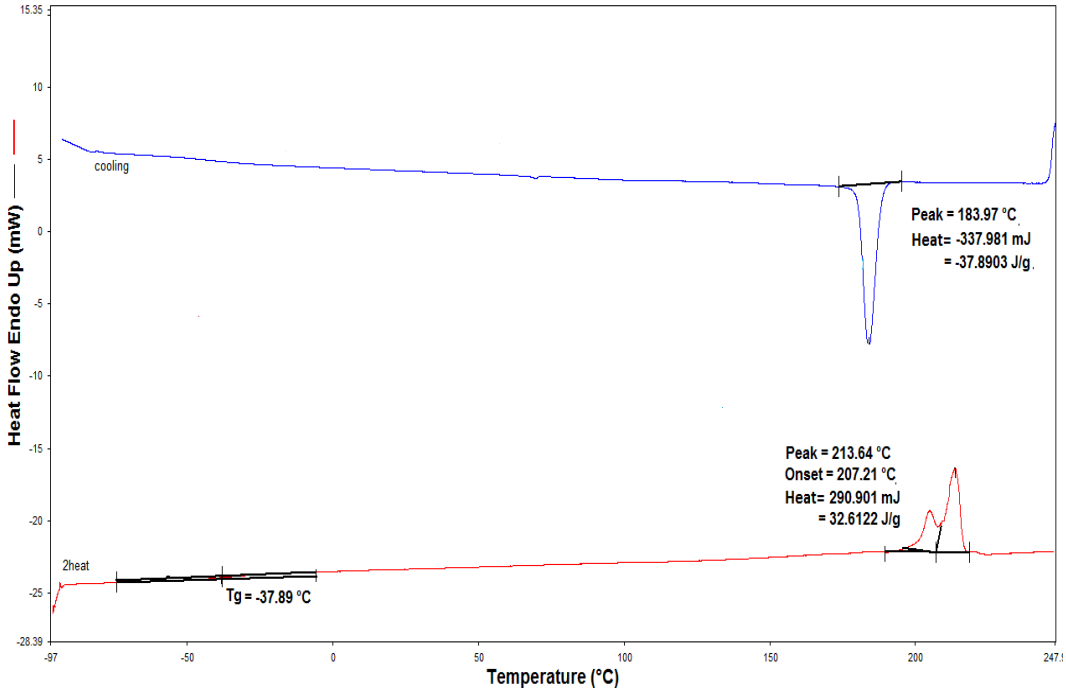

Figure D.19 DSC Analysis of PEE/1000/75 wt%PBT-0.5 % TBHDP-MMT

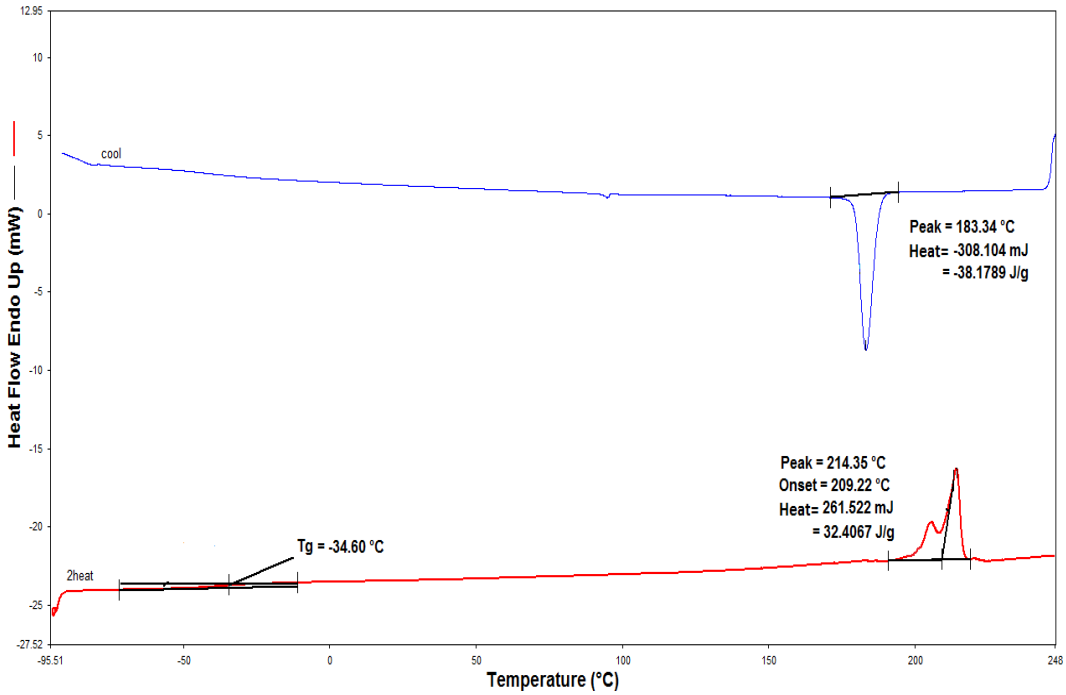

Figure D.20 DSC Analysis of PEE/1000/75 wt%PBT (5) + 0.1 % TBHDP-MMT

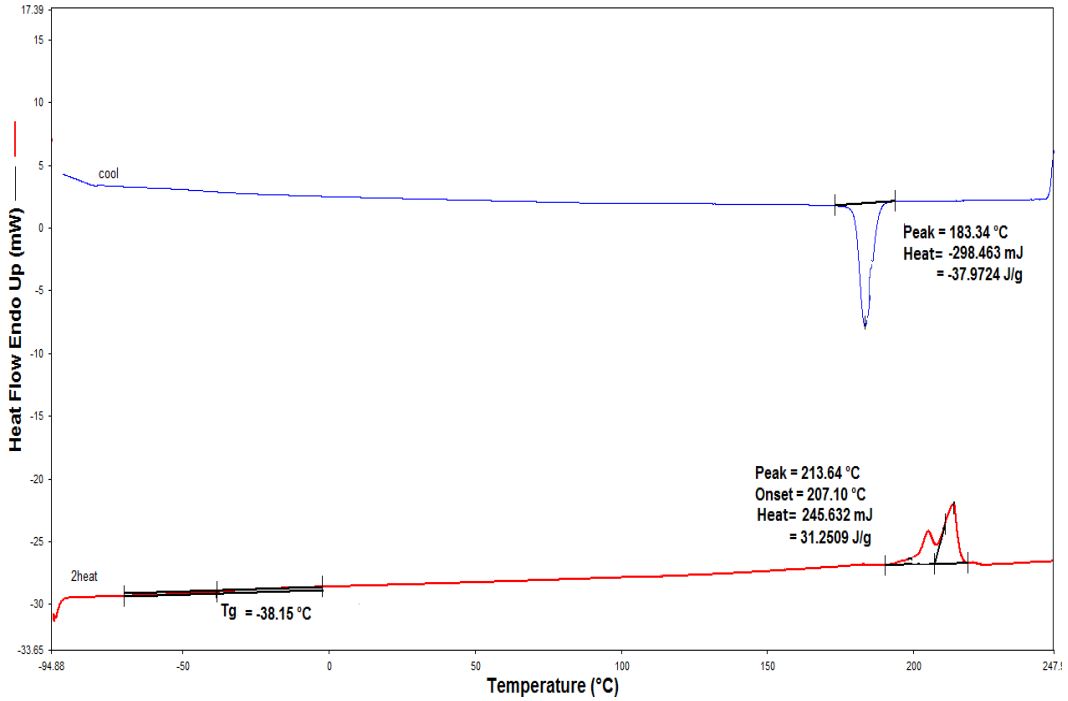

Figure D.21 DSC Analysis of PEE/1000/75 wt%PBT (5) + 0.3 % TBHDP-MMT

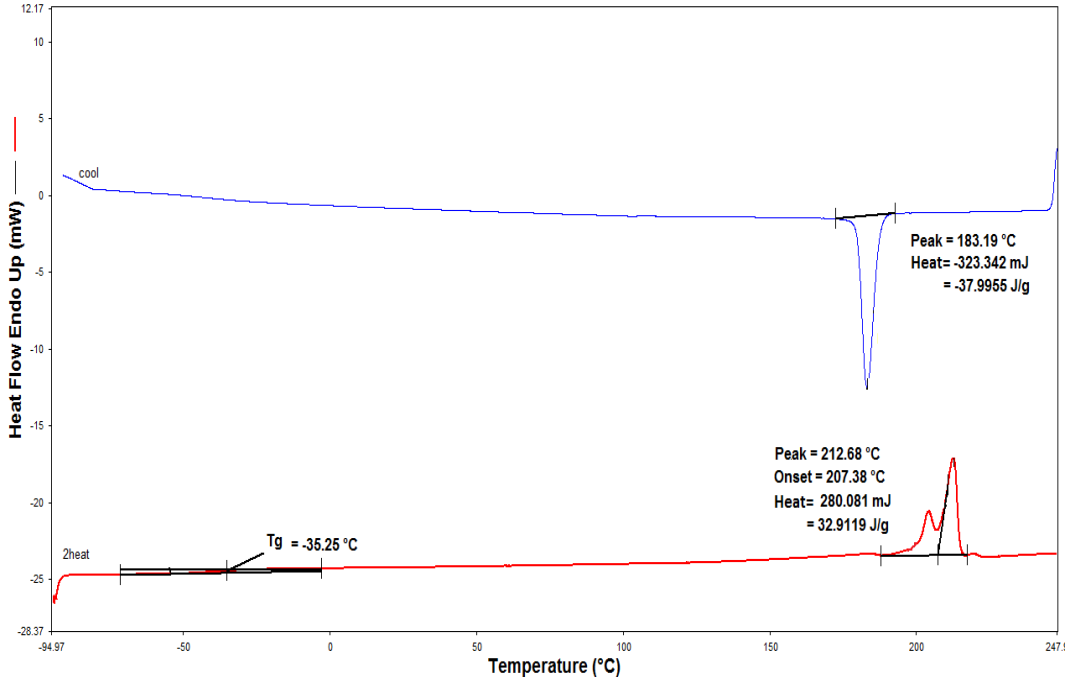

Figure D.22 DSC Analysis of PEE/1000/75 wt%PBT (5) + 0.5 % TBHDP-MMT

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