ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

THERMAL STABILITY INVESTIGATION OF RECYCLED POLYETHYLENE TEREPHTHALATE (PET) THROUGH DYNAMIC RHEOLOGICAL MEASUREMENTS

M.Sc. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

GERİ DÖNÜŞTÜRÜLMÜŞ POLİETİLEN TEREFTALAT (PET)'IN TERMAL KARARLILIĞININ DİNAMİK REOLOJİK ÖLÇÜMLERLE ARAŞTIRILMASI

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Merve Güçlü, a M.Sc. student of ITU Graduate School of Science, Engineering and Technology student ID 515171018, successfully defended the thesis entitled “THERMAL STABILITY INVESTIGATION OF RECYCLED POLYETHYLENE TEREPHTHALATE (PET) THROUGH DYNAMIC RHEOLOGICAL MEASURMENTS”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my mother,

FOREWORD

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ABBREVIATIONS

PET	: Poly(ethylene terephthalate)
R-PET	: Recycled poly(ethylene terephthalate)
PBT	: Poly (butylene terephthalate)
TSE	: Twin screw extruder
TEM	: Transmission electron microscopy
SEM	: Scanning electron microscopy
SSE	: Single screw extruder
IM	: Injection molding
BDO	: 1,4-butanediol
DMT	: Dimethyl terephthalate
TPA	: Terephthalic acid
DSC	: Differential scanning calorimetry
BHET	: Bis-(2-hydroxyethyl)-terephthalate
EG	: Ethylene glycol
PMDA	: Pyromellitic di-anhydride
MFR	: Melt flow rate
DMA	: Dynamic mechanical analysis
FT-IR	: Fourier transform infrared spectroscopy
HPLC	: High performance liquid chromatography
GC	: Gas chromatography
DAD	: Diod-array detector
MS	: Mass spectroscopy
FID	: Flame ionization detector
PVC	: Poly (vinyl chloride)
PE	: Poly ethylene
TCE	: Tetrachloroethylene
PVA	: Poly (vinyl acetate)
TGDMM	: Tetra-glycidyl diamino diphenyl methane
HDT	: Heat deflection temperature
C-NMR	: Carbon nuclear magnetic resonance

SANS : Small angle neutron scattering
H-NMR : Hydrogen nuclear magnetic resonance
XRD : X-ray diffraction
MVR : Melt volume rate
TGA : Thermal gravimetric analysis
WAXD : Wide angle X-ray diffraction
MFI : Melt flow index
MFR : Melt flow rate
TGA : Thermal gravimetric analysis

SYMBOLS

ΔGm : Gibbs free energy of mixing
ΔHm : Enthalpy of mixing
ΔSm : Entropy factor of mixing
η : Intrinsic viscosity
γ : Shear rate
Tg : Glass transition temperature
Tm : Melting temperature
ΔHm-PBT : PBT crystal melting enthalpy
ΔHmr-PET : Recycled PET crystal melting enthalpy
Tcr : Crystallization temperature
ΔHcr : Crystallization enthalpy

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THERMAL STABILITY INVESTIGATION OF RECYCLED POLYETHYLENE TEREPHTHALATE (PET) THROUGH DYNAMIC RHEOLOGICAL MEASUREMENTS

SUMMARY

Today, the use of polymers is becoming more and more common in the industry. Petroleum-derived polymers are frequently used in the industry because of their low cost, easy processing, availability, and easy application. With the growth of the plastics industry, some environmental problems have arisen. One of the biggest problems is that plastics take hundreds of years to disappear completely from nature as an example, a PET bottle wastes disappears completely from nature within 400 years. Due to all these ecological concerns, the industry has focused on recycling of petroleum-based polymer wastes. Recycling of plastic waste is an easy process, and it reduces the amount of plastic waste by re-adapting the plastic waste accumulated in nature to the industry. Today, 30% of the plastics produced can be recycled. However, the recycling of 60% of the produced plastics is what has been targeted for 2030. Therefore, interest and investments increase day by day recycling. The recycling process offers a promising solution to ecological problems caused by the excessive use of petroleum-based polymers that do not degrade in nature.

Poly (ethylene terephthalate) is a semi-aromatic thermoplastic polyester produced by the poly esterification reaction of ethylene glycol and phthalic acid / anhydride. PET is one of the mostly used polymers in the industry due to its high chemical, mechanical and thermal resistance properties. PET is widely used in the production of bottles and food packaging. As a result of these applications, tons of PET waste are generated every year. In addition, PET is not suitable for some applications due to its slow crystallization rate, but studies have increased the crystallization rate of recycled PET. This shows that the field of application can expand.

Recycling processes have advantages as well as various disadvantages. However, these disadvantages have been eliminated with the adoption of newly developed methods. When the properties of the recycled PET are compared with those of PET, some features appear to be decreased. When a material is recycled, the biggest loss will occur at the molecular weight. This results in the molecular weight of recycled materials being lower than the molecular weight of the raw materials. The loss of molecular weight in the structure of PET affects many other properties simultaneously. In particular, the viscosity of PET decreases with the loss of molecular weight. If the viscosity drop is too high, this will seriously affect the processability of PET. This is because of the fact that when the material is exposed to any thermal temperature, it will flow rapidly and accordingly will be difficult to shape. In addition, it will be affected by mechanical properties. The mechanical properties of recycled PET are low compared to raw PET.

Many methods are presented in the literature in order to solve all these disadvantages and improve the properties of recycled PET. They can be modified with chain

extenders when processing recycled polymers by extrusion or other methods in order to be used in the industry and to improve their properties. With the use of chain extenders in recycled polymers, the molecular weight is increased quickly and effectively. Even a small use of the chain extender causes huge effects. In addition, this method is fast, economical and easy to apply. Another method used to improve the properties of recycled polymers is the preparation of polymer blends. A polymer blend is a combination of two or more polymers that are physically mixed to obtain a single phase. This means that instead of obtaining the properties of each polymer individually, a set of properties is obtained by blending several polymers. Therefore, not all polymers may show their desired properties. By using another polymer with better properties and mixing with the other polymer, new polymeric materials having purposeful properties can be obtained. As a result of the studies, it has been clearly observed that the proper polymer blends and the proper chain extenders have positive effects on the mechanical properties, thermal properties and melt rheological properties of the polymers by the use of new polymers.

In this study, our aim is to analyze and improve the thermal stability of recycled PETs after applying the recycling process. It is to show that recycled materials can be used as raw materials after their properties have been improved and become available for industry. Recycled polymer loses its properties during the recycling process, and when an extra thermal process is applied, many problems occur in the industry. Polymers are exposed to temperature by many different methods in order to be processed and shaped as final products. In addition, there are many parameters that affect on thermal behavior,when exposed to temperature. One of these parameters is the shear rate or frequency and in this way there are many process parameters. Therefore, the melt thermal stability of the materials is very important in terms of end product properties and processability. Dynamic rheology measurements can be made to determine these properties. In this context, in order to determine the processability of recycled PETs, their dynamic rheological properties were examined. Thus, how recycled PET will behave in melt state is examined. In these trials, how many parameters will affect the melt behavior of recycled PET is examined. First, the linear viscoelastic region of recycled PET was determined as 1% by strain sweep tests. This test is performed to identify the region where the viscoelastic properties of the material do not change when the strains applied. Time sweep tests were performed at different temperatures to identify thermal stability. In this way, it is possible to observe that how many percentage degredation occured for material. During the time sweep tests, different strains were also used as parameters. Frequency sweep tests were performed to determine the melt rheological behavior of recycled PET whose thermal stability was determined. In this way, rheological behavior, which is of great importance in terms of machinability, has been determined.

Finally, melt behaviors of recycled PET were determined by applying stress growth test. After this point, the disadvantages that occurred with the recycling process were also observed in the structure of recycled PET. The dynamic complex viscosity is quite low. As a result of the studies, it has been observed that both the preparation of polymer blends and chain extenders have positive effects on the mechanical properties, thermal properties and rheological properties of polymers. Our aim in this study is to show that the melt rheological properties of recycled PET are improved and available for industry. In this context, we examined the dynamic rheological properties of recycled PETs to determine their processability. Thus, we have observed how rheological properties change or can be changed as a result of the recycling process. Disadvantages

caused by the recycling process were also observed in the structure of recycling PET. Most importantly, the decrease in viscosity caused by loss of molecular weight was observed for recycled PETs during time sweep rheological experiments indicating its low thermal stability that could negatively affect the melt processing. After this stage, the most important step was to improve the thermal stability with the use of chain extenders and blending. For this purpose, 0.4 wt% and 0.8 wt% of chain extenders were melt mixed with recycled PET using a twin screw extruder and the thermal stability and these compounds were monitored. Considering these results, it has been observed that with the addition of a chain extender, the rheological properties change and the processability properties of the recycled PET vary as well. Moreover, blends of recycled PET with polybutylene terephthalate (PBT) at the blending ratios of 25-75%, 50-50%, 75-25% were prepared through melt blending in a twin-screw extruder. This was because PBT is a polyester polymer that has very similar to the structure of PET. Furthermore, it has very good mechanical, chemical and machinability properties that could also improve the processability and crystallization rate of recycled PET which are considered as PET’s drawbacks. In this way, the effects of the prepared polymer blends on the rheological properties have been examined. Although not being used simultaneously, the preparation of the polymer blends and the use of a chain extender, could both contribute to the rheological properties of recycled materials, a change in their rheological behavior and an increase in their processability properties. In addition, by using different temperatures, the effect of the temperature, that is thermal stability, on the melt rheological properties of all materials was examined. Also, changes in the structure of recycled PET, PBT and their blends during rheological measurements were tested with the FTIR device. It has been concluded that polyesterification reacts to temperature and the use of a chain extender and therefore an increase in viscosity was observed.

GERİ DÖNÜŞTÜRÜLMÜŞ POLİETİLEN TEREFTALAT (PET)'IN TERMAL KARARLILIĞININ DİNAMİK REOLOJİK ÖLÇÜMLERLE ARAŞTIRILMASI

ÖZET

Günümüzde endüstride polimer kullanımı giderek yaygınlaşmaktadır. Özellikle petrol türevi polimerler, düşük maliyetli olmaları, kolay işlenebilmeleri, kolayca temin edilebilmeleri ve kolay uygulanmaları nedeniyle endüstride sıklıkla kullanılmaktadır. Plastik endüstrisinin giderek büyümesi ile birlikte bazı çevresel sorunlar ortaya çıkmaktadır. En büyük sorun ise, plastiklerin doğadan kabolma süresinin yüz yılları almaktadır. Buna örnek verilecek olursa bir PET şişe atığı doğadan 400 yıl içersinde tamamen kaybolmaktadır. Tüm bu ekolojik kaygı nedeniyle endüstri bio-polimer ya da üretilmiş olan petrol bazlı polimer atıklarının geri dönüştürülmesine odaklanmıştır. Plastik atıklarının geri dönüştürülmesi kolay bir proses olmakla birlikte doğada birikmiş olan plastik atıklarının sanayiye yeniden adapte edilmesi ile atık plastik miktarını azalmaktadır. Günümüzde üretilen plastiklerin %30'u geri dönüştürülebilmektedir. Ancak 2030 yılına kadar hedeflenen üretilmiş plastiklerin %60'ının geri dönüştürülmesidir. Dolayısıyla günden güne geri dönüştürme işlemine ilgi ve yatırımlar artmaktadır.

Geri dönüşüm işlemi doğada bozunmayan petrol bazlı polimerlerin aşırı kullanımının neden olduğu ekolojik sorunlara umut verici bir çözüm sunar. Poli (etilen tereftalat) etilen glikol ve ftalik asit/anhidrit'in poliesterifikasyon reaksiyonu ile üretilien yarı aromatik termoplastik poliesterdir. PET yüksek kimyasal, mekanik ve termal dayanım özellikleri nedeniyle endüstride en çok kullanılan polimerlerden bir tanesidir. PET yaygın olarak şişe ve gıda ambalajı üretiminde kullanılmaktadır. Bu uygulamalar neticesinde her yıl tonlarca PET atığı oluşmaktadır. Oluşan bu atıkların geri dönüşümü ile sanayiye kazandırılması gelecek açısından çok önemlidir. Ayrıca PET bazı uygulamalar için yavaş kristtalenme hızından dolayı uygun değildir ancak yapılan çalışmalarda geri dönüştürülmüş PET'nin kristallenme hızında artışlar meydana gelmiştir. Bu da uygulama alanının genişleyebilceğini göstermektedir. Geri dönüşüm işlemlerinin avantajları olduğu gibi çeşitli dezavantajları da olmaktadır. Ancak bu dezavantajlar geliştirilen yeni yöntemler ile giderilmeye başlanmıştır.

Geri dönüştürülmüş PET'nin özellikleri, ham PET'nin özellikleri ile karşılaştırıldığında bazı özelliklerde düşüşler ya da kayıplar meydana gelmektedir. Bir malzeme geri dönüşüm işlemine tabii tutulduğunda karşılaşacağı en büyük kayıp molekül ağırlığında meydana gelmektedir. Bu da geri dönüştürülmüş malzemelerin molekül ağırlığının ham malzemelerin molekül ağırlığından düşük olduğu sonucunu vermektedir. PET'nin yapısında meydana gelen molekül ağırlığı kaybı diğer birçok özelliğide eş zamanlı olarak etkilemektedir. Özellikle, molekül ağırlığı kaybı ile PET'nin viskozitesi de düşmektedir. Eğer viskozite düşümü çok fazla olursa bu da PET'nin işlenebilirliğini ciddi derecede etkileyecektir. Çünkü malzeme herhangi bir termal sıcaklığa maruz bırakıldığında hızlıca akması gerçekleşecektir ve

şekillendirilmesi açısından zorluk yaşanacaktır. Bunun yanı sıra, mekanik özelliklerde etkilenecektir. Geri dönüştürülmüş PET’nin mekanik özellikleri ham PET ile karşılaştırıldığında düşüktür. Tüm bu dezavantajların çözülebilmesi ve geri dönüştürülmüş PET’nin özelliklerinin iyileştirilebilmesi için literatürde bir çok yöntem sunulmuştur. Geri dönüştürülmüş polimerlerin endüstride kullanılabilmesi ve özelliklerinin iyileştirilmesi için ekstrüzyon ya da diğer yöntemlerle işlenmeleri sırasında zincir uzatıcılarla modifiye edilebilirler. Geri dönüştürülmüş polimerlerde zincir uzatıcı kullanımıyla birlikte molekül ağırlığı hızlı ve etkili bir şekilde yükseltilir. Zincir uzatıcının az miktarda kullanımı bile çok büyük etkilere yol açmaktadır. Ayrıca bu yöntem hızlı, ekonomik ve kolay uygulanabilirdir. Geri dönüştürülmüş polimerlerin özelliklerinin iyileştirilmesinde kullanılan diğer bir yöntem ise polimer harmanlarının hazırlanmasıdır. Bir polimer harmanı, tek bir faz elde etmek için fiziksel olarak karıştırılan iki veya daha fazla polimerin bir kombinasyonudur. Bu, her polimerin özelliklerini ayrı ayrı elde etmek yerine, birkaç polimerin harmanlanmasıyla bir özellik kümesi elde edildiği anlamına gelir. Bu nedenle, her polimer kendi istenen özelliğini göstermeyebilir. Özellikleri daha iyi olan başka bir polimerin kullanılmasıyla ve diğer polimerle karıştırılmasıyla amaca yönelik özellikler taşıyan yeni polimerik malzemelerin elde edilebilmektedir. Yapılan çalışmalar sonucunda, uygun polimer harmanlarının hazırlanması ve uygun zincir uzatıcıların polimerlerin kullanılşmasıyla polimerlerin mekanik özellikleri, termal özellikleri ve dinamik reolojik özellikleri üzerinde olumlu etkiler gösterdiği açıkca gözlemlenmiştir.

Bu çalışmada amacımız geri dönüştürülmüş PET’lerin geri dönüştürme prosesi uygulandıktan sonra kaybettikleri termal kararlılıklarının incelenenip ve geliştirilmesidir. Geri dönüştürülmüş malzemelerin özelliklerinin iyileştirilip endüstri için kullanılabilir bir hale geldikten sonra hamadde olarak kullanabilir olduğunu göstermektir. Geri dönüştürülmüş polimer geri dönüşüm işlemi sırasında özelliklerini kaybettiği gibi bir de ekstra termal bir işlem uygulandığında, endüstride bir çok sorun yaşanmaktadır. Polimerler işlenebilmeleri ve son ürüne olarak şekillendirilebilmeleri için birçok farklı yöntemle sıcaklığa maruz bırakılmaktadırlar. Ayrıca sıcaklığa maruz kaldığında ortamda termal davranışı etkileyen bir çok parametre bulunmaktadır. Bu parametrelerden biri de kesme hızıdır ve bu şekilde bir çok proses parametresi bulunmaktadır. Dolayısıyla malzemelerin eriyik halde termal stabiliteleri son ürün özellikleri ve işlenebilirlikleri açısından çok önemlidir. Bu özellikleri belirmek için dinamik reoloji ölçümleri yapılabilmektedir. Bu bağlamda, geri dönüştürülmüş PET’lerin işlenebililiğini belirlemek amacıyla eriyik halde dinamik reolojik özellikleri incelenmiştir. Böylece geri dönüştürülmüş PET’nin eriyik halde nasıl davranacağı incelenmiştir. Bu denemelerde bir çok parametrenin geri dönüştürülmüş PET’nin eriyik halde davranışı üzerine nasıl etki yapacağı incelenmiştir. İlk olarak recycled PET’nin lineer viskoelastik bölgesi gerinim tarama testleri ile %1 olarak belirlenmiştir. Bu test uygulanan strainlerde malzemenin viskoelastik özelliklerinin değişmediği bölgeyi tanımlamak için yapılmaktadır. Ardından termal stabiliteyi tanımlamak amacıyla zaman taraması testleri farklı sıcaklıklarda gerçekleştirilmiştir. Bu sayede malzemenin hangi sıcaklıkta ve % kaç degredasyona uğradığı gözlemlenebilmektedir. Zaman tarama testleri sırasında farklı gerinimler ayrıca parametre olarak kullanılmıştır. Termal stabilitesi belirlenen geri dönüştürülmüş PET’nin eriyik reolojik davraışının belirlenmesi için frekans tarama testleri yapılmıştır. Bu sayede işlenebilirliği açısından büyük önem taşıyan reolojik davranış belirlenmiştir. Son olarak stres büyüme testi de uygulanıp geri dönüştürülmüş PET’nin eriyik haldeki davranışları belirlenmiştir.

Bu noktadan sonra geri dönüşüm işlemiyle meydana gelen dezavantajlar geri dönüştürülmüş PET'nin yapısında da gözlemlendi. Dinamik kompleks viskozitesi oldukça düşüktür. En önemlisi molekül ağırlığı kaybından dolayı ortaya çıkan viskozite düşüşü geri dönüştürülmüş PET'ler için zaman taraması testi ile gözlemlendi. Bu aşamadan sonra en önemli adım geri dönüştürülmüş PET'nin termal kararlılığının iyileştirilmesi olacaktır. Bu amaçla geri dönüştürülmüş PET'lerin yapısına 0.4 wt% ve 0.8 wt% oranlarında zincir uzatıcılar eklenerek termal stabilitenin nasıl değiştiği rapor edildi. Bu sonuçlar göz önünde bulundurulduğunda zincir uzatıcı eklenmesiyle birlikte termal stabilitenin arttığı ve geri dönüştürülmüş PET'nin işlenebilirlik özelliklerinde iyileşmeler gözlemlenmiştir. Ayrıca geri dönüştürülmüş malzemelerin işlenebilirlik özelliklerinin iyileştirilmesinde kullanılan yönremlerden bir tanesinin polimer harmanları hazırlamak olacaktır. Bu bağlamda, mekanik, kimyasal ve işlenebilirlik özellikleri çok iyi olan, yapısı PET'nin yapısı ile çok benzeyen ve bir poliester polimer olan PBT ile çift vidalı ekstrüder vasıtasıyla farklı oranlarda polimer harmanları hazırlanmıştır. Ayrıca PBT PET'nin yavaş kristalizasyon özelliğini de iyileştirecektir. Bu oranlar, %25-75, %50-50, %75-25 şeklindedir. Bu sayede hazırlanan polimer harmanlarının reolojik özellikler üzerine nasıl etki yaptığı incelenmiştir. Hem polimer harmanı hazırlamak hem de incir uzatıcı kullanmak hatta bu iki yöntemi aynı anda kullanmak geri dönüştürülmüş malzemelerin reolojik özelliklerine büyük katkı yaparak termal davranışını değiştirmiştir ve işlenebilirlik özelliklerini arttırmıştır. Ayrıca farklı sıcaklıklar kullanılarak sıcaklık etkisinin tüm malzemelerin termal stabilitesi incelenmiştir ve uygun sıcaklık aralığı seçilmiştir. Aynı zamanda reolojik ölçümler sırasında, geri dönüştürülmüş PET'nin, PBT'nin ve polimer harmanlarının yapısında meydana gelen değişiklikler FTIR cihazı ile test edilmiştir. sıcaklıkla ve zincir uzatıcıyla polikondenzasyon reaksiyonlarının devam ettiği ve bu sebeple viskozite artışının gözlemlendiği sonucuna varılmıştır.

1. INTRODUCTION

The processing of used polymers is as important as the production and use of polymers. In this context, recycling is of great importance. However, the slow developments that occur at the recycling stage cause a major problem for environmental and ecological balance. Every year, hundreds of millions of tons of used polymer waste remains in the environment. As a result of their accumulation, costs and environmental damage are increasing gradually [1]. However, contrary to the recycling of metals or ceramics, some properties are lost during the recycling processes of polymers. One of the most widely used thermoplastic polyesters in the industry is polyethylene terephthalate (PET) which is one of the most important thermoplastic from the polyester group. It may be semi-crystalline or amorphous for use due to its slow crystallization. PET behaves flexibly when it is heated above 72 °C, i.e. above the glass transition temperature (T_g). In these conditions, linear chains are reduced and can be used in the production of bottles or films as uniaxial or biaxial. Then it takes time to form and becomes opaque. In this case, when cooled rapidly, the chains solidify and exhibit high plastic behavior. Owing to its excellent physical and chemical properties, it has enormous applications in food and beverage packaging. Thanks to its high mechanical, thermal and chemical stability, it is widely used in food packaging and beverage bottle. One of the ways to reduce the amount of accumulated PET waste is to recycle the waste and ensure their reuse in the industry. This is very important for the environment. Because the uncontrolled accumulation of PET waste causes serious problems for the environment [4,5]. More than 60% of the PET produced in general is used in the textile industry and in bottle and packaging production. Other areas of use are audio tapes, x-ray films, automotive parts, household products. In this context, PET is a very suitable polymer for recycling and reuse [6,7]. Many researchers have the minimum features required to obtain recycled PET, which will be used successfully in many studies. These properties include the amount of contaminated and physical properties of recycled PET shown in Table 1.1.

Table 1.1 : Minimum requirements to use of recycled PET [3].

Property	**Value**
Intrinsic Viscosity [η]	>0.7 dL.g^{-1}
Melting Temperature Tm	>240℃
Water content	<0.02 wt%
Dye content	<10 ppm
Yellowing index	< 20
Metal content	< 3 ppm
PVC content	< 50 ppm
Polyolefin content	<10 ppm

During the recycling process, number of changes occur in the properties of PET. Thermal and hydrolytic degradation reactions will occur when recycled PET is exposed to high temperatures during processing. The reason that lies behind these reactions is the pollutants that exist in the structure. Since these reactions will cause molecular weight decrease, intrinsic viscosity will decrease accordingly. In addition, an increase in carboxyl and hydroxyl end groups will be observed during these reactions. Many new developments and methods have been reported in order to overcome and protect the decrease in Mw, [η] or mechanical properties of R-PET. In this way, the use of recycled PET is becoming common in the industry [8,9]. In this thesis, studies on the rheological properties of the recycled PET have been carried out to determine the processability of R-PET. First, the rheological properties of raw PET were examined. In order to observe the way through which the rheological properties of PET change as a result of the recycling process, the rheological properties of R-PET have been examined and compared. In addition, while examining the rheological properties, experiments have been carried out between 250 ℃ and 300 ℃ in order to find the temperature at which the two different materials can remain stable. In this way, the effect of temperature on the rheological properties was investigated. After the recycling process of R-PET, a decrease in viscosity was observed due to loss of molecular weight. Two different methods have been considered in order to develop these features. Chain extenders in different ratios have been used to increase the processability of R-PETs. In this way, improvements in rheological properties and rheological behavior were observed. In addition, a second method was used to prepare polymer blends. Firstly, the rheological properties of PBT were studied and their effect on R-PET were investigated. It was observed that PET and PBT behave very differently when exposed to heat. Specifically, while there was an increase in the viscosity of PET, there was a decrease in the intrinsic viscosity of PBT. When these results were evaluated, the degradation of PBT was observed. However, in order to explain this behavior in recycled PETs, FTIR analysis was applied. It was concluded that with the FTIR analysis and literature studies, the reason of the increase in intrinsic viscosity in the rheological measurements of R-PET is poly esterification reactions. In addition, the effects of the use of chain extenders on the rheological properties of the blends were investigated. Rheological behavior significantly determines the processability of a polymer. Initially, R-PETs showed Newtonian behavior. In fact, it is expected to observe shear thinning behavior, which is the type of non-Newtonian behavior in applications. This behavior was observed with the use of chain extender.

2. LITERATURE REVIEW

2.1 Polyethylene Terephthalate (PET)

Polyesters are types of polymers formed by a condensation reaction of two small monomers. There are many types of polyester used in the industry, but the most commonly used polyester is Poly(ethylene terephthalate). Poly(ethylene terephthalate) is obtained by condensation reaction of terephthalic acid or its derivatives (e.g. dimethyl terephthalate) between ethylene glycol [10]. An example of the condensation reaction is given in Figure 2.1.

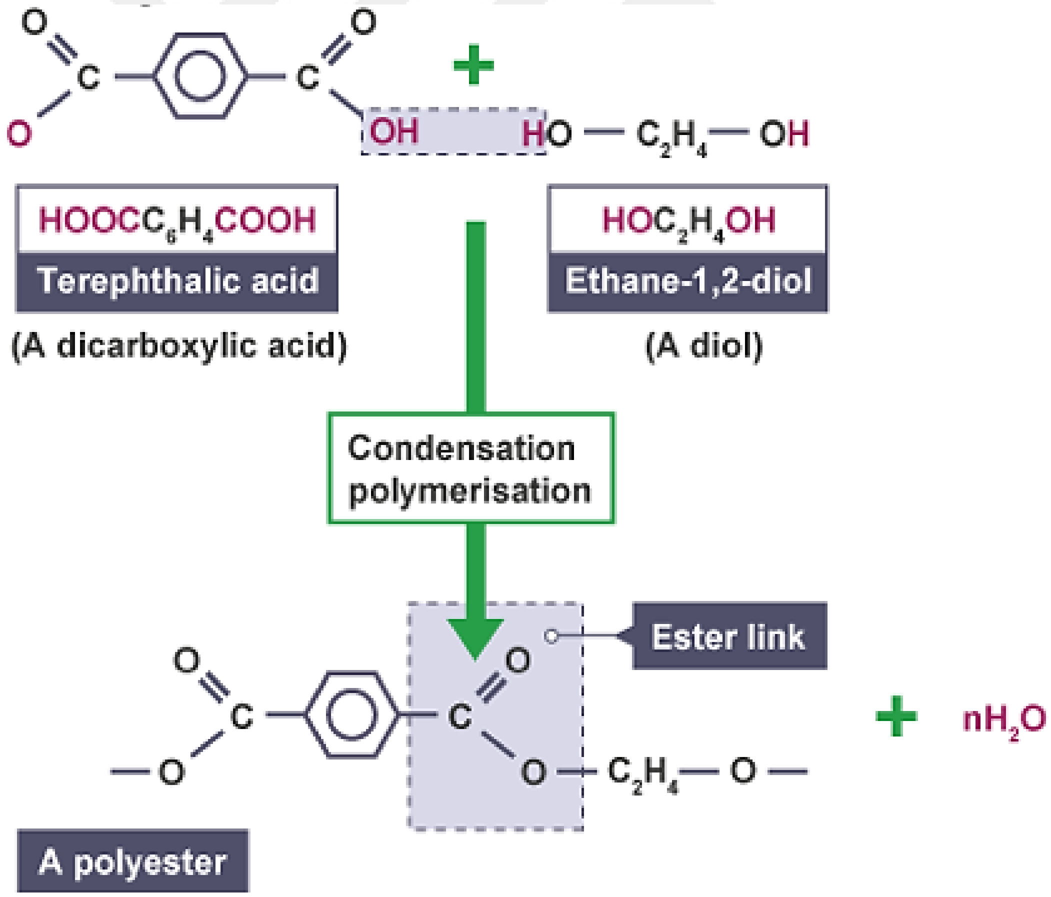

Figure 2.1 : A simple condensation reaction [11].

Poly (Ethylene Terephthalate) (PET) is a commercially important material in the industry. Poly (ethylene terephthalate) is often used as PET. Many companies use different names for their commercially produced PET. Some of the trade names of PET are given in Table 2.1 [12,13].

Table 2.1: Trade Names of PET [12].

Trade name	Manufacturer
Hostadur	Farbwerke Hoechst AG
Arnite	DSM Engineering Plastics
Diolen	ENKA-Glazstoff
Eastapac	Eastman chemical company
Mylar	E. I. Du Pont de Nemours & Co., Inc.
Melinex	Imperial Chemical Industries Ltd.

Poly (ethylene terephthalate) (PET) is one of the major commercial engineering plastics with good thermal and mechanical properties, but with low permeability and chemical resistance [14]. Polyethylene terephthalate (PET) has become one of the widely used thermoplastic polyesters in recent years place in the plastic bottle industry. It is also used in packaging, engineering, automotive industry, fibers making, clothing and beverage containers making. Moreover, it can have biomedical applications. So, there are hundreds of different applications in the industry [15]. PET is also used as an insulation material for cloths and as fiber filling for furniture and pillows. PET can be used in artificial silk if it is produced in very fine filaments, as well as in carpets if produced in large diameter filaments. PET's industrial applications include yarns used in automobile tires, drive belts, reinforcing materials for fire hoses, seat belts (an application that largely replaces nylon), nonwoven fabrics for stabilizing drainage ditches, grilles, and rail bearings. and nonwoven fabrics for use as diaper top sheets and disposable medical garments. [16,17].

The standard physical and chemical properties of PET are shown in Table 2.2.

Table 2.2: The standard physical and chemical properties of PET [16].

Property (Unit)	Value
Molecular Weight of repeating unit (g/mol)	192.2
Weight Average MW (g/mol)	30.000-80.000
Glass transition Temperature (°C)	69-115

Table 2.2 (continued): The standard physical and chemical properties of PET [16].

Property (Unit)	Value
Melting Temperature (°C)	265
Heat of Fusion (j/g)	166
Specific Density (g.cm^{-3})	1.37-1.42
Water Absorption Rate (%):	min: -4
Breaking Strength (MPa)	50
Elongation (%)	70
Tensile Strength (psi)	6600
Compression Strength (psi)	14000
Flexural Strength (psi)	16000
Flexural Modulus (psi)	400000
Impact (Izod ft. lbs/in)	0.8
Hardness	R120
Deflection Temperature (° F)	@ 264 psi: 212
Utilization Temperature (° F)	max: 212
Melting Point (° F)	480
Coefficient of Expansion	0.000039
Arc Resistance	80
Dielectric Strength (kV/mm)	20
UV Resistance	Good
Acids Resistance	Good
Alkalis	Good
Solvents	Good

2.1.1 Synthesis of PET

Polyethylene terephthalate (PET) is a stable polyester due to its chemical structure. Its area of use has significantly increased over the past decade, with a wide range of applications ranging from beverage bottles, food containers to electronic components to fiber in the textile industry. Usually, recycled PET bottles are used to make polar clothes as well as plastic bottles. The most common usage area of PET is the production of drinking water bottles [2,18]. Reaction of alcohol groups with acid groups and separation of water is called polycondensation [19]. Polyesters have low intermolecular cohesion (less inter-chain non-binding interactions) so that Poly (ethylene terephthalate) (PET) can be used commercially as a fiber. Chemical structure of PET is shown in Figure 2.2.

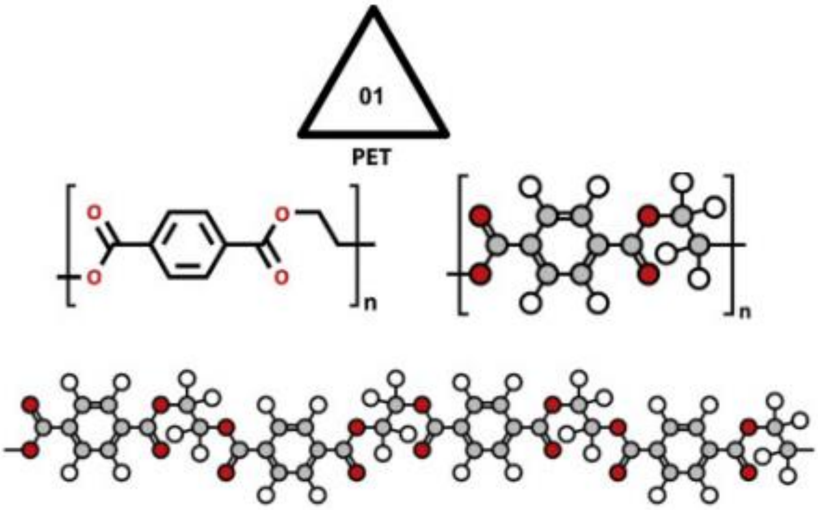

Figure 2.2 : Chemical Structure of PET [19].

PET can be prepared by a polyesterification reaction between 1,2-ethane diol (ethylene glycol) and terephthalic acid, usually using a strong acid or acid catalysts prepared with strong compositions. However, thermally induced side reactions (hydrolysis) of the monomer or oligomer can affect polyesterification under the required high temperature conditions. In addition, there is transesterification, which is a faster reaction and does not allow time for possible side reactions, and so is usually the preferred method [20]. PET is a polymer produced by a polycondensation reaction. A polymerization reaction and molecular structure are determined by esterification and transesterification, which are reorganization of functional groups. The polycondensation reaction of PET takes place in two stages. In the first stage, bis (2-hydroxyethyl) terephthalate (BHET) exits as an intermediate and is carried out commercially in different way. The synthesis initially begins with dimethyl terephthalate (DMT) or purified terephthalic acid (TPA). Dimethyl terephthalate (DMT) or terephthalic acid (TPA) reacts with ethylene glycol. While forming bis (2-hydroxyethyl) terephthalate (BHET), it also causes the formation of by-products, methanol, or water. The second step is the one in which the separation of ethylene glycol and a transesterification reaction of BHET takes place. This step takes place at 270-285°C, which is a higher temperature than esterification. Since the final product has a low viscosity, it provides a thorough mixing of the melt necessary for the evaporation of the produced ethylene glycol [19]. Otherwise, the reversible reaction prevents the formation of a higher molecular weight polymer [21]. When it comes to high temperatures, homolytic breaks occur. A commercial method has been developed to prevent this. High technical applications of PET techniques are processed by solid polymerization (SSP) to prevent homolytic breakage. An inert atmosphere is required for solids polymerization and SSP operates below the melting point. [22]. The composition is very important for this system, but the catalyst also has a big effect. Especially, it has been reported that two different catalysts or combinations of different ratios used for the polycondensation reaction reduce or increase the solution viscosity of PET for a long time during the reaction [23]. Reaction conditions should be considered. PET synthesis consists of two different steps. These two reactions are the initial reaction. During the reaction of the first step, terephthalic acid (TPA) undergoes an esterification reaction with ethylene glycol (EG) at a temperature of between 240°C to 260°C and a pressure of between 300 to 500 kPa. The second reaction is a trans-esterification reaction between dimethyl terephthalate (DMT) and ethylene glycol (EG) at 150°C, 180°C-210°C, 140-220°C and 100 kPa. The trans-esterification reaction is a more preferred reaction. It is preferred because it is easier to purify. The result of these two steps is bis (hydroxyethyl) terephthalate (BHET). The process until BHET reaches 30% polymerization degree (DP) is called Pre-polymerization. The reaction conditions of pre-polymerization were between 250-280°C and 2-3 kPa [2]. The stages of PET synthesis are shown in Figure 2.3 and Figure 2.4. The third step is the final step and the polycondensation process in which the degree of polymerization is increased to 100 and the conditions of this process are 280-290°C [21], 270-285°C [22] and 50-100 Pa. The final stage is the step in which the molecular weight increases. The polymerization reaction will be completed at this stage. Prior to this step, the molecular weight is low, and the PETs produced in this process are important for applications that do not require high molecular weight (MW) applications. Examples are fibers. If high molecular weight PET is to be produced, solid state polymerization (SSP) is required.

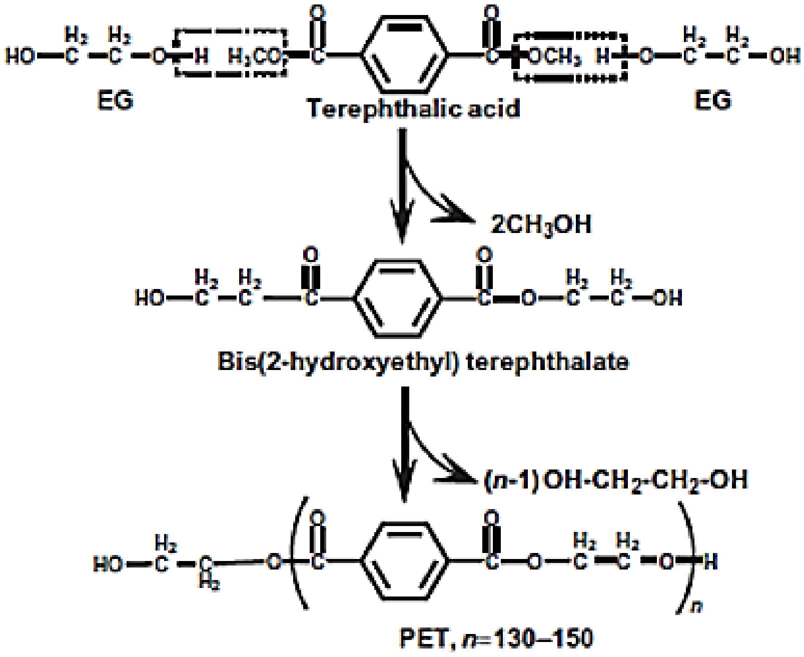

Figure 2.3 : Synthesis of bis(2-hydroxyethyl) terephthalate and polymerization of the same to PET [24].

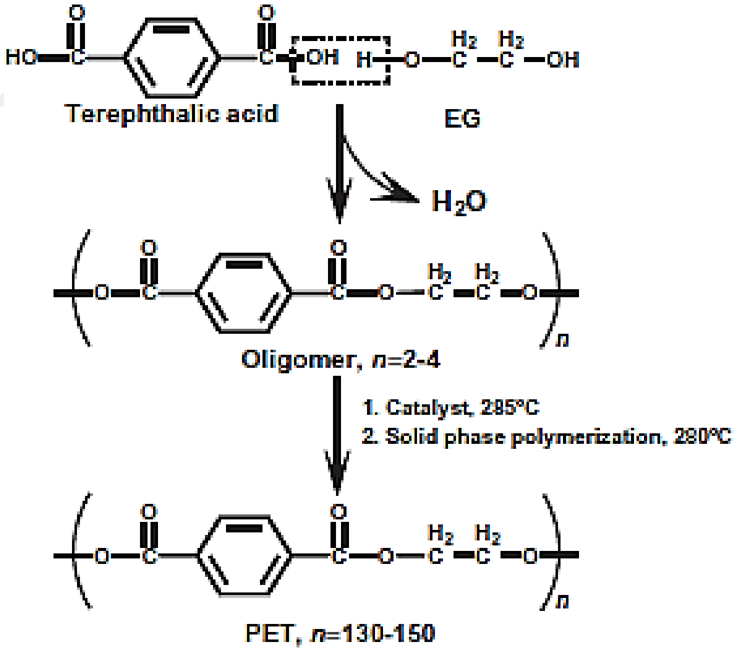

Figure 2.4 : Manufacture of PET by direct esterification reaction [24].

Solid state polymerization (SSP) is used to increase the degree of polymerization (DP) up to 150 as well as to increase the molecular weight (MW) of the polymer to be produced. When the operating conditions for solid state polymerization are investigated, polymerization occurs at a pressure of 100 kPa and 200–240°C in 200–25 h The gradient PET with an intrinsic viscosity [η] of 0.7-0.81 dl/g and used as a field of application is produced by gradient PET solid state polymerization at 210°C for about 15-20 hours [15,16].

2.1.2 Thermal Properties of PET

Since PET is an important engineering polymer, its processability depends largely on its thermal properties, while its thermal properties depend on the degree and quality of crystallinity. PET crystallizes over a wide temperature range. While PET crystallizes, samples with the same degree of crystallinity at different temperatures may exhibit different melting properties, while these samples exhibit multiple endotherms during thermal transitions [25,26]. PET has aromatic benzyl groups at positions 1,4 (para) and the presence of these groups greatly affects and determines the thermal properties. In addition, these aromatic groups determine the hardness and stiffness of the repeating units of the polymers. These are helped to clarify thermal stability for a polymer of PET. The value of the melting temperature of the PET was experimentally determined. Melting temperature of the commercial PET was defined for the fibers from 250 to 265°C. If the annealing process is applied correctly, it is theoretically possible to observe high values up to 290°C [27]. The glass transition temperature (Tg) is related to the chain structure and arrangement of the polymers. The glass transition temperature (Tg) for PET is 67°C in amorphous state. If we look at the semi-crystalline state, the glass transition temperature will change. The glass transition temperature for PET in the semi-crystalline state is 81 °C. In crystalline state or fully oriented state for PET, the glass transition temperature is 125°C. PET is an aromatic semi-crystalline thermoplastic polyester, but it is possible to obtain PET in amorphous state if rapid cooling is applied. The crystallization rate for PET is very slow and 30% of the crystal phase (triclinic crystal structure) can be observed at these conditions. For amorphous and semi-crystalline PET, the application range is different. In the amorphous state, PET will be transparent and can be used in the production of films or thin sheet. It is also one of the most important properties for

- 65 °C (1.8 MPa) for amorphous PET
- 224 °C (1.8 MPa) for PET with 30 % of glass fibers.

The thermal conductivity values of PET are indicated by a range and vary according to the field of use. The thermal conductivity value varies between 0.15-0.4 W / m.K and the upper working temperature is in the range of 115-170°C [28]. DSC curve of virgin PET is shown in Figure 2.5.

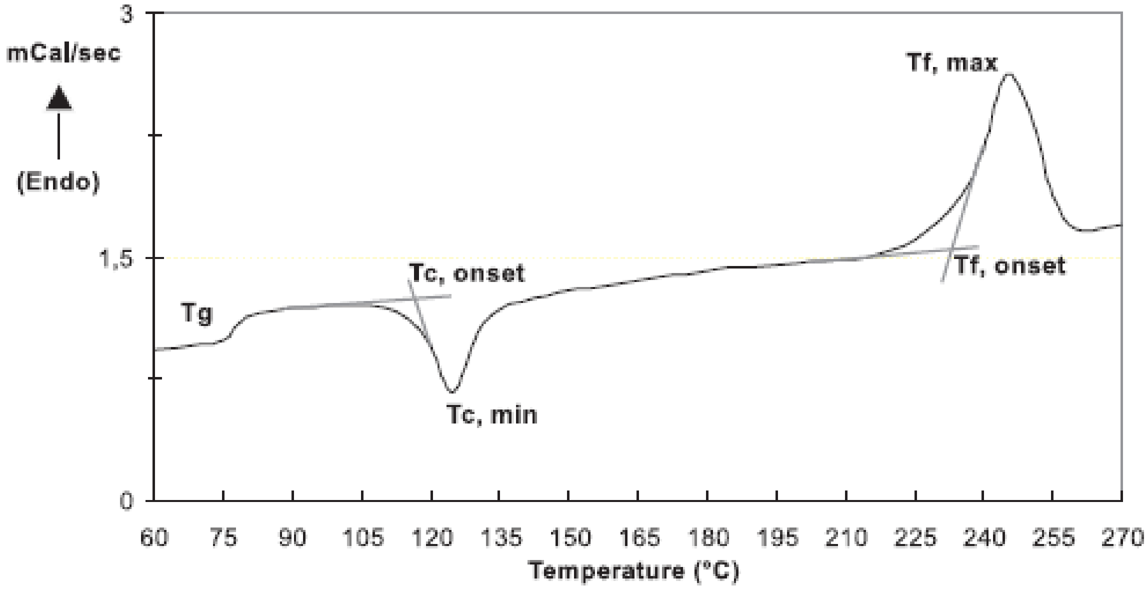

Figure 2.5 : DSC thermogram of virgin PET recorded during the second heating run after quenching from the melt [29].

The results of the glass transition temperature, melting temperature and crystallization behavior obtained from the DSC results are given in Table 2.3.

Table 2.3: DSC results of virgin PET recorded during the second heating run after quenching from the melt [29].

	Tg (°C)	Tc,onset (°C)	Tc,min (°C)	ΔHc (Jg^{-1})	Tm,onset (°C)	Tm,max (°C)	ΔHm (Jg^{-1})	Xc (wt. %)
First Heating Run	-	-	-	-	238	245	63	46
Second Heating Run	81	141	160	15	229	243	22	5

2.1.3 Mechanical properties of PET

Stress-strain curves should be carefully examined to understand the mechanical properties of a polymer. From these values drawn as in accordingly tensile testing, values such as elastic modulus, fracture strength, tensile strength can be determined [28]. Stress-strain curve example is given in Figure 2.6.

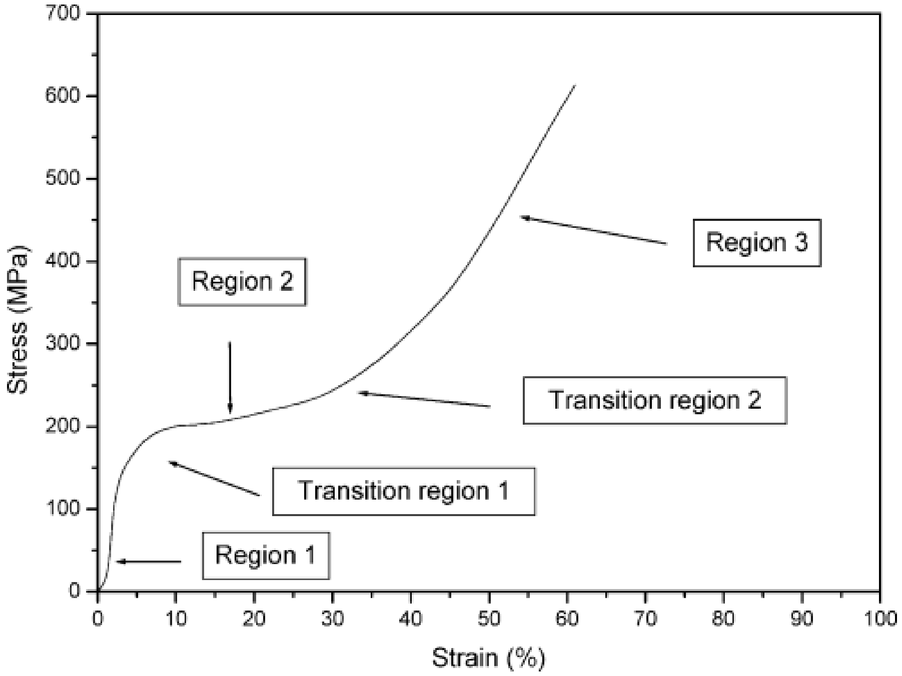

Figure 2.6 : A typical stress-strain curve of PET [106].

Mechanical properties of oriented PET films produced around 250°C by extrusion are shown in Table 2.4. After the PET was exposed to 250°C, its oriented structure was prepared in the extruder. As a result of this process, the material was produced as amorphous. It has been observed that the mechanical properties of the material are better after the applied heat treatment. Elongation at break appears to be higher for amorphous material. But they observed that the films show brittle behavior [28].

Table 2.4: General mechanical properties of PET [28].

Properties	Units	Average Values
Tensile Strength	MPa	55-75
Tensile Elongation	%	50-165
Tensile Modulus	MPa	2000-4000
Izod Notched Impact Strength	J/m	13-35
Ultimate Tensile Strength	MPa	40-45

2.1.4 Rheological properties of PET

The science of rheology defines the ability to process polymeric materials in the molten state and examines the effect of this condition on molecular properties with precision. Polymers can also be defined as macromolecular structures, which exhibit viscoelastic behavior. Viscoelastic behavior can be defined as combined viscous and elastic material behavior. Considering the most important effect on linear viscoelastic behavior, it is the free volume that decreases with increasing molecular weight to a certain extend. As a result, friction and relaxation times increase, which leads to increased viscosity [30]. The elastic part working with entropy and the viscous part consuming energy can be determined by dynamic measurements. The storage and loss module corresponding to these two regions, respectively, can be defined as the angle of loss, representing a solid or more liquid material behavior at different times or frequencies. A phase shift may occur when defining these two regions. The mathematical value of this phase shift allows structural estimates of the behavior of the polymer [31,32]. At high deformation rates, nonlinear behavior occurs on the polymeric material. In particular, when uniaxial elongation tests are performed, it can analyze the melt strength of the polymer. Another important point is that the processability of polymers is largely determined by their elongation properties. The effect of the polymer bulk, which is of great importance in PET processing during the blowing and thermoforming process, on molecular properties can be calculated by structural equations [33]. The behavior of a polymeric material that is in solution or melt depends on time, temperature and intermolecular forces. The presence of the ester group in specifically, its structure which completely determines its behavior, should be carefully examined. PET is a polyester, and if we want to produce a polyester, it is generally caused by the reaction of an alcohol group and an acid group, and as a result of separating the water as a by-product [19]. Since the reaction is reversible, water must be removed from the medium or performed in an open atmosphere. Because water can cause hydrolysis in the formed polymer, damage the structure and cause breaks in the bonds [29]. The structure of PET is determined by the polycondensation reaction followed by the ongoing transesterification reaction [33]. J.R. Whinfield and J.T. Dickson [36] succeeded in obtaining a patent for the viscosity of poly (ethylene terephthalate) under thermal and thermo oxidative conditions. The content of this patent is that the structure of poly (ethylene terephthalate), which is in the melt form is quite complex. They also presented to the literature that PET is a very sensitive material. According to the results observed in the studies conducted in the following years, it was observed that viscosity decreased under both the inert atmosphere and the oxygen atmosphere. In the studies conducted after that, the opposite behavior was observed. According to the results, the molecular weight increase during the kneading of PET was detected in experiments in a torque rheometer under nitrogen atmosphere. With this increase in molecular weight, viscosity increased. They concluded that this result came from esterification or by continuing a transesterification. Although articles have been published on viscosity reduction even under nitrogen atmosphere [37]. They observed that complex viscosity increased in rheological measurements of processed PET performed under nitrogen atmosphere. Given all the experiments, it seems that the thermal behavior of PET has somehow changed in the past 60 years. The strong viscosity reduction behavior observed at the beginning changed over time and evolved to an observed viscosity increase at low shear rates and frequencies. Over the years, mutations of PET's melt properties have been described in two different ways. it is thought to be using large number of model parameters or simplifying kinetics. Frequency dependency is often neglected when considering these [38]. To examine the rheological behavior of a material, using the time shifting factor, PET storage (G ') and loss (G") modules as well as complex PET viscosity (η *) are examined. Matthias Kruse et al. [33] analyzed poly (ethylene terephthalate) with three different polycondensation backgrounds and physical properties with dynamic shear rheology to investigate structural changes caused by thermal exposure. In addition, they examined the nitrogen atmosphere and the effect of air [33]. While the applied modes show a trend that is decreasing first, an increase trend is observed in the continuation. Both graphs clearly show the overall effect of the reaction of polycondensation that occurs in the structure of PET under nitrogen atmosphere, in contrast to measurements in the air. Viscosity first showed a shear-thinning behavior (decreasing operation starting from 500 rad/s), then after the 227 rad/s, it increased strongly at lower frequencies and longer measurement times. This increase in viscosity gave the same result in the second (ascending) study, and after reaching the maximum point, it shifts to shear thinning behavior. When the range of 0.1-100 rad/s is examined, it almost overlaps both for pellets and for samples that have been applied to heat treatment and for the start and end value at 500 rad/s. PET's complex viscosity curve is shown in Figure 2.7. Obviously, viscosity at 500 rad/s has the same start and end value. Therefore, although the increase in viscosity at low frequencies depends on polycondensation reactions and the formation of higher molecular weight species and they obtained shear thinning behavior and chain scission. It is clearly seen that shorter molecules are formed.

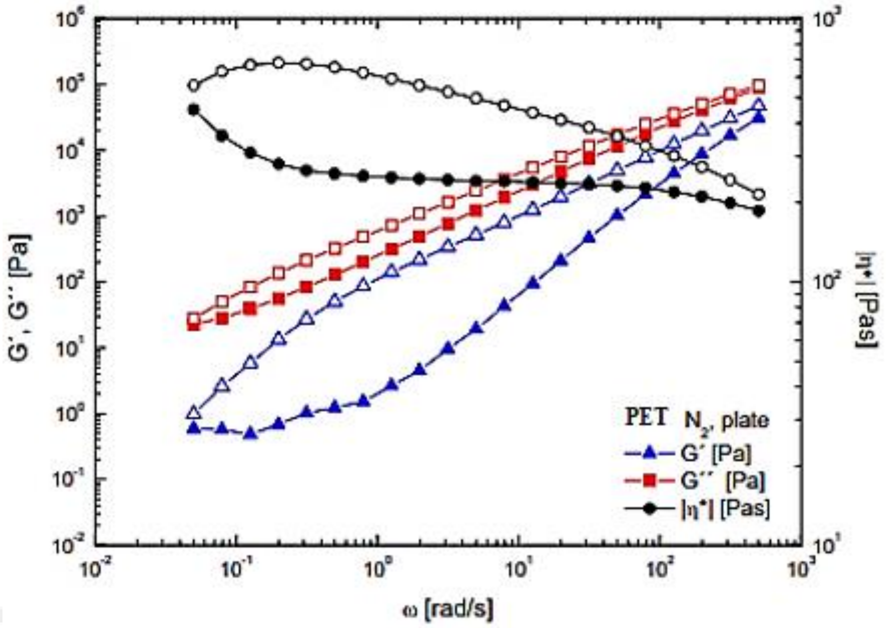

Figure 2.7 : Storage modulus (triangles), loss modulus (squares) and complex viscosity (circles) for an initially decreasing (500 rad.s^{-1} to 0.05 rad.s^{-1}, closed symbols) and subsequently increasing (0.05 rad.s^{-1} to 500 rad.s^{-1}, empty symbols) for a compression molded sample of PET in N_2 [33].

In addition, it can be examined in terms of G '. This can also be examined in terms of G ', which shows a slope of about 2 degrees in the study where the viscosities between 80 rad/s and 1 rad/s decrease, but the slope is smaller in the study where the viscosity is increased The term "nitrogen" is the thermal treatment of the melt material under nitrogen atmosphere. and this increases polydispersity. Polydispersity is known to decrease with degradation resulting from complex viscosity changes [21,33,35-37].

2.1.5 Applications of PET

PET is one of the most widely used engineering plastics in the industry. More than 90% of the PET produced is used in plastic bottle making. However, the structure of PET is polyester and poly alcohols are widely used in its production. The reaction in the production phase is reversible. Therefore, these bottles should be used in products other than alcohol. Otherwise, alcohol triggers the reaction to reverse, causing degradation in the structure. Moreover, PET is widely used in other industries. PET is also commonly used as a fiber in the textile industry. An example of application area of PET is given in Figure 2.8. In addition, it is possible to use it in the automotive supplier industry. PET can be used as Masterbatch, monofilament, electrical insulation material, reinforcement in the construction industry. The use of PET is also common in the packaging industry. It is also suitable for baling and various applications in the industry. In this way, it is an alternative to metal. It is widely used in packaging many products such as Vegetables, Fruits, medicines, beverages. This is due to its cheapness, other physical features, and its strength [29,39].

Figure 2.8 : Examples of PET beverage bottle [40].

2.2 Polymer Recycling

Because of the depletion of resources and the increase of ecological degradation, recycling of polymer materials is needed in the industry. One of the biggest problems faced by the polymer industry is the elimination of the plastic materials produced after use. Because it takes centuries for these plastic wastes to disappear from nature. In order to protect the environment, it is necessary to encourage the polymer industry to recycle waste. Recently, recycling of plastic wastes has been focused on recycling poly (ethylene terephthalate) (PET). Tons of pet bottle waste cannot be disposed of each year and are mixed with nature. Bottle grade PET is one of the most widely used packaging materials for water and beverages [35,36]. Recycling of PET is one of the most accomplished method of polymer recycling and is the most widely used It is possible to divide into 3 different classes. These methods include chemical recycling, mechanical recycling, and energy recovery (i.e., combustion, burning). There are various methods in the literature in relation to how to recycle PET. Compared to other polymer materials, PET waste can be easily collected and converted into useful end products after easy recycling processes. Many researchers have researched PET bottle recycling methods so far and these methods have become available today [37,38].

Plastic recycling refers to the re-processing of a plastic wastes in the industry to get a product that will be used for the same purpose similar to the original plastic. When we wanted to classify plastic recycling methods, we mentioned that there are four different types of plastics: "primary", "secondary", "tertiary" or "energy recovery" recycling. The production of plastic bottles from the mixtures of recycled PET (R-PET) and virgin PET is one of the biggest examples prepared by the method of primary recycling. The secondary (mechanical) recycling process is applied when it is necessary to use it for different purposes other than the original material from which the recycle material is produced. The recovered material generally has lower properties compared to the original material. However, the product obtained by this method does not have chemical decomposition, so that the material obtained is offered as 'down grinding'. The stages of primary and secondary recycling processes are as follows; separating, grinding, washing and extruding that are mechanical processes. Mechanical recycling processes cause different degrees of degradation in polymers, so the number of applications of mechanical recycling processes is limited and applied to the point where the polymer will not degrade. In the tertiary (chemical) recycling method, chemical processes are applied to recover petrochemical components in plastics. An example of this is the pyrolysis reaction that occurs at high temperatures. It is not a widely used method in the industry because it requires the utilization of great amount of energy. Another method of recycling plastic waste is the incineration in plastics. In this method, the energy generated during combustion is used as heat. Once a product is burned, it cannot be recovered. This method is not an application from cradle to cradle [45,46].

2.2.1 Recycling methods and supporting technologies

Recycling of PET is one of the most accomplished method of polymer recycling and is the most widely used It is possible to divide into 3 different classes. These methods include chemical recycling, mechanical recycling and energy recovery (i.e., combustion, burning). There are various methods in the literature in relation to how to recycle PET. Compared to other polymer materials, PET waste can be easily collected and converted into useful end products after easy recycling processes. Many researchers have researched PET bottle recycling methods so far and these methods have become available today [44,45]. Plastic recycling refers to the re-processing of a plastic wastes in the industry to get a product that will be used for the same purpose similar to the original plastic. When we wanted to classify plastic recycling methods, we mentioned that there are four different types of plastics: "primary", "secondary", "tertiary" or "energy recovery" recycling. The production of plastic bottles from the mixtures of recycled PET (R-PET) and virgin PET is one of the biggest examples prepared by the method of primary recycling. The secondary (mechanical) recycling process is applied when it is necessary to use it for different purposes other than the original material from which the recycle material is produced. The recovered material generally has lower properties compared to the original material. However, the product obtained by this method does not have chemical decomposition, so that the material obtained is offered as 'down grinding'.

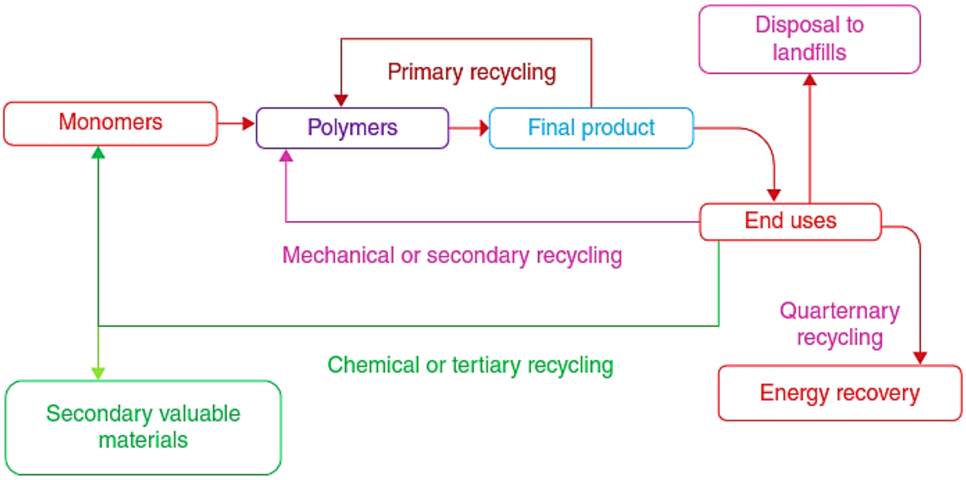

Figure 2.9 : Recycling methods [45].

The stages of primary and secondary recycling processes are as follows; separating, grinding, washing and extruding that are mechanical processes. Mechanical recycling processes cause different degrees of degradation in polymers, so the number of applications of mechanical recycling processes is limited and applied to the point where the polymer will not degrade. In the tertiary (chemical) recycling method, chemical processes are applied to recover petrochemical components in plastics. An example of this is the pyrolysis reaction that occurs at high temperatures. It is not a widely used method in the industry because it requires the utilization of great amount of energy. Another method of recycling plastic waste is the incineration in plastics. In this method, the energy generated during combustion is used as heat. Once a product is burned, it cannot be recovered. This method is not an application from cradle to cradle [45,46]. Recycling methods are given in Figure 2.9.

2.2.1.1 Primary recycling

The recovered plastic is used in products with performance characteristics that are equivalent to those made using virgin plastics. Ideally, closed-loop recycling takes the recovered material and uses it back in the original application. An example of primary recycling is where PET recovered from postconsumer bottles is used in the production of new bottles. In the primary recycling process, plastics containing a minimum number of contaminants are recycled for reuse for the same purpose [47]. Recycled plastic is produced using virgin plastic, which has previously been used for any purpose, and is used in products that have equivalent performance characteristics to virgin plastic. The closed-loop recycling method is the most ideal and allows the recycled material to be reused in the original application. The most common example of the primary recycling method is the use of recycled PET in the production of PET bottles [48]. The first step in primary recycling is to clean the material and separate it from contaminants. As a second step, the material is re-stabilized and adds modifying agents to increase the impact resistance falling with the recycling process. Usually, scrap plastic, cleaning materials, products with specification problems are used for the primary recycling process. Given specific examples, large parts used in areas such as automotive bumpers, instrument panels, refrigerator panels, and vinyl seat covers are the source of raw materials for primary recycling. Other major sources of raw materials are components of building materials such as roofs and windows. In addition, olive coatings made of nylon, polyester fibers are among the most important raw material sources for the primary recycling method [49].

2.2.1.2 Mechanical recycling (Secondary recycling)

Secondary mechanical recycling is one of the most widely used recycling methods in the industry. Mechanical recycling has become widespread in Europe recently, there are approximately 3000 companies working in this field and there are approximately 100 companies that purchase mechanically recycled plastics to produce new products. Materials produced by secondary recycling are often used in intermediates or semi-productions such as pellets. Only 13% can be used directly on final products such as floor coverings, culvert and plant pots [50]. Secondary recycling of plastics is applied to products where performance is least needed compared to the original application. Floor coverings made from mixed polyolefins are an example of secondary recycling [49]. In the secondary and primary recycling method, only thermoplastic polymers can be reprocessed because the chemical structure of thermoset materials is changed when they are exposed to heat and cannot be recycled. There is no changed in the chemical structure of the polymer during secondary recycling, but the presence of water and trace amounts of acid in the medium leads to chain scissions and the molecular weight of the polymer decreases. The decrease in molecular weight that occurs during secondary recycling also leads to a decrease in the mechanical properties. Additives can be used to stabilize the material and restore lost properties, or this problem can be solved partially by intensive drying a of vacuum degassing [51]. If there is contamination in the main polymer, the mechanical properties may decrease again. The reason for this is that there is no compatibility between the contamination and the main polymer matrix. In general terms, the recycled form of a pure polymeric material has better mechanical properties than a recycled mix polymeric material [52]. Mechanical recycling is a physical method in which plastic wastes are reused by cutting, crushing or washing the appropriate quality granules, flakes or pellets to produce new products. After these steps, as a final step, the new product is melted by extrusion and takes its final form.

Figure 2.10 : Mechanical recycling steps [14].

Recycled material and virgin material are generally used for polymer blends prepared to improve the properties of recycled materials [53]. Mechanical recycling steps are shown schematically in Figure 2.10. This method has its advantages as well as its disadvantages. The most important disadvantages are that solid wastes are heterogeneous. Also, if the molecular weight of virgin material is low, this is a disadvantage. Because, during the recycling process, as the material will lose some of its molecular weight, it causes loss and loss of product properties in each cycle. Intensive drying has been recommended and chain extender additives are used to eliminate molecular weight losses. In addition, after vacuum degassing, it can be reprocessed. It is a very economical method considering commercially [14].

2.2.1.3 Chemical or feedstock recycling (Tertiary recycling)

In the chemical recycling method, unlike other recycling methods, chemical structure of the material changes as well as its physical structure changes. It is known that the chemical structure does not change while the physical structure changes in other methods. The new recycled material by this method is used to reproduce virgin material [46]. Chemical recycling is also known as tertiary recycling. This method involves the total depolymerization step for the conversion of virgin polymer to monomers, or partial depolymerization step for oligomers. Monomers produced after depolymerization the polymer are polymerized [54]. Chemical recycling is an advanced technology that transforms polymers into raw materials such as monomers, oligomers or mixtures of other hydrocarbon compounds, making them suitable for use as input for the production of a new product [55]. This method is called chemical recycling in that it leads to chemical changes in the structure of the polymeric material. When the product formed after chemical conversion is considered as a fuel, it is suitable for use and has been proven as a result of the studies on it. This approach is an important step in ensuring sustainability [55]. Tertiary recycling method is more important than other recycling methods due to its use as an energy source. Tertiary recycling method is more important than other recycling methods due to its use as an energy source. Chemical recycling is carried out in a number of different ways. The method called thermolysis has drawn a lot of attention. The reason for this is that thermolysis is carried out in a high temperature and non-oxidative environment [56]. Chemical recycling implies that the chemical structure of the material is changed. This means that the resulting chemicals can be used to produce the original material again [57]. Chemical or feedstock recycling (tertiary recycling) is defined as the process leading to the total depolymerization to the monomers, or partial depolymerization to oligomers and other chemical substances. The monomers could subsequently be repolymerized to regenerate the original polymer [54]. In other words, chemical recycling is an advanced technology that transforms plastic materials into smaller molecules, mostly liquids or gases, suitable for use as feedstock material starting with monomers, oligomers, or mixtures of other hydrocarbon compounds, or as input for the production of new plastics and petrochemicals by means of heat or chemical agents [50]. The term chemical is used because a change occurs to the chemical structure of the polymer. The final output in chemical recycling is very useful as a fuel, which has been proved scientifically. It uses a technique called depolymerization, which can be very profitable and beneficial from the sustainability point of view [50]. Tertiary recycling is attracting much attention because of its possible use as an energy resource. Chemical recycling methods include various methods. These include chemolysis/solvolysis (hydrolysis, alcoholysis, glycolysis and methanolysis), cracking (catalytic cracking, hydro cracking, thermal cracking) and gasification or partial oxidation [45].

2.2.1.4 Energy recovery or quaternary recycling

With this method, the energy contained in the plastic is recovered. Energy recovery is carried out by reducing the volume of organic substances by burning. This method is a very good solution as the polymers have high energy consumption. However, this method is dangerous in terms of ecological balance. The reason for this is toxic substances that will be released into the air during the combustion process, for example, heavy metals, polymers containing chlorine or toxic carbon as well as free radicals during the combustion process, and these radicals cause various problems for human and environment. Therefore, this method is not sustainable. Considering all recycling methods, chemical recycling is the most sustainable method and allows to reach monomeric structure during recycling [46,58,59]. The advantages and disadvantages of all methods are given in Table 2.5.

Table 2.5: Summary of discussed recycling methods [14].

Method	Advantages	Disadvantages
Mechanical recycling	Cost effective	Degradation of materials structure
Chemical recycling	Simple technology for PET	Limited to polyesters
Energy recovery	Generates considerable energy	No ecologically suitable

Recycling PET bottles has become common in recent years. PET is used as beverage bottles in many countries; after the recycling process, recycled PET is brought back as the bottle form, is filled with beverage and offered for re-use. This process is done very precisely. Otherwise, when PET is refilled, it will transfer the pollutants it contains to food or beverages. It is also a known fact that the PET bottle is polyester and uses various poly alcohols in its production. If alcohol is desired to be stored in the PET bottle, it is possible that various side reactions as well as unpredictable degradation might occur in the structure of recycled PET. All recycling methods have been tested many times until now. There are advantages as well as disadvantages inherent to all methods. One of the disadvantages of the mechanical recycling method is that it is only suitable for thermoplastic polymers. In addition, even the minimum impurity level changes the properties of the polymer and prevents the production of quality products. Therefore, recycled polymers are generally gray. Moreover, the hydrogen gas used for the hydrogenation process is very costly. At the same time, ambient conditions require high pressure and this situation is dangerous. In the chemical recycling method, it is difficult to apply to the additional polymer and processes cannot be performed in a single step. All processes are carried out by uniting. In the thermal cracking process, the low concentration structure of the monomer is obtained. This structure is formed by obtaining a hydrocarbon mixture. In the catalytic cracking process, the compounds in the structure of the waste plastic cause poisoning of the catalyst and the catalyst becomes deactivated. For this reason, a carbonaceous residue is formed after a while and this causes an increase in viscosity in plastic. In such structures, heat flow is blocked due to viscosity [56-58].

2.3 Recycled PET

One of the biggest problems facing the plastic industry is the disposal of plastic waste. Recycling of plastic materials is a promising technology in terms of environmental pollution. Poly (ethylene terephthalate) (PET) is already recycled and is widely used in the industry. From these wide variety of recycled materials, there will be many applications for recycled polyesters, depending on the properties of the resin as well as the additives used to increase the properties of the material [60]. With the increasing interest in recycling in recent years, the recycling of disposable Beverage bottles has found a major place in the industry. Poly (ethylene terephthalate) (PET) material recovered from bottles is used in the construction of chemicals, fiber filling, fabric, automotive parts, industrial strapping, sheet and film, new containers for both food and non-food products, containers for baked goods, hiking boots and most clothing made of polyester. In addition to these areas of application, it is observed that many properties have improved thanks to the blending process of virgin PET and recycled PET, so that blends have become trendy worldwide [61]. PET recycling process can be carried out by two different methods as mechanical recycling and chemical recycling. However, mechanical recycling method is widely used in the industry. In mechanical recycling, PETs are collected, washed and grinded. Recycled PETs obtained as products are prepared with different percentages of polymer blends with virgin PET. R-PET is a raw material source for many industries due to its good thermal and chemical properties [62]. One of the most common problems that occur during the processing of recycled PET is that the polyester reaction is reversible. Hydrolysis reaction can occur with thermal exposure and the reaction can be reversed. For this reason, molecular weight losses are experienced [63]. During the recycling process, the molecular weight of PET decreases due to moisture absorption, biological contamination, oxidation, thermal decomposition [64]. Chemical and mechanical degradation occur in the structure of PET during recycling processes. These distortions have a serious effect on the mechanical properties of recycled PET [65]. The recycled PET's chemical resistance and melt viscosity is lower compared to virgin PET. Factors that reduce the physical, chemical, and rheological properties of recycled PET also cause the material to show a brittle behavior. These factors could also result in the reduction of the melting elasticity behavior of recycled PET [62].

2.3.1 Thermal properties of recycled PET

Thermal properties of recycled PET are defined by glass transition temperature (Tg), melting temperature (Tm), melting enthalpy (DHc) and maximum crystallization temperature (Tc, max.). To predict the rate of crystallization in more detail, the minimum crystallization temperature (Tc, clear and Tc, min, respectively) and DTc (Tc, Tc, min) start and values have a significant effect. In general, it is known that the DTc value decreases when the crystallization rate increases. PET has a slow crystallization rate. So, it is a very important feature for R-PET [66]. Hao Wu et al [67] investigated thermal properties of different grade R-PET. They explained the effect of microstructural change that results from multiple processing cycles on thermal properties. The recycled form of PET was used. However, REPET1 means that it has been recycled once. They used two different methods. First one is eccentric rotor extrude, defined as ERE, and second method is twin screw extruder, defined as TSE. They compared the thermal properties of all these materials with virgin PET. In their study, they showed how many times the recycled material was exposed to the same cycle with values of 1-2-3. The results of DSC analysis are given in Figure 2.11.

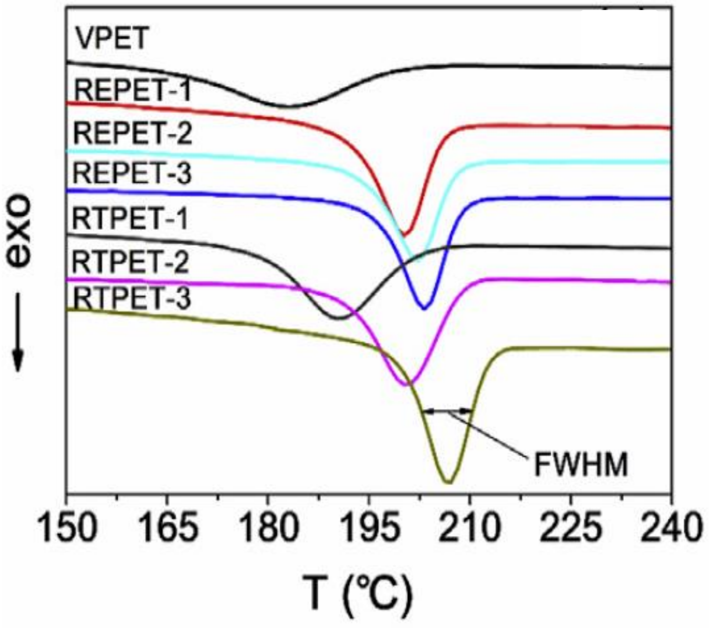

Figure 2.11 : DSC thermograms of virgin and reprocessed PET: (a) crystallization scan, b) FWHM of the crystallization peak [67].

They observed that as the number of recycling cycles increased with ERE methods, the Tc value increased slightly by 3°C when going from REPET-1 to REPET-3. In contrast, for recycled PET processed through TSE, an increase in the number of extrusions observed a high increase in the Tc value from 190.4 °C to 206.1°C. From Figure 2.11 (a), we can also see that the crystallization peaks of REPET-1 are not as sharp as the RTPET-1 crystallization peaks when the crystallization peaks of VPET with RTPET-1 and REPET-1 are compared. FWHM is defined as the crystallization rate, and if FWHM is smaller, the crystallization rate is higher. They observed that the crystallization rate from Figure 2.11 (b). Recycled PET was faster than virgin PET, and the rate of crystallization increased as the number of extrusions increased. It is also known that the crystallization rate is low for virgin PET [61]. DSC results are given in Table 2.6.

Table 2.6: DSC results of R-PET [67].

	Cooling Scan			Reheating Scan		
Material	Tc (℃)	ΔHc (J/g)	Tg (℃)	Tm (℃)	ΔHm (J/g)	Xc (%)
VPET	174.4	-29.6	82.2	248.4	31.8	21.5
R-PET (ERE)	200.3	-41.9	81.5	245.2	32.9	23.5
R-PET (TSE)	190.4	-43.2	78.7	251.4	36.3	25.9

2.3.2 Mechanical properties of recycled PET

It is a fact that the molecular weight decreases as the material is recycled. In this way, the crystallinity of the recycled material increases. Although virgin PET samples are transparent, recycled PET samples display an opaque appearance. The reason for this is the increased crystallinity. Due to the high crystallinity of R-PET, tensile strength and Young's modulus are expected to increase. However, impact resistance decreases [69,70]. Igor Sbarski et. al. [68] have been investigated mechanical properties of R-PET, PET, and their blends. When the mechanical properties were examined, they first applied tensile test. They applied this test to virgin PET, recycled PET, and their blends of 90-10, 80-20, 70-30 and 50-50. These results showed that the materials used had almost similar tensile strength. They used two different 100% recycled PET. These recycled PETs showed a tensile strength of 66 MPa, while other PETs showed that they had a tensile strength of about 57MPa. This is due to the higher crystallinity of recycled PETs, which were previously emphasized in thermal properties, compared to virgin PETs. As shown in Figure 2.12, the young modulus is more corresponding to the virgin PET and recycled PET (food and fiber grade) compared to their polymer blends in different ratios. Comparison of the mechanical properties of the recycled pet is given in Figure 2.12.

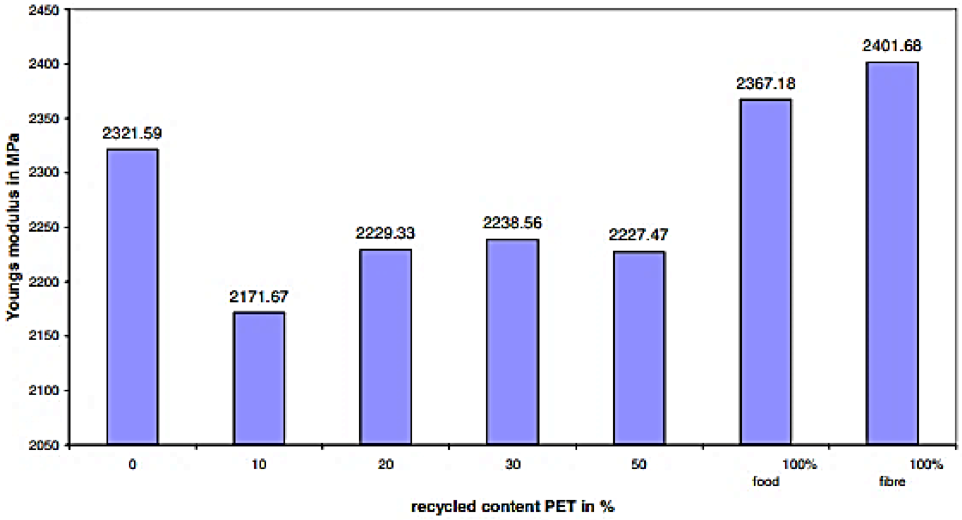

Figure 2.12 : Young's modulus diagram of recycled PET at ambient temperature [68].

However, when this experiment is not performed under ambient conditions, the results are the opposite. The results of the mechanical tests carried out at 110°C are given in Figure 2.13. Tensile strength and modulus of elasticity of recycled PET at high temperatures is lower than virgin PET. The mechanical properties for virgin PET and R-PET are compared in Figure 2.14.

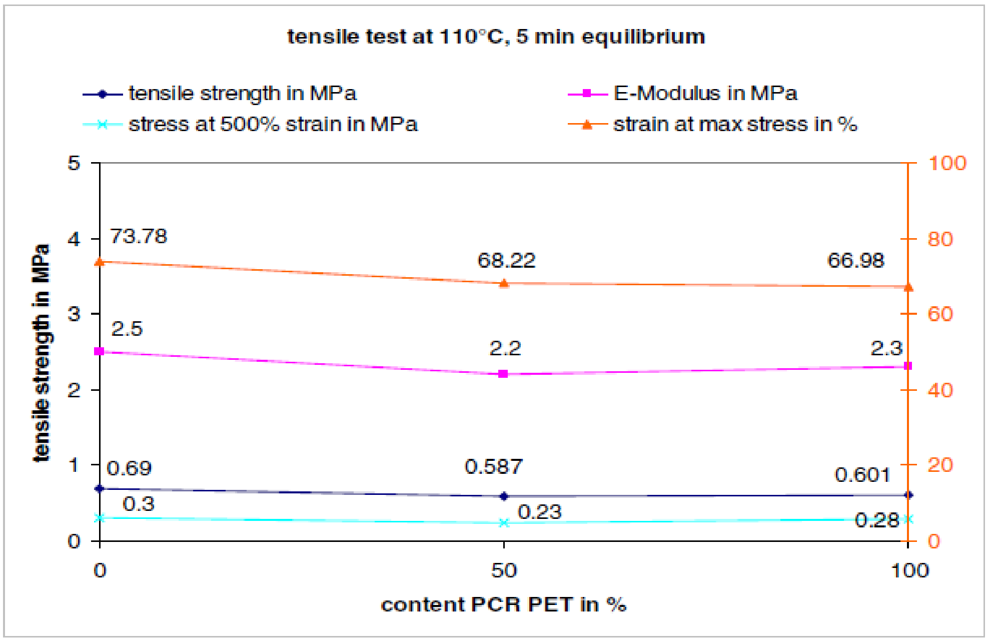

Figure 2.13 : Mechanical properties of PET blends at 110 °C [68].

Hao Wu et. al [67] reported the mechanical properties of Virgin PET and recycled PET processed using different methods. The comparison of mechanical properties is given in Figure 2.14. When the processing cycle of recycled PET produced with ERE method also increased tensile strength increased. But when the recycled PET processed with twin screw extruder, the tensile strength decreased. These two methods showed opposite result. Young modulus values of recycled PET in both methods are greater than the young modulus of virgin PET and showed an increasing trend as the number of cycles increased. They explained that these results are due to the increased crystallinity of the recycled PET with decreasing molecular weight. With multiple extrusion processes, molecular weight and polydispersity index reduction and thermomechanical chain scission are promoted. In addition, the increased crystallinity is explained by the fact that virgin PET is transparent and recycled PET is opaque [67].

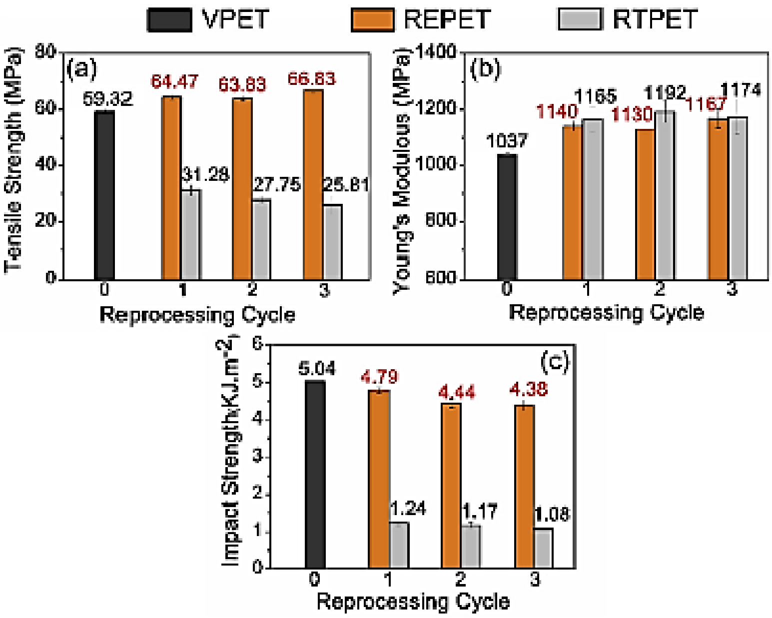

Figure 2.14 : Mechanical properties of recycled PET [62].

2.3.3 Rheological properties of recycled PET

When the rheological properties for R-PET are examined, the first thing to notice is that the intrinsic viscosity decreases. This happens for the sake of the molecular weight losses that occurs during the recycling process. For this reason, the power law index will increase. Moisture or impurities have a major effect on R-PET. It is, therefore, inevitable to have thermal or hydrolytic degradations. R-PET is a more sensitive material than virgin PET because it has formerly been subjected to heat treatment and may contain contaminants. These impurities can also have effects on decreasing molecular weight and viscosity value [107]. Dynamic rheological measurements were carried out to determine the rheological properties of the samples at 280°C under the nitrogen atmosphere [71]. Dynamic time sweep test and frequency sweep test results are shown in Figure 2.15 and Figure 2.16, respectively. The complex viscosity of Virgin PET at all frequency values of 1 to 100 rad/s during measurements was observed to be higher than the complex viscosity values of R-PET (with 0.0% PMDA by weight) in the same frequency range. The complex viscosity of R-PET increased with increasing the amount of PDMA. Moreover, the molecular weight increased with an raise in the amount of PDMA.

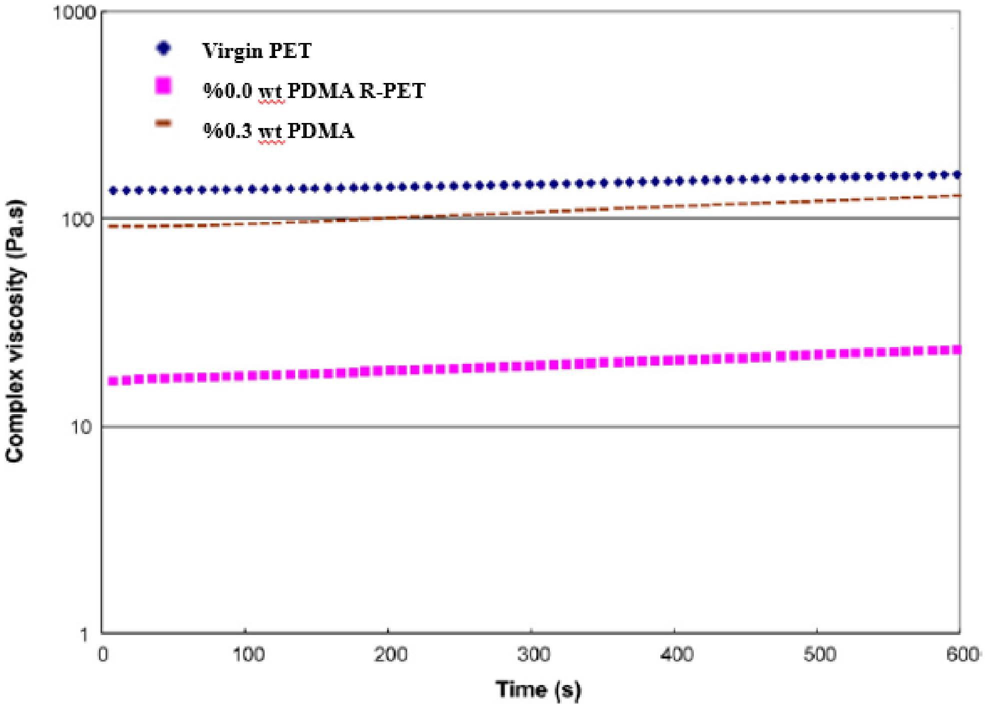

Figure 2.15 : Complex viscosity changes with time for R-PET [71].

While the Neat R-PET sample showed Newtonian behavior, shear thinning behavior was observed at high frequencies. Virgin PET's complex viscosity value is higher than recycled PET at all frequency values between 1 and 100 rad/s. Newtonian behavior was observed for R-PET and PET [72].

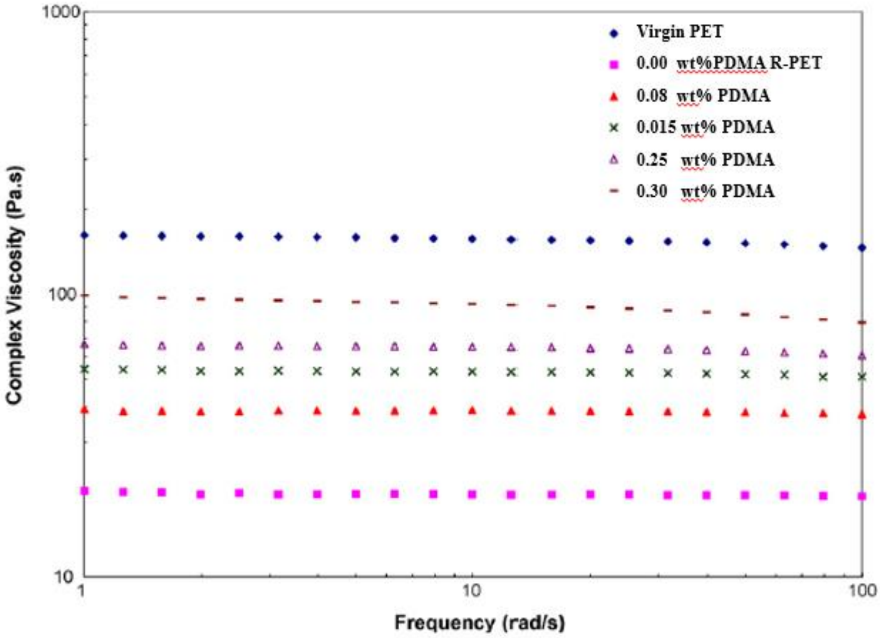

Figure 2.16 : Complex viscosity curve of R-PET and their chain extended samples [71].

The rheological properties of R-PET, which have not been modified from Figure 2.17.

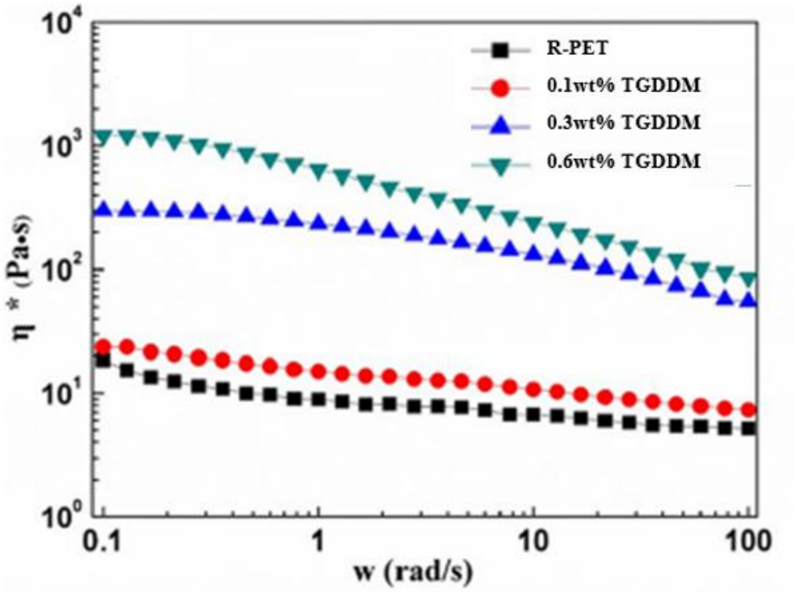

Figure 2.17 : Complex viscosity changes with frequency for R-PET [73].

In another study, similar results were found. The complex viscosity of the raw R-PET does not show any discernible variation across the applied frequency. It preserves almost Newtonian behavior across all frequencies [73].

2.3.4 Application of recycled PET

One of the most common uses of PET is food packaging and bottles. These areas are important market for recycled PET. For this reason, it is widely used in the production of plastic products in contact with food. Bottle-bottle recycling application is widely used in the USA. Recycled PETs are used in bottle production again. Thanks to these applications, the recycling rate in the USA has increased up to 40%. In addition, PET food packaging is produced from 100% recycled PET bottles. That one may perform this process, raising the viscosity of recycled PET has become ready for use with solid state polymerization method. Polymer blends were prepared in various combinations with recycled PET and started to be used in different applications. For example, polymer blends prepared with the use of 54% recycled PET and 46% PP are used in the production of light weight containers [74]. This blend is thought to be durable in hot climatic conditions. It also increases PP moisture resistance. To summarize, recycled PET uses as a packaging material in the food industry with or without food grade, as a reinforcement in the construction industry, and as a reinforcement for the automotive supply industry and composites. In addition, it is widely used in cosmetic and health care bottles. these are also, other application areas clothing products, fabrics and fibres, wind turbines, printing paper [75].

2.4 Chain Extended and Branched PET

Poly (ethylene terephthalate) (PET) is widely used today in the production of soft drink bottles, packaging films and textile fibers. PET recycling is of great interest today due to the growing concern of PET waste on environmental issues. In addition, various distortions occur in the structure of PET during the recycling process. These degradations can be chemical, mechanical, thermal, or oxidative degradations. Due to these degradations, there are many reductions in the molecular weight, melt strength and mechanical properties of the polymer. Chain extenders are usually small molecules and molecules that react with the carboxylic and / or hydroxylic end groups in the structure of macromolecules to form new covalent bonds. However, chain extenders must contain at least two or more functional groups [76]. ‘’Chain extenders react with the functional end groups of PET. For this reason, they are expected to be di/polyfunctional. Therefore, chain extenders can be classified according to functional end groups of PET. Chain extenders, besides the chain extension process, protect the molecular weight loss that occurs during the melt process and reduce the carboxyl group content, which reduces thermal stability. Basically, the application and the way it works are based on this [78]. The content of hydroxyl and carboxyl end groups in R-PET or PET plays a decisive role in increasing or decreasing the molecular weight of the material during processing. [78]. When the Post Consumer PET is processed in the molten state, a reduction in molecular weight occurs. There are also increases of carboxyl content in the melt state [79]. Also, the increase of Carboxyl end groups is an indication that there is thermal degradation in the structure. In other words, thermal degradation and speed can be determined precisely with the increase of carboxyl end groups [80]. In their study, Bikiaris and Karayannidis [94] observed that the carboxyl end group content of PET encourages PET to oxidation during thermal processing. They also observed that the reduction in Carboxyl end groups reduced thermo-oxidative degredation and increased stability for chain extended PET groups. Chain extenders may cause the material to have different properties after the reaction. This depends on the reaction medium, reactivity and number of functional groups. During the Melt process, chain scissions occur in the carboxyl and / or hydroxyl end groups of PET or recycled PET. These broken chains are repaired by reacting with low molecular weight di- poly-functional materials. In this way, chain extension occurs. [3]. During this process, 3 different reactions occur in the structure of PET.

(1) An extender chain molecule reacts with a PET chain. It is called as blocking reaction.

(2) This step is the main target in a chain extension process. A pair of chain extender molecules join two PET chain.

(3) No reaction occurs in the chain extender molecule at the last stage.

The blocking reaction is the first step, and this step is the start for coupling reactions. The reaction rate is determined by the chain extender concentration. In these three types of reactions, highly controlled reactions must be made using di-functional chain extenders. Otherwise, branching reactions will occur. It is an important method to prefer to apply by reactive extrusion so that prevent viscosity decreases that may occur during the chain extension process. It is cheaper and easier to apply than solid state polymerization. [77,78,81]. The carboxyl end groups of the chain elongated PET are consumed by the polyester reaction that takes place during the melt process. The poly esterification reaction of glycol with carboxyl end groups is shown Figure 2.18.

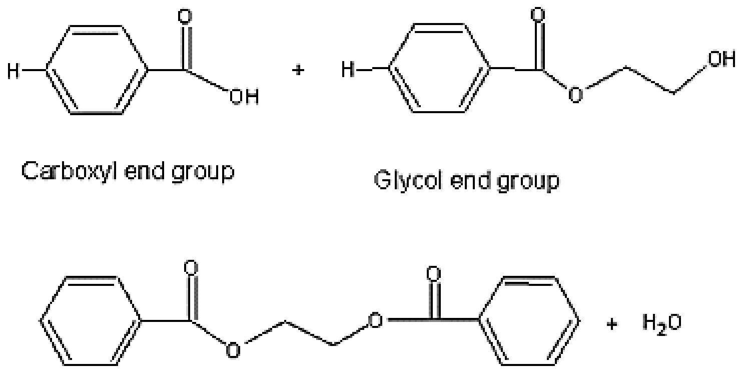

Figure 2.18 : Polyesterification reaction of glycol with carboxyl end groups of PET [82].

We can also classify chain extenders as carboxyl reactive and hydroxyl reactive extenders. 2,20-bis (2-oxazoline), 2,20-bis (5,6-dihydro-4h-1,3-oxazin), N, NO-hexamethylene-bis (2). -carbonyl 1,2-oxazoline) are example of carboxyl reactive chain extenders [82]. When using hydroxyl reactive chain extenders for PET produced by melt process, the viscosity will increase rapidly, because of the increase in molecular weight. 2,20-bis(3,1-benzoxanin-4-one) are example of hydroxyl reactive chain extenders [83]. Examples of chain extender are given in Figure 2.19.

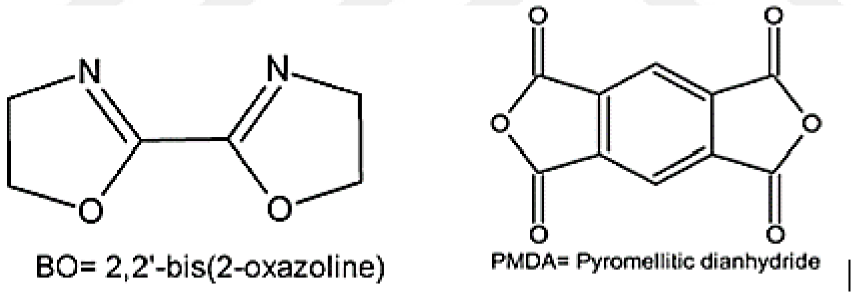

Figure 2.19 : Examples of chain extenders [84].

The reactions with PET for different chain extender types are shown in Figure 2.20, Figure 2.21 and Figure 2.22.

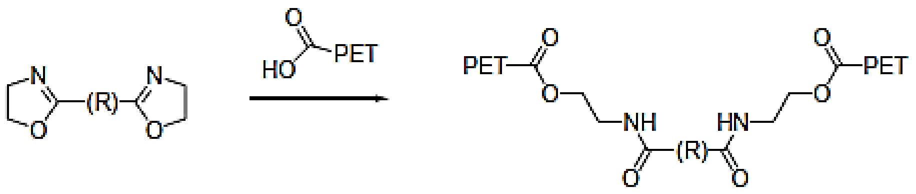

Figure 2.20 : Chain extension reaction of PET with a generic bis-oxazoline [84].

Bis-oxazoline have bis-amide bridging structures. These structures react quickly with the carboxylic end groups present in the structure of PET. In this way, linear chain elongation occurs in the structure of PET [84].

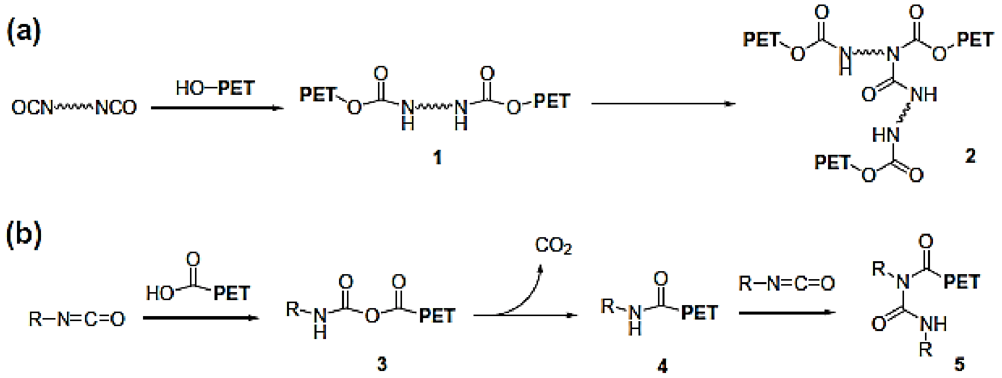

Figure 2.21 : Chain extension and secondary branching reactions of PET with di-isocyanates [84].

In these two reactions, di-isocyanates, and di-epoxides, which are widely used in the industry, have been used as chain extenders. The reaction will take place between di-isocyanates and both hydroxyl end groups of PET and the carboxyl groups. In its reaction with hydroxyl group, carbamate molecule is formed. This reaction is as stable as fast. It then gives a termination reaction with the carboxyl ends of PET. As a result of this reaction, O-acyl carbamate is formed. This structure is unstable and carbon dioxide loss occurs during the reaction and these losses provide decomposition to amides. Also, temperature is a very important factor for this process. The designated processing temperature of PET is between 260 and 280℃. However, urethane, known as carbamate, cannot maintain its stability at these temperatures. different reactions prevent by using high concentrations of isocyanate, which leads to the formation of branched structures [84].

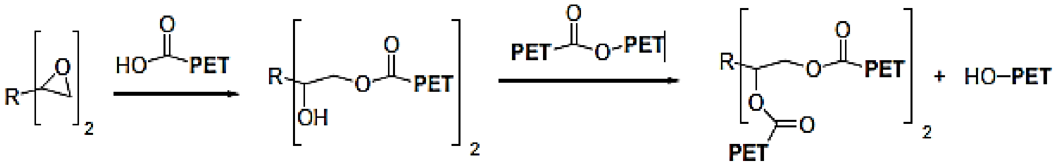

Figure 2.22 : Chain extension and secondary branching reactions of PET with di-epoxides [84].

Unlike isocyanates, epoxide structures prefer to react only with carboxyl end groups in the structure of PET. This reaction is an esterification reaction and leads to the formation of esters. Also, hydroxyl group formation takes place with this reaction. These hydroxyl groups formed undergo transesterification reaction with other PET chains. Chain branching or chain scission is expected at the end of this reaction [84].

2.4.1 Thermal properties of chain extended PET

The effect of using chain extender on the thermal properties of PET has been studied by many researchers [86]. The thermal properties of Virgin PET using differential scanning calorimetry (DSC) have already been studied in many studies. However, unlike all these, how and in which direction the chain extender usage changed the glass transition temperature, crystallization temperature, melting temperature was determined by differential scanning calorimetry (DSC). In these studies, it was observed that chain extensions affect Tg, Tm, Tc, and crystallinity in decreasing direction [83]. Bikiaris et al. [87] used di epoxide chain extenders for virgin PET in their study, and as a result, they observed that the glass transition temperature was not affected by their thermal analysis, but the melting point decreased. In the researches, they have different opinions on this subject. Inata et. al. [83] used different concentrations of chain extenders for PET in their study, and they claimed a completely opposite view from other studies. In other words, they observed that the use of chain extender would not cause major changes on the melting point. Degree of crystallinity determines the application area of PET and Its crystallinity relates to molecular structure and conditions. With the chain extender process, branching reactions and chain entanglements occur in the structure of PET. Therefore, decreases in crystallinity are expected [88]. It has been reported when the degree of branching depends significantly on the concentration of the chain extender used. If the crystallization process is carried out at high temperatures, crystallinity will increase due to the ease of movement of the chains and the ability to regulate themselves [89]. Impurities that occur during the recycling process cause different properties in the R-PET structure. The most important of these is that it increases crystallization. Many studies have reported that they act as nucleating agents in the building [86]. F. Awaja et. al. [86] have been investigated thermal properties of R-PET, PET and different ratio of chain extended R-PET samples. DSC results are given in Figure 2.23

They reported that R-PET samples showed two different melting peaks in this study. In fact, similar results have been observed in previous studies. It is anticipated that crystals with different lamella thickness or partial melting- recrystallization- r1e-melting system will have been realized. Since exothermic events caused by recrystallization do not occur in heat flow curves, this result has been proved not to be partial melting-recrystallization-re-melting. All things considered in previous studies, it was concluded that two melting peaks are isothermal crystallization. In contrast to this behavior, virgin PET showed a single melting peak. This represents the homogeneity of the structure of virgin PET. The crystallization range is wide for amorphous PETs. The cold crystallization peak for amorphous PET was seen only in the extruded sample**.** How the glass transition temperature (Tg), melting temperature (Tm), crystallization temperature (Tc) change in different concentrations of the added chain extender is shown Figure 2.24.

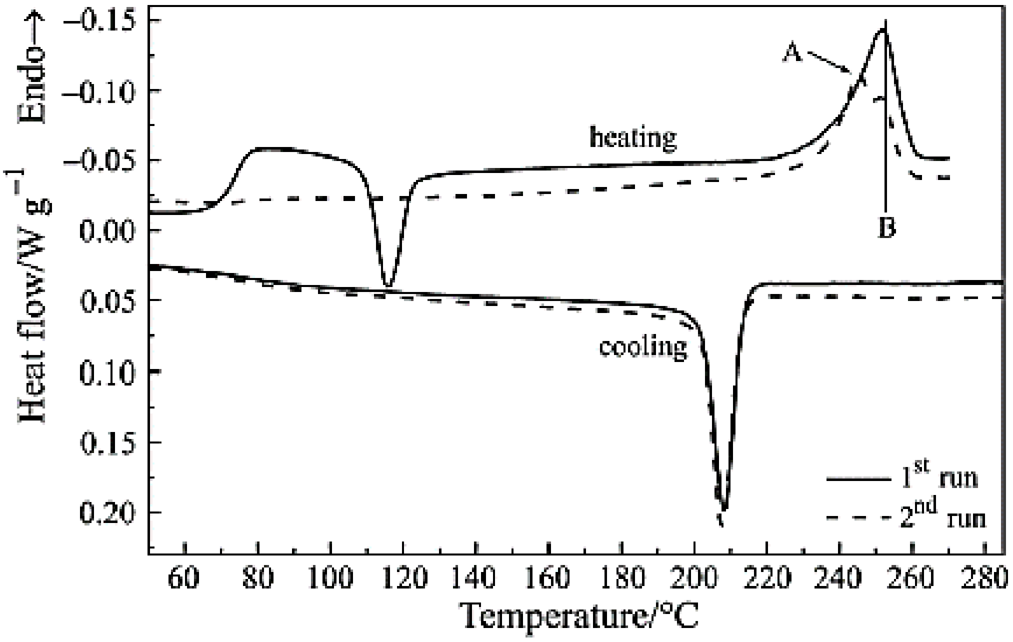

Figure 2.23 : DSC curve of chain extended PET [86].

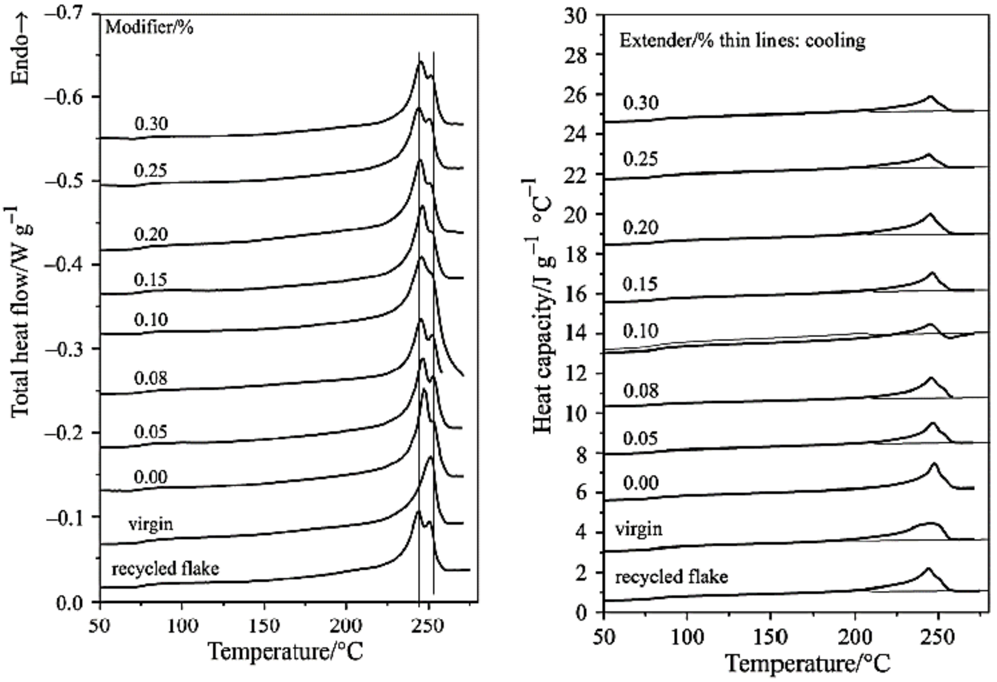

Figure 2.24 : (a) Total heat flow curve of PET (b) Heat capacity curve of PET [86].

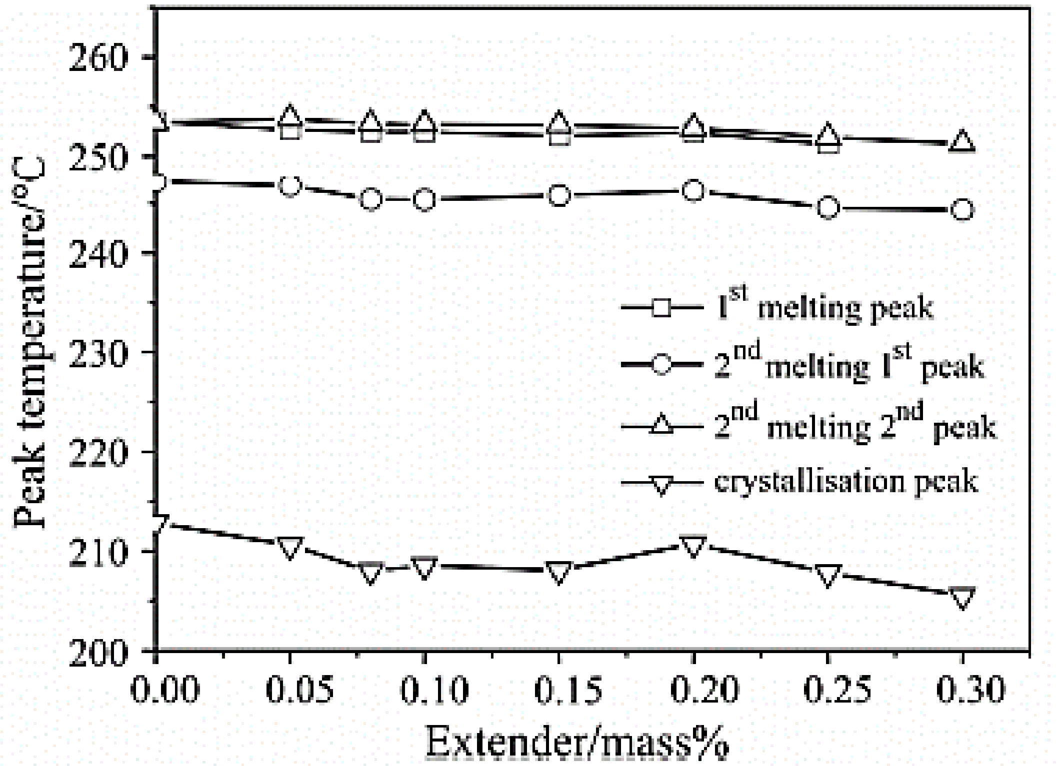

Figure 2.25 : Melting peak temperature of chain extended R-PET [86].

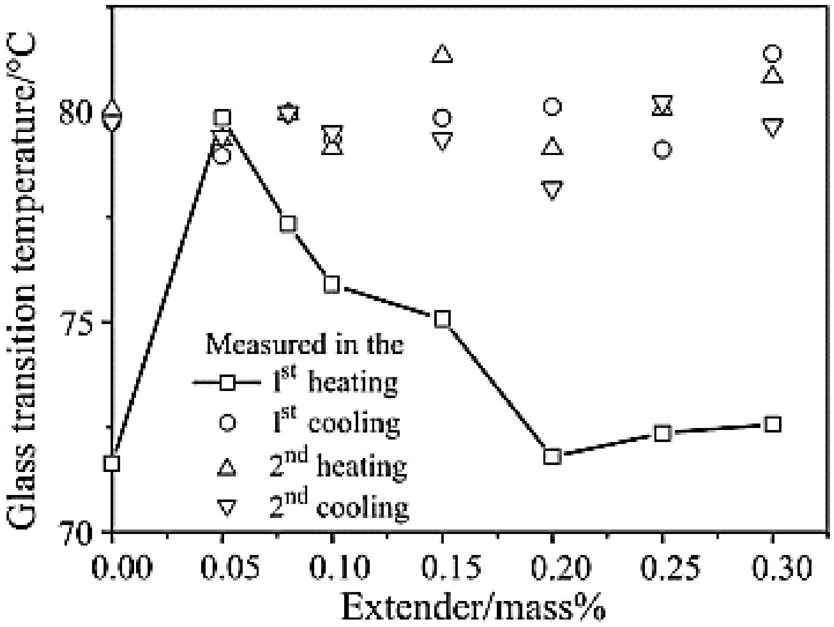

Figure 2.26 : Glass transitions temperature of chain extended R-PET [86].

In Figure 2.25 and Figure 2.26, they observed that melting temperatures and crystallization temperatures are decreasing with increasing chain extender ratio. For virgin PET, a melting temperature of 254°C is observed, while the 0.2% chain extended version of R-PET melts at this temperature. The expected behavior here is the increased viscosity reduction of T_m and T_c. This result proves that chain expansion has taken place. The main factor affecting Tg is the ability of the chains to move and the degree of crystallinity of the structure. Due to reactions such as cross-linking in R-PET and chain extended samples, increases in T_g may be predicted. However, in the experimental results, they observed that there was not a big difference in the Tg of all samples [86].

2.4.2 Mechanical properties of chain extended PET

The tensile properties of the chain extended PET and virgin PET are compared with the tensile test performed and are shown in Figure 2.27. They observed that the general behavior of the materials was hard and tough. In addition, while exhibiting high tensile strength behavior, it also observed high elongation break values. Samples were prepared as amorphous films. However, they observed an opaque appearance due to the orientation of the molecules after yield points. Materials were transparent before application. In stress-strain graphics, breaking strength, elongation at break, Young's modulus can be determined.

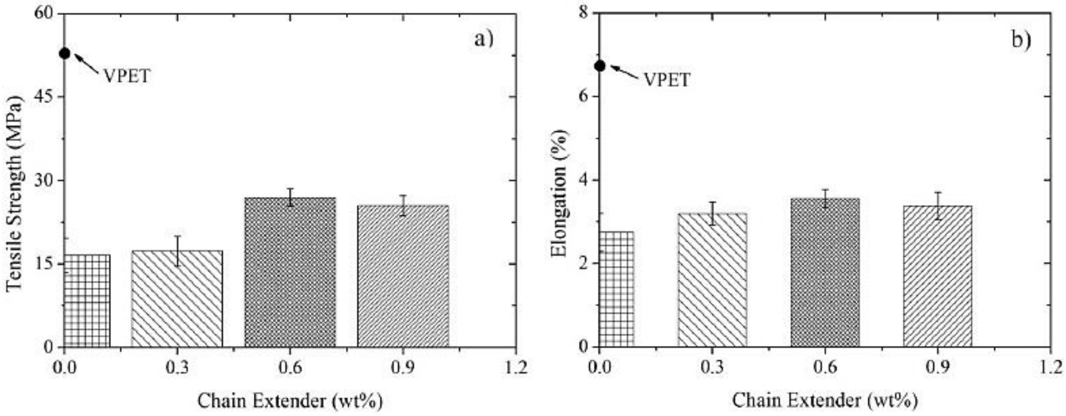

Figure 2.27 : Mechanical properties of chain extended recycled PET (a) Tensile strength (MPa) (b) Elongation (%) [109].

These data play an important role in determining the mechanical properties of materials. These results are summarized in the Table 2.7. They emphasized that it was interesting that the tensile strength of virgin PET (sample 1) raised from 31.14 to 62.3 MPa for sample 5, where the chain extender content was highest. They argued that this was due to cross-linking and branching reactions. In addition, a second result supporting this result occurred in the young module. It was observed that the virgin PET (sample 1) young module increased from 1315 to 1852 MPa (sample 5). In addition, sample 5 has % 350 elongation at break [90]. Supawee Makkam and Wanlop Harnnarongchai [110] investigated mechanical properties of chain extended recycled PET. They prepared chain extended recycled PET with Joncryl which is epoxy based chain extender.

Table 2.7: Mechanical Properties of Chain Extended PET Samples [90].

Sample	Chain Extension Time (min)	Tensile Strength (MPa)	Elongation at Break (%)	Yield Stress (MPa)	Elongation at Yield (%)	Young’s Modulus (MPa)
1	0	31.4	275	43.4	3.9	1315
2	10	36.2	300	50.8	5.0	1455
3	20	43.3	315	61.3	6.5	1767
4	30	52.9	335	63.7	6.5	1826
5	60	62.3	350	66.3	6.5	1852

When the amount of chain extender was 0.6% by weight, they observed an increase in tensile strength and elongation, but When the amount of chain extender was 0.9% by weight, they observed a slight decrease in tensile strength and elongation. They reported that an increase in tensile strength and elongation was observed as a result of the reaction of the broken ends in the structure of R-PET with the chain extender. They reported that when the chain extender amount was 0.9% by weight, reductions in crystallinity reduced tensile strength and elongation [109].

2.4.3 Rheological properties of chain extended PET

It is possible to produce high or low molecular weight for PET. Molecular weight and distribution significantly affect rheological properties. PET with low molecular weight or narrow molecular weight distribution is not suitable for some processes due to its rheological properties. Peculiarly, blow molding, extrusion or foaming processes are among the unsuitable ones. There are many ways to improve the rheological properties of the thermoplastic materials, that is, viscoelastic behavior. These can be additives, branching, chain extension, grafting, controlled cross-linking, or controlled degradation [91]. In this way, molecular weight and distribution can be increased to the desired level and rheological properties can be improved. PET can be modified by many different methods. In this way, melt strength is increased. The most important of this is to perform branching reactions using chain extenders. This method is carried out using different types of materials. Examples of these materials include carboxyl / hydroxyl polyester end groups and anhydride, epoxy, oxazoline, isocyanate, carbodiimide, hydroxyl, tertiary-containing di- or multifunctional reactants [92]. Rheological modification process for PET is performed in three different stages. These are given below, respectively.

1) Modifier can be added while performing polycondensation reaction.

2) Modifiers can be added before the reaction takes place.

3) It can also be made using the reactive extrusion method. This is usually called as reactor modification method.

When a reaction mechanism proposed with PMDA, a chain extender used to improve the rheological properties of PET, is examined, linear elongation occurs at the first stage. This step is the reaction of polyester hydroxyl end groups anhydride with functional groups [93]. As a result of this reaction, two carboxyl groups are formed for per associated PDMA component. The reaction system continues as the esterification or transesterification which forms branching or cross-linking structures after the initial reactions. This reaction shows that chain extension reaction occurs by glycidyl functional group in the PDMA structure esterification reaction of carboxyl end groups or etherification reaction of hydroxyl end groups. These structures promote the polymer to branching or crosslinking [94]. Based on all these inferences, Kai Wang and his colleagues examined and compared the rheological properties of R-PET and their chain extended samples. In this study, the complex viscosity η*, storage modulus G' and loss modulus G" graphs of chain extended R-PET with different SAG-008 / TGDDM concentrations at a screw rotation speed of 60 rpm are shown in Figure 2.28 and in Figure 2.29. Considering the graphic for R-PET. They observed that the complex viscosity of crude R-PET exhibited Newtonian behavior with non-variable behavior. For chain extended R-PETs, they showed shear thinning behavior by decreasing complex viscosities at low frequencies. However, this behavior decreases gradually with increasing frequency values. Especially with the increase in the amount of chain extender used, non-Newtonian behavior was observed, but there was a serious decrease in complex viscosity.

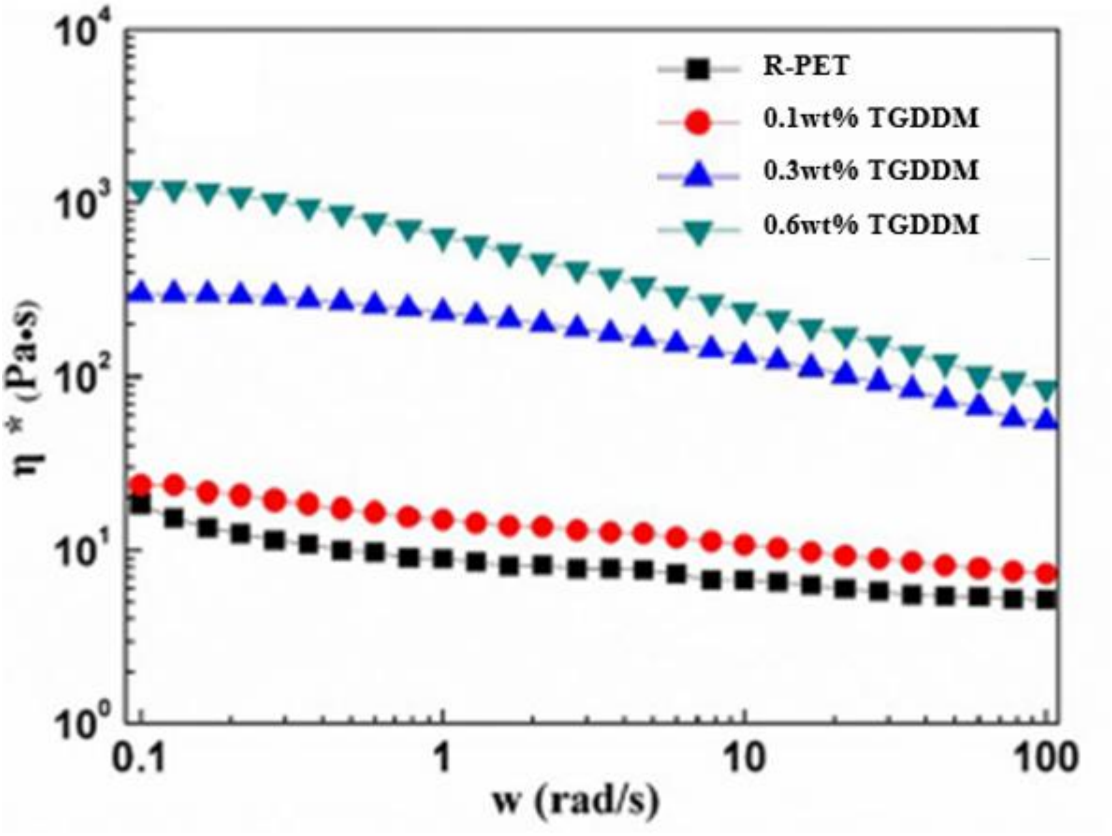

Figure 2.28 : Complex viscosity, as a functional of frequency of R-PET and their chain extended sample [73].

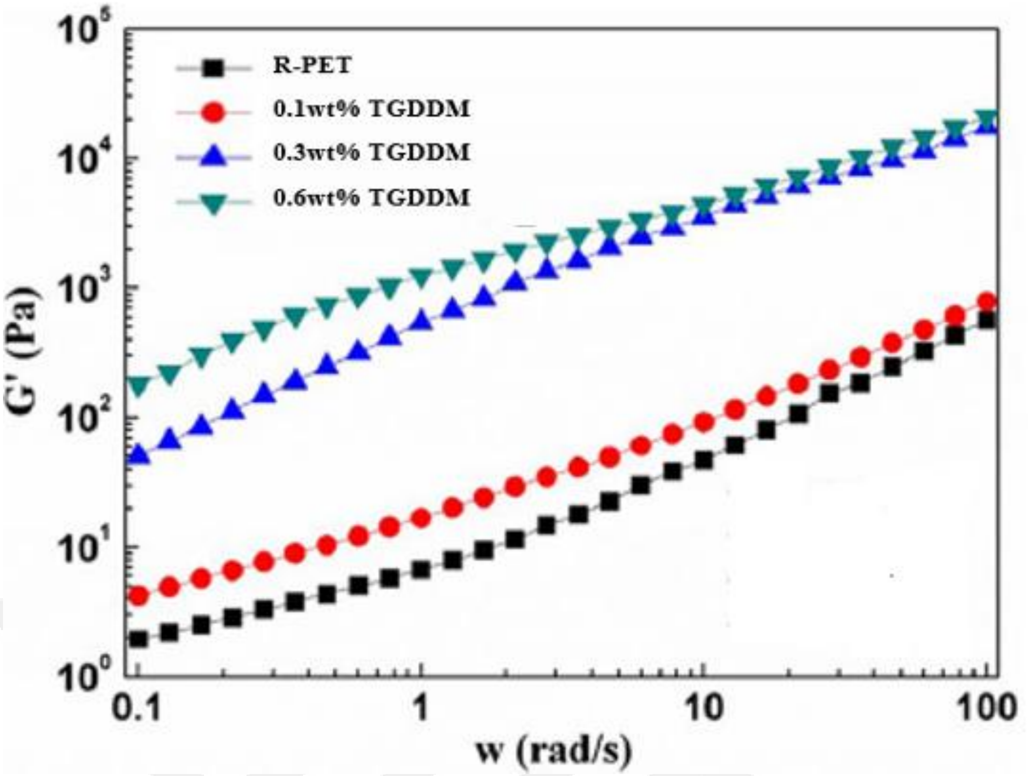

Figure 2.29 : Storage modulus, as a functional of frequency of R-PET and their chain extended sample [73].

In addition, loss modulus and storage modulus have increased. These results are due to the branching and chain extension reactions occurring in the R-PET structure. They associated the cause of this behavior of complex viscosity with the molecular weight distribution. They plotted the Cole-Cole curves to relate the structure of the chain elongated R-PET to the molecular weight distribution. In this study, the graphics were not related to Molecular weight but reported that Mw / Mn is related to chain branching. They also reported that with the increase of the chain extender content, the curve approached the diagonal line. They interpreted this as the increase in the chain extender content as well as the increase in molecular weight distribution. It has been observed that rheological properties are improved [73].

2.5 PET/PBT Binary Blends

Poly (ethylene terephthalate) (PET) and poly (butylene terephthalate) (PBT) are both semi-aromatic thermoplastic polymers. PET is generally used in food packaging and film production, while PBT is generally used in injection molding applications. If a higher heat deflection temperature and more hardness are required in the application, PET is more suitable to use. However, due to its low melt strength and slow crystallization rate, PET has very low processability. Compared with PET, PBT has high moldability properties due to its fast crystallization rate [95,96].

PBT / PET polymer blends are specially designed to increase the processability of PET, heat deviation temperature (HDT) of PBT, in generally, to improve the impact resistance and dimensional stability, surface appearance according to the application [96]. In addition, these polymer blends produced are frequently used in applications requiring high hardness and heat resistance and are also widely used in applications where the surface appearance should be bright. the most common application areas are electrical and automotive applications. The preparation of PBT / PET polymer blends has important advantages. PET is a cheap material, but the crystallization rate is slow. The crystallization rate of PBT is high. Therefore, it provides a great advantage in the industry by reducing the cost and increasing the crystallization rate [98].

2.5.1 Miscibility and morphology of PET/PBT binary blends

PBT and PET can form stable polymer blends in amorphous phase without requiring any compatibilizer [99]. In the study by Avramova [100] PET and PBT showed a single glass transition temperature (Tg) in the amorphous phase. But separate melting peaks have been observed. They also observed changes in the melting point of a component in Blend's structure. They argued that this was related to the existence of the other component. However, it has been observed to be compatible with PET and PBT with only glass transition temperature seen in the amorphous phase. Avramova7 also examined PET / PBT mixtures microscopically. He observed that the crystallization of both components was in the form of spherulite. Escala and Stein [99] suggest that the compatibility of PBT / PET polymer blends is due to transesterification reactions. compatibility of PBT / PET polymer blends is due to transesterification reactions. He also reported that copolymers could be formed during melt processing. With the transesterification reaction, there are block copolymers in the first stage and then random copolymers can be formed. Therefore, transesterification reactions play an important role in determining the morphology of blends using two polyester. It may increase the miscibility of polymer blends, but if this reaction takes place too much, a decrease in performance may occur in the final product [86]. G. Aravinthan, D. D. Kale [101] prepared PET / PBT blends in different proportions and examined their morphology. They examined the morphological properties of PET / PBT mixtures with scanning electron microscopy. The results of the SEM (scanning electron microscope) are shown in Figure 2.30.

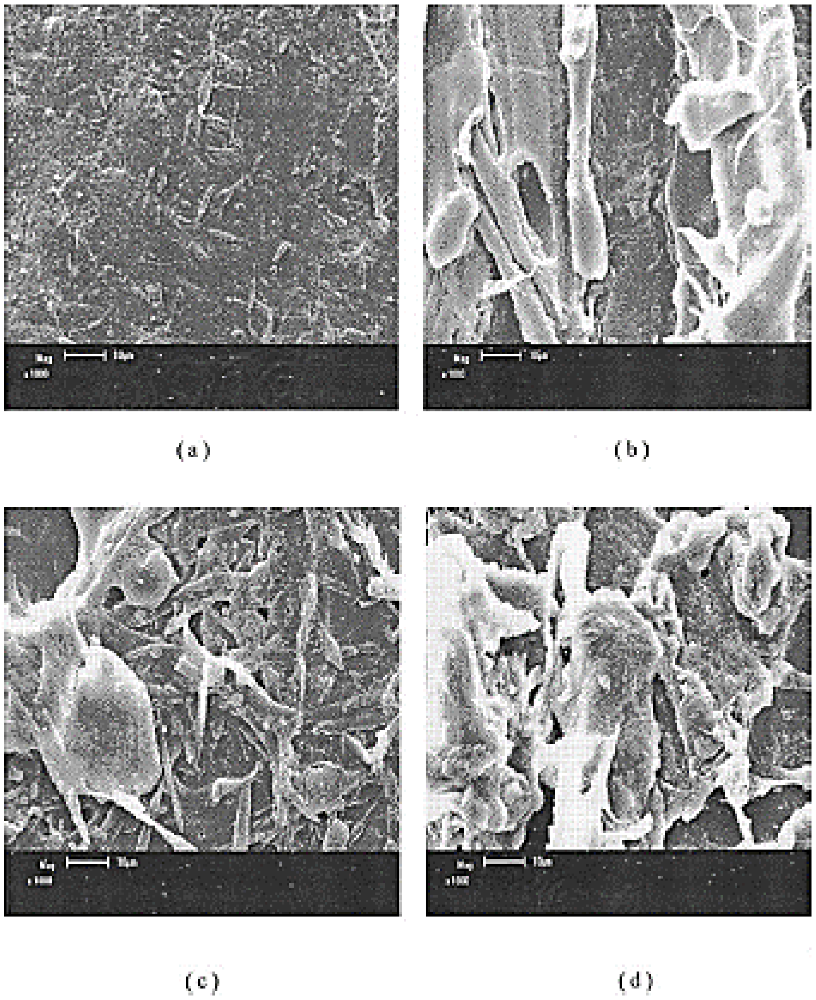

Figure 2.30 : SEM imagine of PET/PBT blends in different ratios (a) 20:80 (b) 60:40 (c) 50:50 (d) 40:60 [101].

When the morphology of PET / PBT blends prepared at the ratios of 40:60 and 60:40, they reported a co-continuous structure. [Sec. 4 (b - d)]. PET / PBT blend prepared in the ratio of 50:50 and 40:60 observed fibril morphology in their blends. However, it showed a co-continuous and unique structure at 50:50.

They observed that the dispersed phase (PBT phase) in the polymer blends with high PET ratio in the prepared blends was larger than the dispersed phase (PET) in the polymer blends with high PBT ratio. They reported that PET and PBT are miscible the entire composition range. They reported that fibrillar structure was formed in polymer blends with high PET usage ratio and the co continuous morphology was reported for 40:60,50:50,60:40 blends. The morphology and compatibility of polymer blends depend on the properties of each component where polymer blends are created, but it is also very important how polymer blends are prepared. Processing conditions also have a significant impact on morphological properties.

2.5.2 Thermal properties of PET/PBT binary blends

PET has a slow crystallization rate. This is a disadvantage for the processability of PET. The rate of crystallization will rise, and the crystallization temperature will decrease with the preparation of PET / PBT polymer blends. In this way, processability will increase and will be easier. In general studies, the miscibility of the blend is understood by examining the thermal properties with DSC. In previous studies, a single glass transition temperature was observed in the DSC results of PET / PBT polymer blends. They reported that this result showed that the mixture was miscible. However, two melting peaks were observed. There are some studies in the literature about the thermal properties of PET and PBT polymer blends [95,96]. G. Aravinthan, D. D. Kale [101] explained the thermal properties with DSC analysis by preparing PET / PBT polymer blends in different ratios. PET / PBT DSC results are shown in figures 2.31 and Figure 2.32. All mixtures except PET / PBT polymer blends prepared at 80:20 ratio showed two different melting point peaks. The polymer blend prepared in the ratio of 50:50 is the mixture that melts at the lowest temperature. In addition, two different melting temperatures were observed separately in the prepared blend. However, the melting temperature of PET determined in polymer blends is lower than that of virgin PET. This result is the same in PBT. They reported that the decrease in melting temperatures was related to (ΔHm) values. In mixtures with high PET ratio (ΔHm) value is higher than calculated and expected value. For PBT, on the contrary, (ΔHm) value is lower than expected. They reported that this was due to the difference in miscibility in the compositions. However, all mixtures showed a single Tg value in accordance with other literature studies. A single Tg observation shows that the miscibility in the amorphous phase is high. These results are similar to those previously reported by Avramova [100]. DSC thermogram of PET/PBT blends in different ratios is given in Figure 2.31 below.

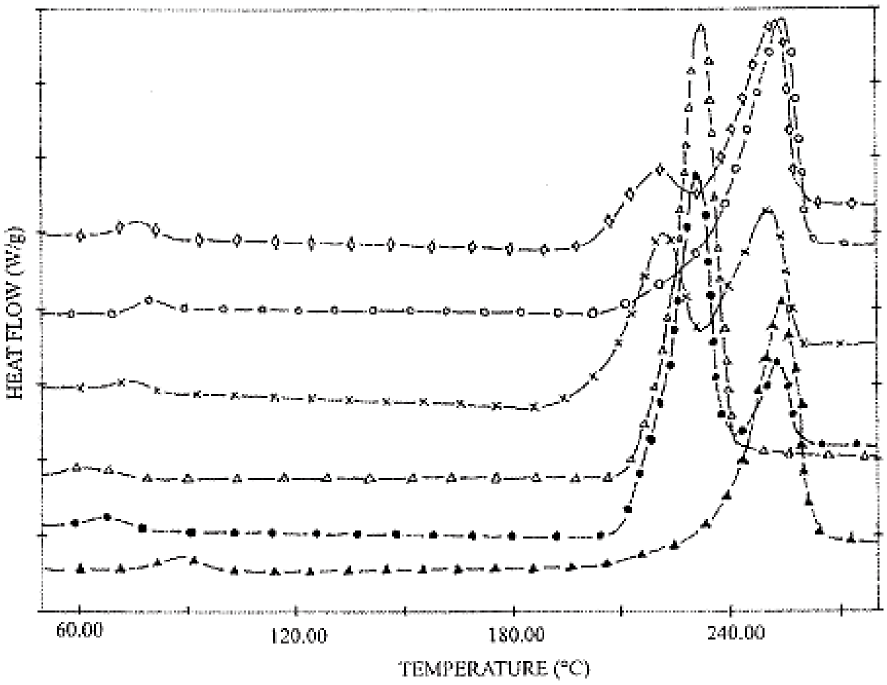

Figure 2.31 : DSC thermograms of PET/PBT blends in the heating cycle▲ PET,
◊ PET 80, ○ PET 60, X PET 50, △ PET 20, ● PBT [101]

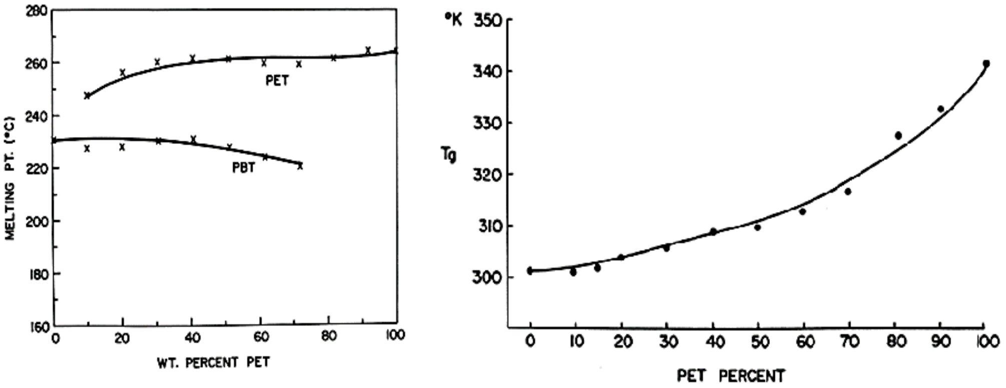

Figure 2.32 : (a) Melting temperature of PET/PBT blend in different ratios (b) Glass transition temperature of PET/PBT blend in different ratios [99].

Escala and Stein [99] have been studied on the thermal properties of PET / PBT blends in different proportions. They observed the Single Tg peak and the double melting peak, as in correspond to the precursory studies. Escala and Stein [99], also have been reported that the compatibility of PBT/PET polymer blends is due to transesterification reactions. After this approach, many researchers have examined the transesterification reaction for PET / PBT blends. Ito et al. [102] examined the transesterification of the PET / PBT components and how their crystallization behaviors changed upon these approaches. They reported that transesterification reactions would occur when extrusion processing at high temperatures for PET / PBT blends. They stated that the temperature and transesterification reactions were directly proportional. In addition, with this study, they observed that crystallization increased with transesterification reactions. With the presence of PET crystals at temperatures above 200 ℃, the crystallization of PBT has been increased. Nofar R. and Oğuz H. [108] investigated melt behavior, phase miscibility, crystallization behavior, solid viscoelastic properties,tensile and impact properties of the PBT/recycled PET blends and analyzed using differential scanning calorimeter (DSC), melt flow indexer (MFI), dynamic mechanical analyzer (DMA),and tensile and Izod notched impact testing, respectively.

Schematic representation of the crystallization behavior of PBT /recycled PET blend is given in Figure 2.33. In this study, during the first heating, a single Tg value was observed for rapidly cooled processed samples. However, two separate melting peaks of the crystals of PBT and r-PET were observed. PBT/recycled-PET mixtures are completely miscible in the amorphous phase, while the crystalline phases are not miscible after a rapid cooling. It was reported that PBT crystallizes rapidly at higher temperatures while, the crystallization of PET occurs at lower temperatures. Because PBT crystals increase the crystallization rate of PET and PET crystals are heterogenous nucleated in the crystalline phase at low temperatures. On the other hand, it was reported also the heating thermograms of the slowly cooled samples. In the first heating, almost one large peak was observed, where the separate melting peaks resulting from rapid cooling were combined as a result of slow cooling. Therefore, it was reported that during slow cooling rates, low perfused crystals containing both PBT and r-PET molecules co- crystallized. Therefore, when blends are slowly cooled, the full miscibility of both amorphous and crystalline phases can be observed. It was emphasized that rapid cooling caused that PBT crystallized earlier due to the rapid crystallization kinetics.

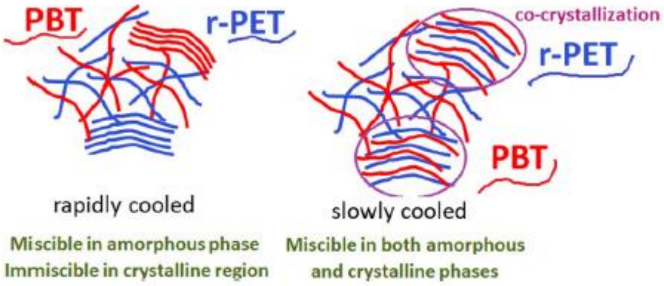

Figure 2.33 : Crystallization behavior of PBT / recycled PET blend [108].

2.5.3 Mechanical properties of PET/PBT binary blends

PET has a slow crystallization rate and its processability is low compared to PBT. However, there is not much difference between its mechanical properties. In the literature, there are studies examining the changes in mechanical properties by preparing PET / PBT polymer blends at different rates. In the literature, there are studies examining the changes in mechanical properties by preparing PET / PBT polymer blends at different ratios [103].

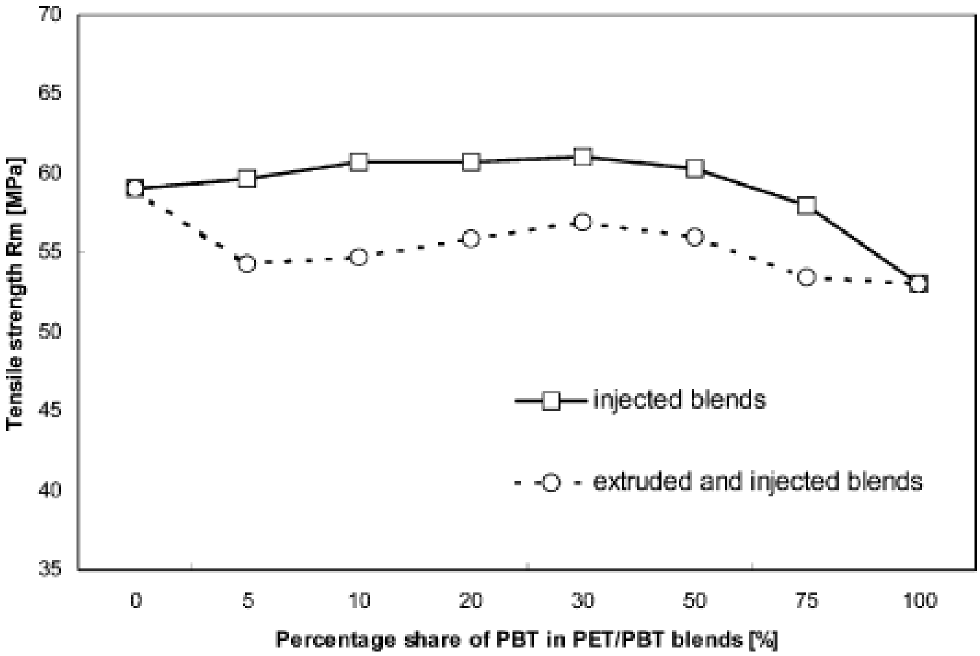

Figure 2.34 : Tensile strength of PET/PBT blends [103].

The results of the mechanical properties of PET / PBT mixtures are shown in Figure 2.34 and Figure 2.35. The tensile strength values are very close for polymer blends prepared with both injection and extrusion. With the increase of PBT ratios in prepared blends, a significant decrease was observed in elongation breaks for both methods. As the PBT rate rises, the hardness will increase in prepared in two different methods of blend. Summarizing the mechanical properties of PET / PBT blends, Elongation breaks decreased as the amount of PBT added into the PET increased, while the hardness and impact strength increased, but the tensile strength did not change [103]. Aravinthan and Kale [101] reported that the PET / PBT polymer prepared at a ratio of 50:50 has higher tensile and impact strength than other PET / PBT polymer blends. They explained the reason for this with the definition of co-morphology.

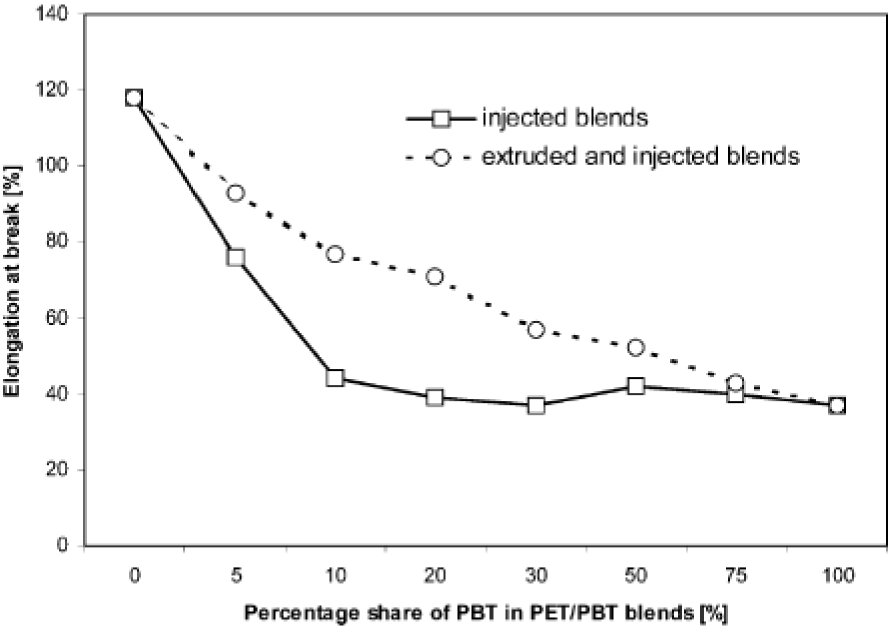

Figure 2.35 : Elongation at break of PET/PBT blends [99].

2.5.4 Rheological properties of PET/PBT binary blends

Mishra and Deopura [104] examined the rheological properties of PET / PBT polymer blends. With the addition of PBT to PET, an increase in molecular weight occurred. This increased when up to 4% PBT was added to PET. However, they also observed an increase in viscosity with an increase in molecular weight. Fakart observed a decrease in viscosity when more than 4% PBT was added. They explained the reason for this as phase separation. Anton Marcincin and Eva Körmendy [105] examined the PET / PBT viscoelastic properties prepared in different proportions. The effect of PBT concentration on viscosity is shown in Figure 2.36. They applied rheology tests to different ratios of PET / PBT at 275°C. These compositions observed a close to 10% change in the dynamic viscosity of PET. However, the preparation of the polymer blends affected the rheological behavior of PET and PBT, and the polymer blends deviated slightly from Netwtonian behavior. The rheological properties of PET and PBT are similar and their miscibility in the amorphous phase is quite high. For this reason, they emphasized that PET / PBT blends exhibit synergistic behavior. They observed a decrease in experimental viscosity in blends where the PBT was less than 15% by weight in the PET / PBT blend. They explained this by the reduction of aromatic rings in the unit volume in the polymer blends and the presence of more flexible PBTs. They also stated that the viscosity reduction is predictable when the polymer blend prepared in heterogeneous morphology [105].

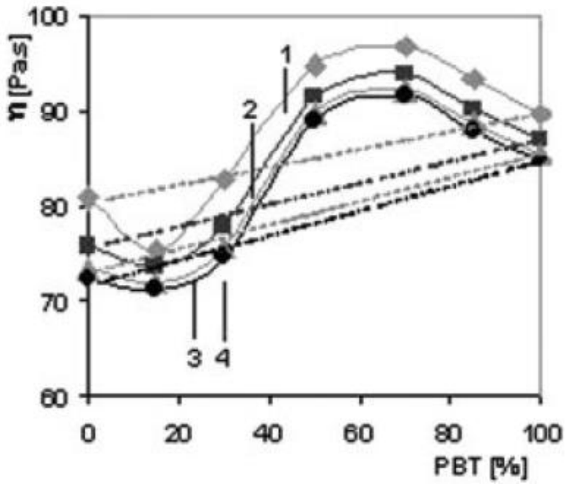

Figure 2.36 : Impact of PBT concentration on viscosity of PET/PBT blends [105].

To the best of acknowledge the reological properties of recycled PET/PBT blends have not been reported yet. In this study, the thermal stability and rheological behavior of recycled PET / PBT blends with dynamic rheological measurements were investigated.

3. EXPERIMENTAL DESIGN

3.1 Materials

Recycled PET has been supplied from Adana / Turkey Çevre PET Inc. PBT has a melt volume ratio of 17 ± 4 cm^3 / 10 minutes and has been supplied from Sasa Polyester Inc. Co. from Co. Properties of supplied recycled PET is given in Table 3.1. Chemical structure of Joncryl ADR 4468 is given in Figure 3.1.

Table 3.1 : Properties of supplied recycled PET.

Property	Value
Intrinsic Viscosity [η]	0.65-0.75 $dL.g^{-1}$
Water Content	0.3-0.7 wt%
Flake Size (D)	8-10 mm
White Color Ratio	75-85 %
Blue Color Ratio	15-25 %
Metal Content	10 ppm
PVC Content	20 ppm
Paper and Fiber Content	10 ppm
Adhesive Content	10 ppm

Joncryl ADR 4468 ® chain extender has been supplied from BASF. Phiysical properties of Joncryl ADR 4468 ® chain extender is shown in Table 3.2.

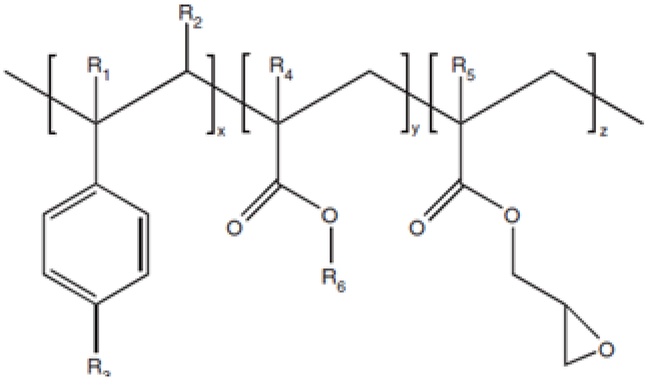

Figure 3.1 : Chemical structure of Joncryl ADR 4468 ®.

The chain extender structure is a multifunctional styrene acrylic oligomer containing epoxy reactive groups.

Table 3.2 : Physical properties of Joncryl ADR 4468 ®.

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

3.2 Sample Preparation

In order to improve the rheological properties of r-PET, R-PET/PBT blends were prepared with twin screw extruder using different ratios and chain extended R-PET were prepared in different ratios. Joncryl mixed with recycled PET flakes in different proportions. These mixtures were extruded. The composition ratios of these prepared mixtures are summarized in Table 3.3 and Table 3.4. Preparation methods are shown in Figure 3.2.

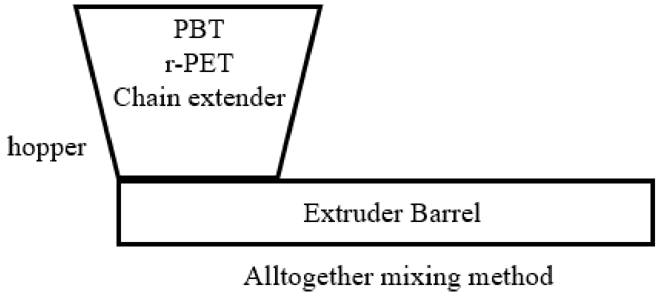

Figure 3.2 : Preparing methods of chain extended R-PET and r-PET/PBT blends.

The disk shape rheological samples (25mm diameter and 1.5mm thickness) were prepared through compression molding. The compression molding was conducted at 255 °C for 5 minutes by gradually increasing the pressure up to 1.5 ton. After 5 minutes, the samples were fast cooled with water before taken out from mold. Before molding, pellets were dried under vacuum overnight 60°C.When preparing the samples, 255°C was preferred which PBT and PET can work without degradation. Molded samples are shown in Figure 3.3. Since the rapid degradation occurs for polyesters in air atmosphere. Preparation of samples and rheological measurements were carried out under nitrogen atmosphere. The prepared samples are shown in Figure 3.6.

Table 3.3 : List of chain extended samples.

Recycled PET/Joncryl	Recycled PET (wt%)	Joncryl (wt%)
r-PET	100	0
r-PET+J0.40	99.60	0.40
r-PET+J0.80	99.20	0.80

Table 3.4 : List of R-PET/ PBT blends and their chain extended samples.

PBT (wt%)	Recycled PET (wt%)	Chain Extender (wt%)
75	25	0
75	25	0.20
50	50	0
50	50	0.20
25	75	0
25	75	0.20

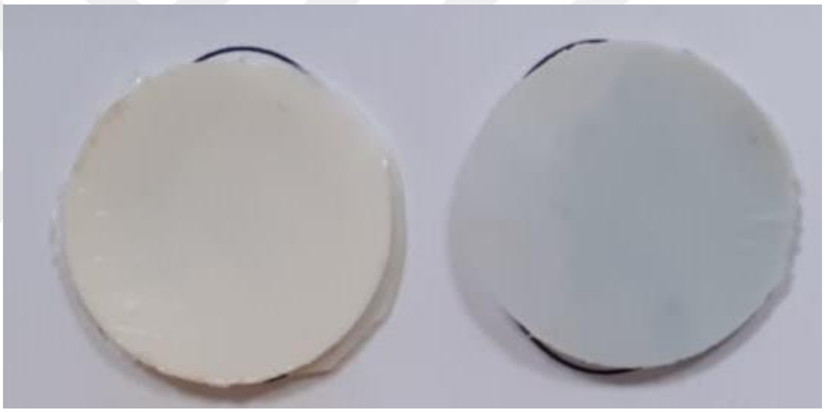

Figure 3.3 : Molded PBT(right) and R-PET (left).

The thermal properties of R-PET and PBT used in the measurements are summarized in table 3.5 below.

Table 3.5 : Thermal properties of R-PET and PBT [108].

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

3.3 Rheological Analysis

Rheological measurements were performed at 240°C, 270°C, 285°C, 300°C with the MCR-301 rotational rheometer equipped with a parallel-plate geometry (plate diameter 25mm) with a gap of 1 mm. (Anton Paar, Austria) shown in Figure 3.4.

Figure 3.4 : MCR-301 rotational rheometer (Anton Paar, Austria).

When the stress is applied to the material, the microstructural properties begin to change at the point where the yield stress is exceeded. Since the linear viscoelastic behavior changes. It is very important to define the Linear Viscoelastic Region (LVR) to run rheological tests in consistency. Strain sweep test was carried out for PET at 270 ℃, 285 ℃ and 300 ℃. It was carried out at 270 ℃ and 300 ℃ for PBT. The behavior of the material at fixed frequency, amplitude and temperature is determined by time sweep test to observe the material's thermal stability over time. Due to the sensitivity of recycled PET and PBT to thermal degradation, the time sweep test was carried out at different temperatures to determine thermal stability. The time sweep test was carried out at 270℃, 285 ℃ and 300 ℃ using strain amplitude of 0.01 and frequency 1 rad/s for PET, while at 240℃, 255℃, 270℃, 285 ℃ and 300℃ for PBT. In order to make comparisons, measurements were made at 10 rad/s under the same conditions. From the results obtained, it was calculated how much degradation at which temperature. The frequency scanning test defines the deformation interval of the material that occurs over time. At high frequencies, the material is given a short time periods, while at low frequencies, deformations are determined for much longer periods. In this way, the behavior of the polymers and their stability are determined in the long or short term. First, the linear viscoelastic region was determined as 1% for 1 rad/s constant frequency value with strain test from 1% to 100%. Frequency sweep test was applied starting from ω = 665 rad / s and decreasing to 0.1 rad / s. Frequency Scan test was carried out for R-PET, R-PET + 0.4 wt% CE, R-PET 0.8 wt% CE samples at 270 ℃, 285℃ and 300℃.

3.4 FTIR Analysis

FTIR spectrometers (Fourier Transform Infrared Spectrometry) are one of the commonly used analysis methods in organic synthesis, polymer science, petrochemical engineering, pharmaceutical industry. Fourier Transform Infrared Spectroscopy is used to identify materials. Chemical properties of test samples are identified by scanning by infrared light. FTIR analysis was performed to determine the chemical structure and changes in the structure all of samples. Each sample was shaped by compression molding before dynamic rheology tests. FTIR was subjected to analysis after compression molding application. In this way, the structure has been defined. After the time sweep, frequency sweep and stress growth applied, FTIR analysis was done again. With this application, the changes in the chemical structure of the samples were determined as a result of rheological measurements. Samples were grinded with grinder for FTIR analysis to give better results. The FTIR device is shown in Figure 3.5.

Figure 3.5 : An example of FTIR device.

4. RESULTS AND DISCUSSION

4.1 R-PET and PBT

In this study, the change in rheological properties of neat R-PET and PBT were examined.

4.1.1 Rheological analysis of R-PET and PBT

Strain sweep test was performed to identify the linear viscoelastic region. In order to examine the thermal stability, time sweep tests were performed. Frequency sweep tests were carried out to examine the time dependent behavior of samples in non destructive deformation range. Stress growth tests were performed to determine the transient viscosity

4.1.1.1 Determination of linear viscoelastic region (LVE)

Strain sweep tests were accomplished for PET at 270°C, 285°C, and 300°C. It was also performed at 270°C, and 300°C for PBT. Results of strain sweep test as complex viscosity (η*) versus strain (γ) are shown in Figure 4.1 and Figure 4.2.

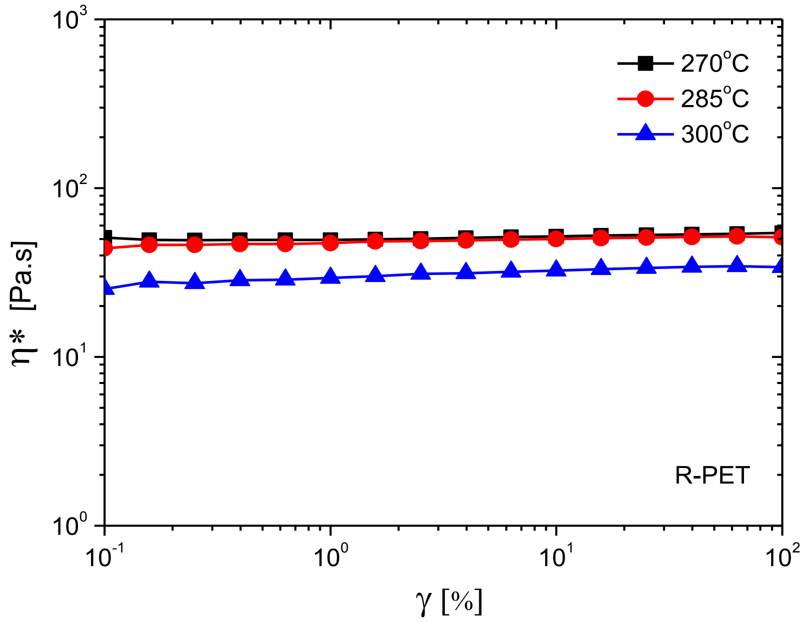

Figure 4.1 : Strain Sweep Test at 270°C, 285°C, 300°C 1 rad/s for R-PET.

The linear viscoelastic region was determined as 1% for 1 rad/s constant frequency value with strain test from 1% to 100% for R-PET and PBT.

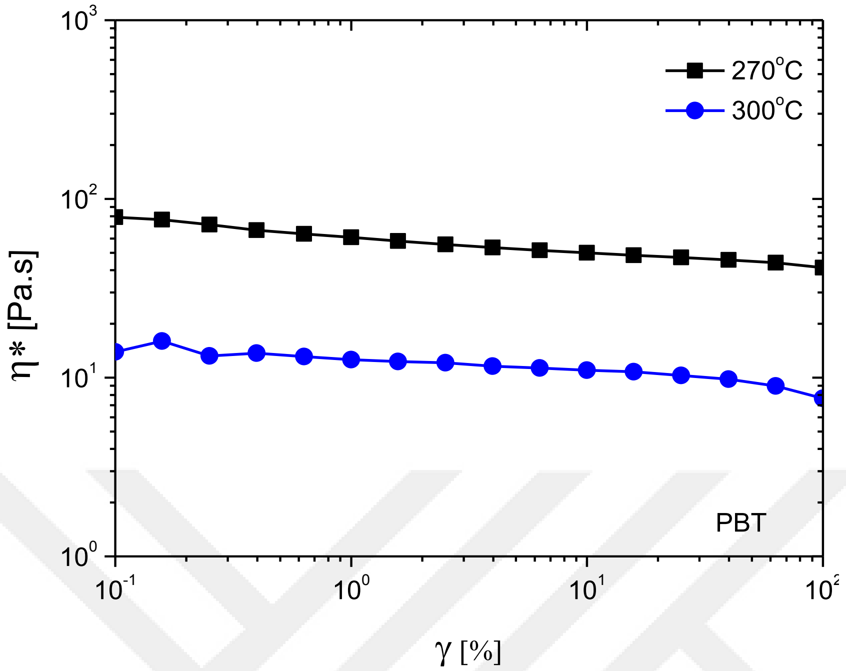

Figure 4.2 : Strain Sweep Test at 270℃, 300℃ 1 rad/s for PBT.

4.1.1.2 Thermal stability analysis

The time sweep test was carried out for R- PET at 270℃, and 285℃ using the strain amplitude of 0.01 and frequency 1 rad/s, and for PBT at 240, 255, 270, 285℃ to determine the thermally stable time zone in which the viscosity drop was monitored as a function of time. For the sake of comparisons, all measurements were made with the strain of 1 rad/s under the same conditions. The complex viscosity (η*) obtained from the time sweep measurements of the R-PET and PBT are reported in Figure 4.3 and Figure 4.4. The complex viscosity of R-PET is stable over time and the increase in viscosity was calculated to be 5%. As the temperature increased the complex viscosity value decreased.

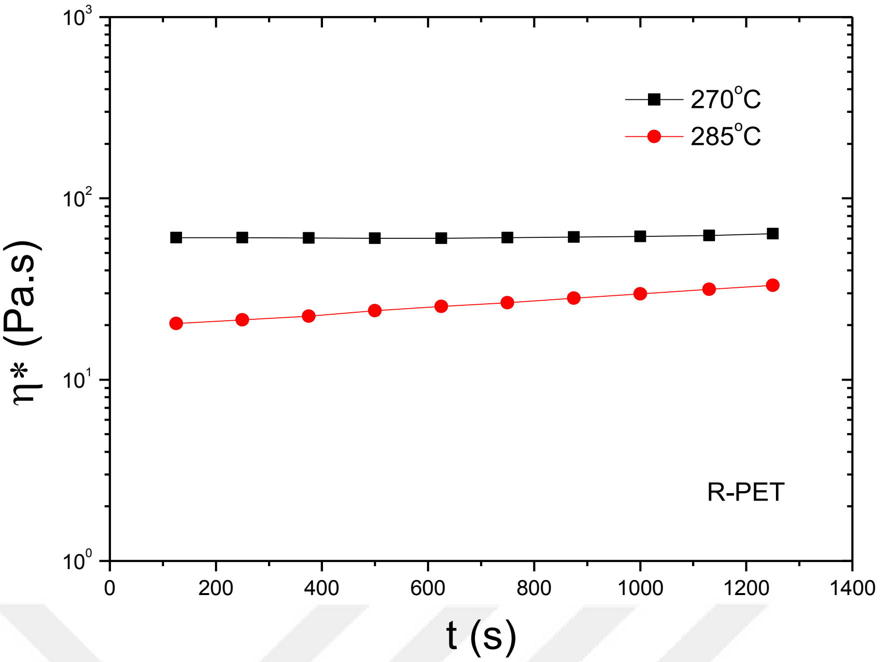

Figure 4.3 : Complex viscosity of R-PET at 270°C, 285°C.

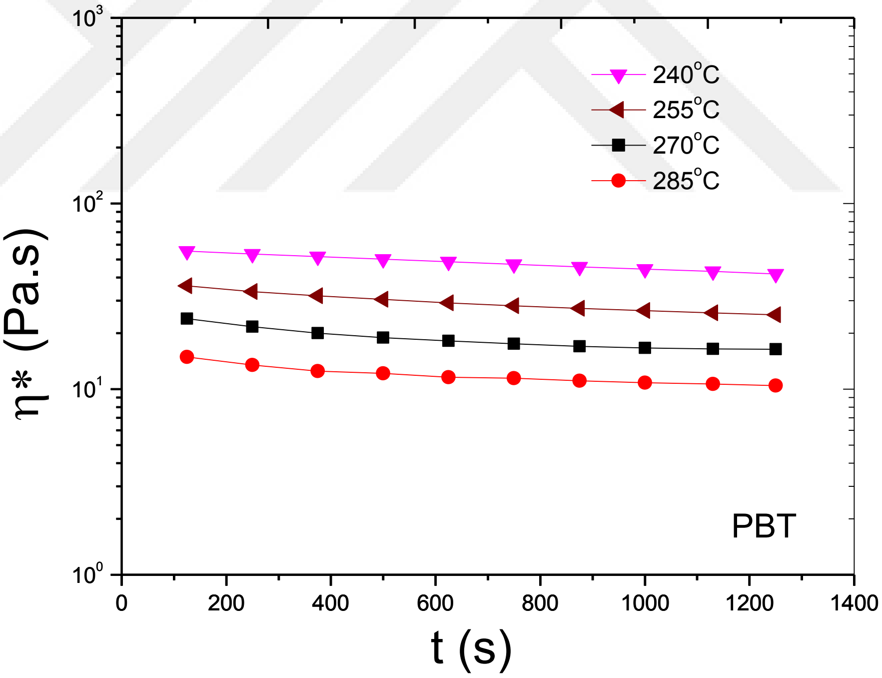

Figure 4.4 : Complex viscosity of PBT at 240°C, 255°C, 270°C, 285°C at 1 rad/s for time sweep test.

Viscosity increase trend is observed again. To observe shear rate effect on thermal stability the time sweep test was carried out at 270°C at at 1 rad/s and 10 rad/s. Results of time sweep test in different shear rate as complex viscosity (η*) versus time (t) are shown in Figure 4.5. However, when applied 1 or 10 rad / s shear rate have not been caused major changes for R-PET. The thermal stability of the material has not been changed. Complex viscosity changes that occurred during the time sweep test are shown in the Table 4.1.

Table 4.1 : Complex viscosity changes during time sweep test for R-PET and PBT after 20 min.

	R-PET	**PBT**
270°C	(+) %5	(-) %39
285°C	(+) %47	(-) %40

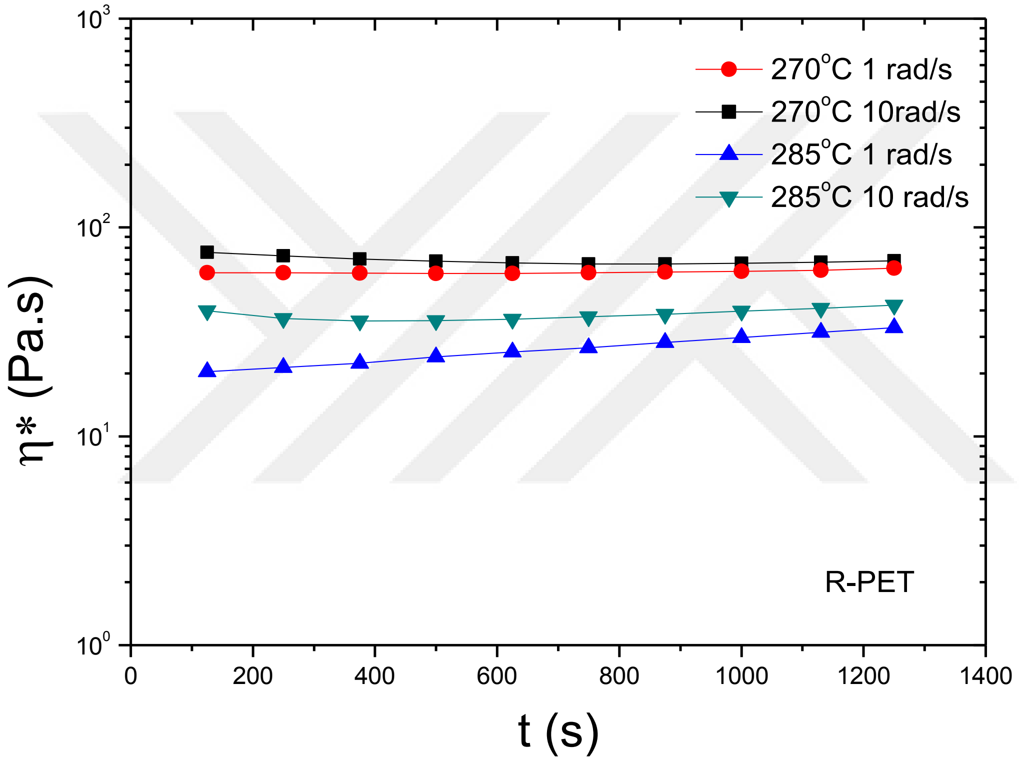

Figure 4.5 : Effects of shear rate on complex viscosity of R-PET at 270°C and 285°C for time sweep test.

4.1.1.3 Stress growth test

Transient viscosity is defined by the stress growth test with data at certain time steps. Non-linear viscoelastic behaviors were analyzed with the correlation of stress applied with relaxation time to this test. The stress growth test was carried out for recycled PET in the intervals of 0.01,0.05 and 0.1 s^{-1} at 270°C. Transient viscosity curve of R-PET are given in Figure 4.6. In this figure, transient viscosity increases were not clearly observed and slightly increases were obeserved an these increases were examined with polycondensation reactions.

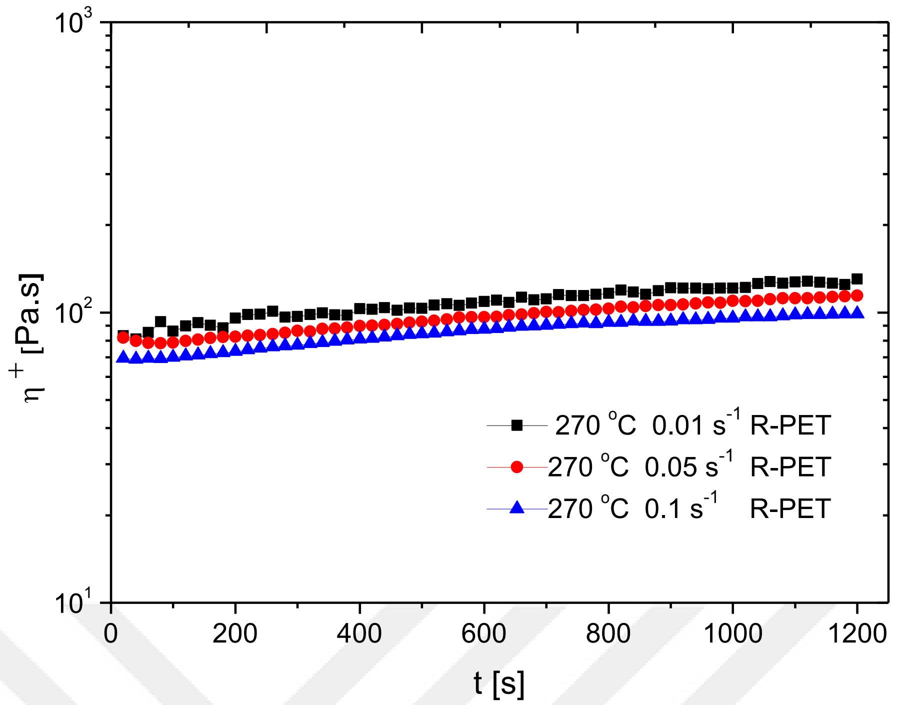

Figure 4.6 : Transient viscosity changes of recycled PET at 270°C.

4.1.2 Structure analysis of R-PET

4.1.2.1 FTIR analysis

An increase in viscosity was observed in the structure of R-PET during time sweep or frequency sweep tests. These viscosity increases during the rheological measurements of R-PET after processing could be regarded as a consequence of molecular weight increase which resulted from polycondensation reactions in the structure of R-PET between broken functional end groups which are carboxyl and hydroxyl. The predicted reaction mechanism of polycondensation reaction is displayed in Figure 4.7. FTIR analysis was performed in order to observe the structural changes during the dynamic rheological measurements resulting from these polycondensation reactions. The FTIR spectrum of R-PET is given in Figure 4.8. The most sharp peak visible in the FTIR spectrum which is the carbonyl peak of carboxylic acid at 1712 cm^{-1} was normalized. It expected that decreases in some -OH peaks during the polycondensation reaction.

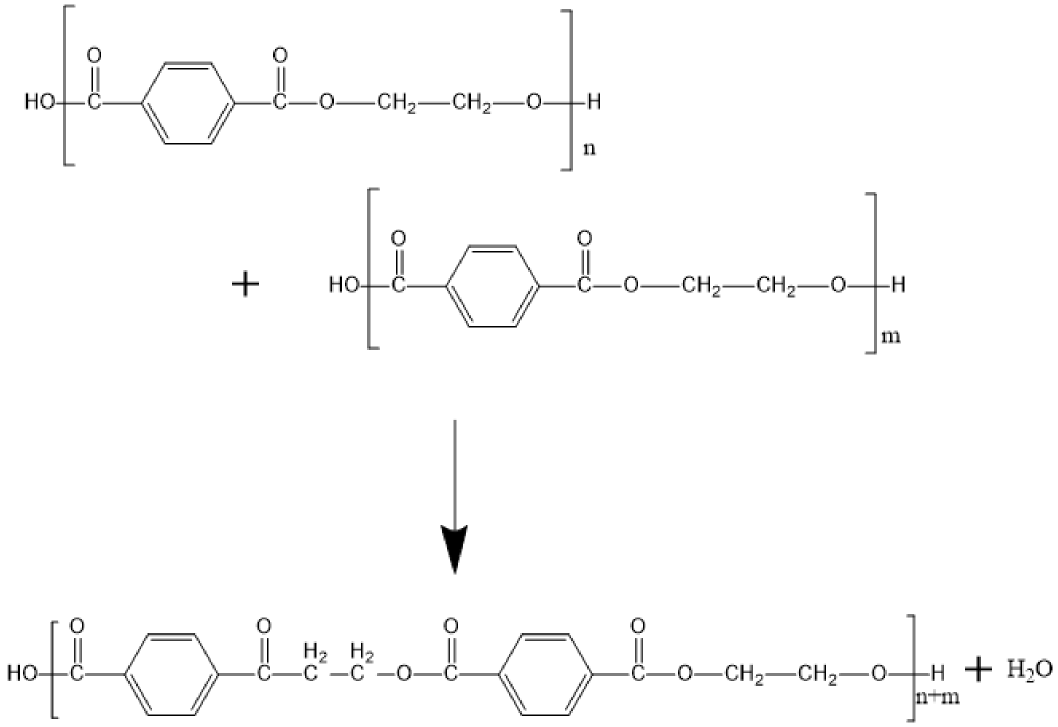

Figure 4.7 : Polycondensation reaction mechanism of R-PET.

During the polycondensation reactions given by R-PET, unreacted functional end groups reacts with increasing temperature. In Figure 4.8 (c), the intensity of carboxylic acid -OH streching vibration peak at 2958 cm^{-1} is observed to decrease as the temperature increases. Also, the intensity of the -OH bending vibration peak of the end-group carboxylic acid (1340 cm^{-1}) decreases during the dynamic rheological measurements with increasing temperature. This situation could be regarded as a succesful polycondesation reactions between -COOH and -OH end functional groups of different PET chains. While functional end groups (carboxylic or hydroxyl) are consumed, an increase in the intensities of the C-O stretching vibrations in aliphatic and aromatic ester groups is expected. In Figure 4.8 (b), the intensity increase at 1365 cm-1 (aromatic ester C-O streching) and 1179 cm-1 (aliphatic ester C-O streching) proves the assumption that as a result of polycondensation reactions, newly formed esters are observed.

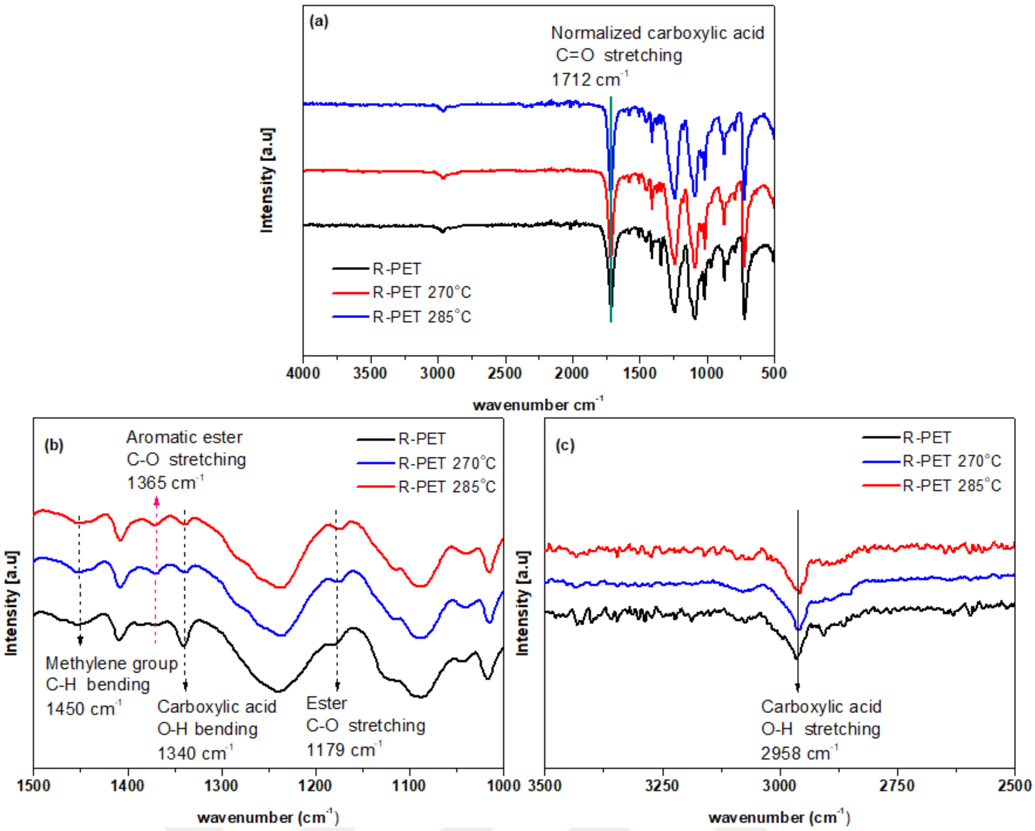

Figure 4.8 : FTIR Spectrum of R-PET between (a) 4000-500, (b) 1500-100, and (c) 3500-2500.

4.2 Chain Extended R-PET

4.2.1 Rheological analysis of chain extended R-PET

Chain extender was used to improve the thermal stability of recycled PET.Chain extenders reacted with carboxylic and / or hydrocyclic (alcohol) end groups at the broken end groups in the structure of the R-PET. The effects of chain extender on thermal stability and processability were determined by dynamic rheological measurements.

4.2.1.1 Thermal stability analysis

The Time sweep test was carried out at 270 °C and 285 °C at 1 rad/s shear rate. During the melting process, chain extenders reacted with the functional end groups of R-PET. The amount of hydroxyl and carboxyl end groups in R-PET plays a significant role in molecular weight of the R-PET during the process. In the structure where carboxyl end groups thermal degradation will occur, and thermal stability will decrease. Results of time sweep test in as complex viscosity (η*) versus time (t) are shown for R-PET and their chain extended samples in Figure 4.9 and Figure 4.10. However, as seen in the time sweep test results, polycondensation reactions have increased with the use of a chain extender. Increases in molecular weight and viscosity are observed with raising polycondensation. A increase in viscosity was observed when the amount of chain extender used raised. This shows that polycondensation reactions increase with the amount of chain extender. In addition, when the amount of chain extender increased, more viscosity raise was observed, and polymerization reactions increased. . This indicates that the carboxyl end groups in the structure of R-PET decreased. Since the polymer used was recycled, it was observed the high amount of broken end groups and polymerization reaction increased when the temperature has risen. In addition, unreacted chain extender end groups reacted with R-PET with the effect of temperature. As the amount of chain extender increases, the complex viscosity has increased significantly. Highly branching structure has been formed with increasing the amount of chain extender. In addition, molecular mobility of polymers increases with increasing temperature.

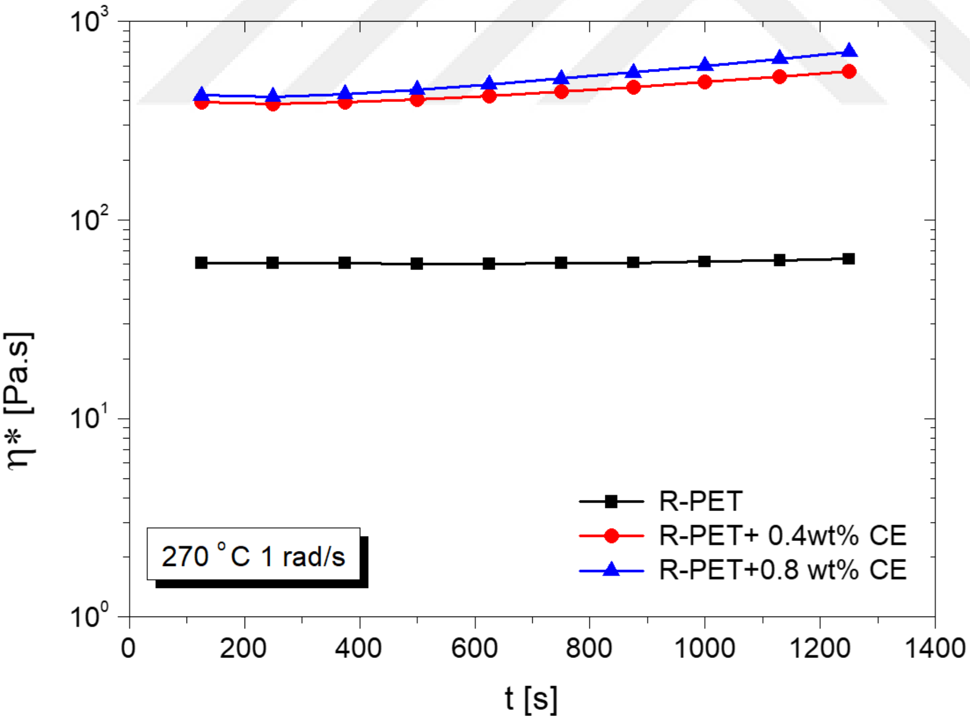

Figure 4.9 : Effects of Chain extender usage on complex viscosity at 270°C for time sweep test.

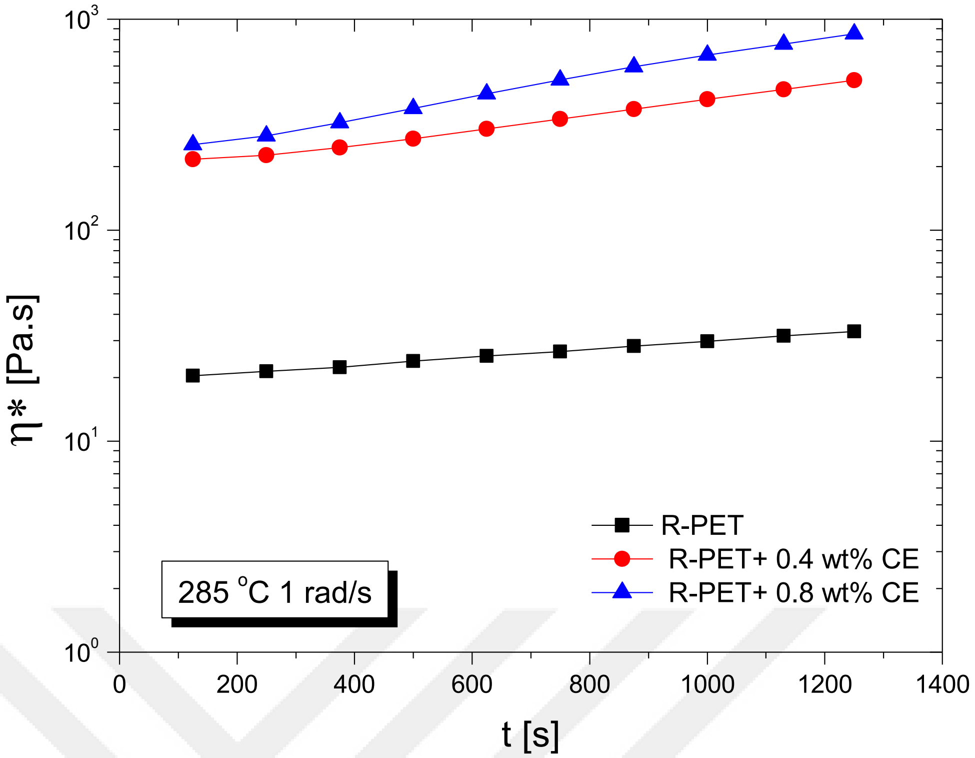

Figure 4.10 : Effects of chain extender usage in different ratios on complex viscosity at 285°C for time sweep test.

They can move more easily and react more easily. For this reason, reactions of polycondensation and unreacted chain extenders at 285°C have increased and significant increases in viscosity have been observed. However, it is undesirable to observe decrease or increase of the complex viscosity to prevent thermal degradation and enable thermal stability. However, it was observed an increase in the complex viscosity of recycled PET. In addition, thermal degradation was not observed in the sttructure of recycled PET during time sweep test. Matthias Kruse and Víctor H. et. al. [33] were reported that polycondensation reactions occurred because of frequency sweep tests performed under nitrogen atmosphere. They first observed that Newtonian behavior occurred. But they reported sharp increases in viscosity at low frequency values. All this will be support and decide with FTIR analysis results.

4.2.1.2 Frequency sweep test

The frequency sweep experiments were conducted for samples at 270°C and 285°C. The applied frequency was within the linear viscoelastic region (strain of 0.01) which was determined from the strain sweep experiments since not to destroy the structure of the system by the applied excessive strain. All frequency sweep measurements were also performed within the thermally stable time zone which was also determined from the time sweep experiments during which the viscosity drop was monitored as a function of time and the as the thermal degradation initiation. It is a known fact that polyesters undergo partial degradation in air atmosphere. Therefore, when they contact with air, molecular weights and viscosities will decrease over time. To observe this, frequency sweep tests were repeated at different time intervals and the results were compared. All tests were carried out in a nitrogen atmosphere to prevent possible degradation. First, the linear viscoelastic region was determined as 1% for 1 rad/s constant frequency value with strain test from 1% to 100%. Frequency sweep test was applied starting from ω = 665 rad / s and decreasing to 0.1 rad / s. Frequency sweep test was carried out for R-PET, R-PET + 0.4 wt% CE, R-PET 0.8 wt% CE samples at 270 ℃, 285℃. The complex viscosity (η*) obtained from the frequency sweep measurements of the R-PET and their corresponding chain extended samples 0.4 wt% and 0.8 wt% are reported in Figure 4.11. In Figure 4., It was observed almostly Newtonian more clearly at high temperatures. However, at low frequencies, increases in viscosity were clearly occurred. The reason for this is thought to be polycondensation reaction and high temperature triggered these reactions. It was observed similar increases for chain extended samples at 270 ℃. However, viscosity increases are much higher at 285℃. This indicates that with the increase in temperature, the polycondensation reactions and the reactions of the unreacted chain extenders increase. With the increase in temperature, molecular motion has increased and molecular diffusion has been facilitated. Therefore, an increase in reactions has been observed.

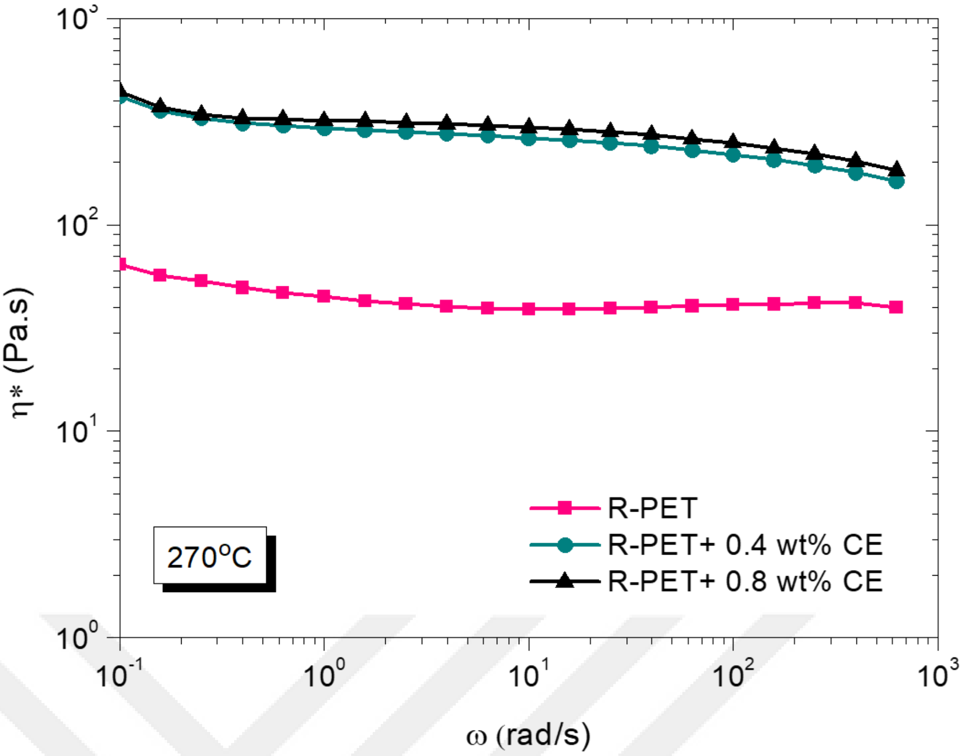

Figure 4.11 : Frequency sweep test results of chain extended R-PET at 270°C.

This increase led to increases in molecular weight and directly complex viscosity was increased. As the amount of used chain extender increases, the unreacted end groups increase. İt was observed that complex viscosity was high for 0.8 wt% chain extended R-PET in both temperatures. These reactions progressed faster at higher frequencies at 270 °C. Viscosity increases of chain extended samples at low frequencies are clearly seen.. It is an indication that the reactions between the chain extender and R-PET were carried out. The frequency sweep test was performed in 40 minutes for R-PET and 0.8 wt% chain extended R-PET after the 20 min. treated at 270°C and the result of these treatment is shown in Figure 4.11. The recycle material was exposed to 270°C for a long time. No degradation was observed during this period. Complex viscosity of R-PET has significantly increased. Viscosity increases seen when R-PET was treated for 20 minutes due to polycondensation reactions. Frequency sweep test applied after teratment, the condensation reactions that is carried out in the structure of R-PET have been completed. Results of frequency sweep test (270°C) of previously treated R-PET and chain extended R-PET is given in Figure 4.13. For this reason, significant viscosity increases were not observed during frequency sweep test. On the other hand, the viscosity of 0.8 wt% chain extended R-PET has increased significantly during frequency sweep test. Serious polycondensation reactions was observed.

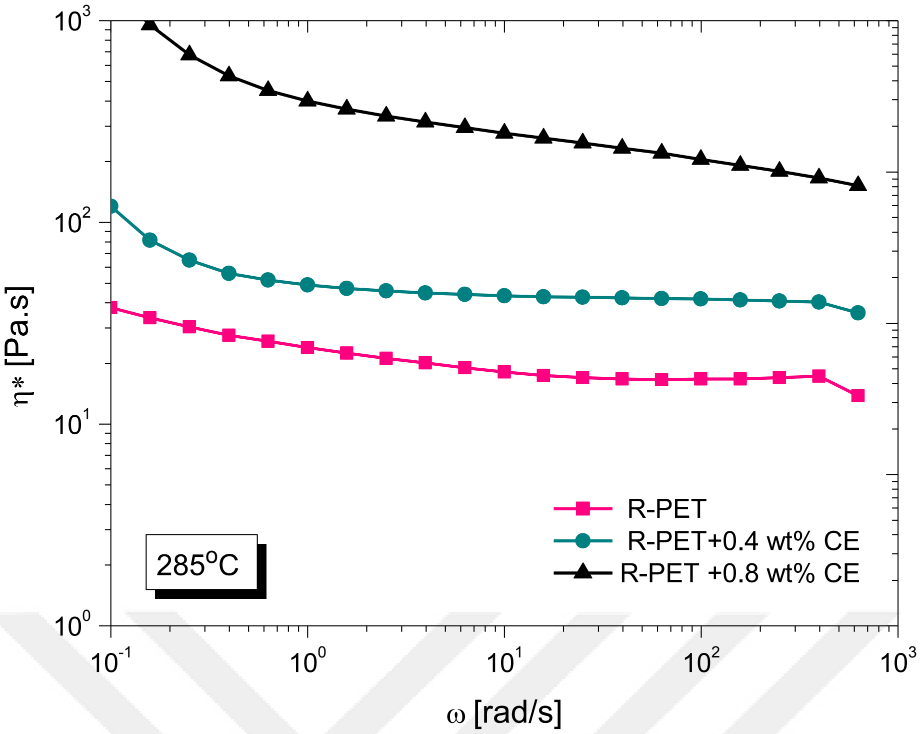

Figure 4.12 : Frequency sweep test results of chain extended R-PET at 285℃.

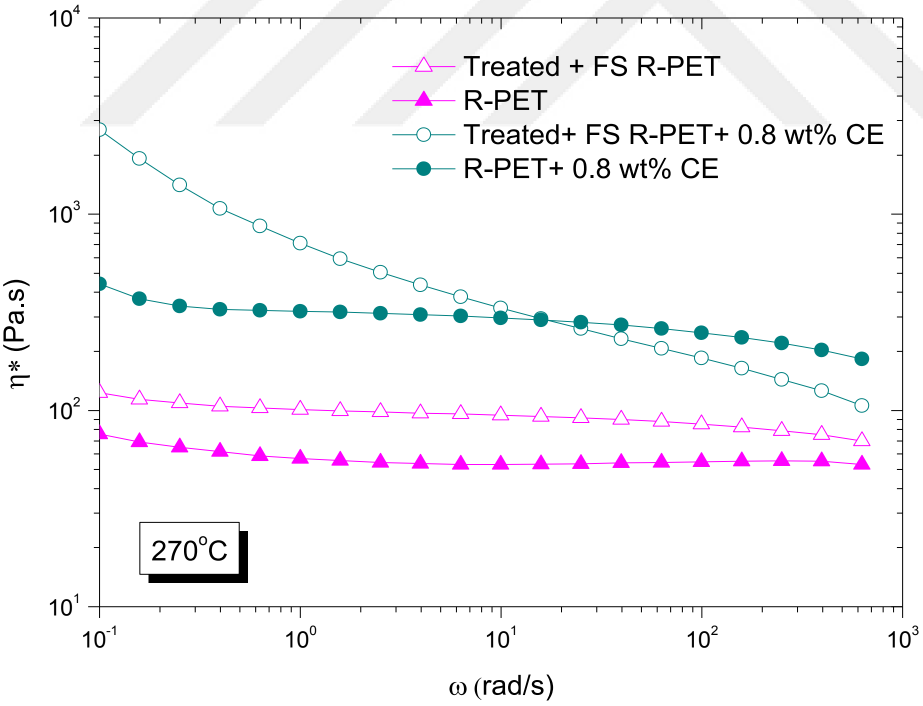

Figure 4.13 : Results of frequency sweep test (270℃) of previously treated R-PET and chain extended R-PET.

Viscosity increases are quite large compared to the samples that are applied only to frequency sweep tests. Especially for the sample with 0.8 wt% CE, after the treatment, unreacted chain extender reactions were but when the extra minutes frequency sweep test was applied, the viscosity increases increased considerably. When 40 minutes treatment then 20 minutes frequency sweep test were performed, the reactions of the unreacted chains were almostly completed for R-PET but highly branched structure was occured for 0.8% wt CE R-PET. Shear thinning behavior was observed for 0.8% wt CE R-PET at low frequencies.

4.2.1.3 Stress growth test

Transient viscosity is defined by the stress growth test with data at certain time steps. Non-linear viscoelastic behaviors were analyzed with the correlation of stress applied with relaxation time to this test. The stress growth test was carried out for chain extended recycled PET at 0.05 s^{-1} at 270°C. Transient viscosity curves are given in Figure 4.14 for R-PET and their chain extended samples. In Figure 4.14, transient viscosity increases were clearly observed with the increasing the amount of chain extender. Polycondensation reactions occurred and increased with the increasing temperature. Reaction of unreacted chain extender end groups with R-PET was occured. With the addition of the chain extender caused complex viscosity increases. As the amount of chain extender increased, these reactions increased, thereby serious increases in viscosity were observed.

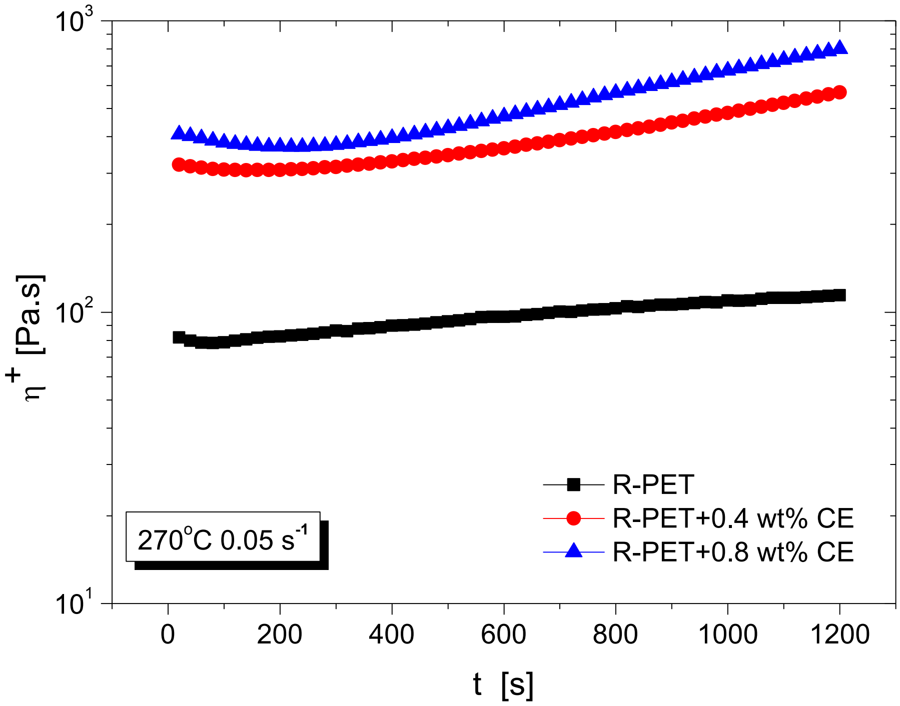

Figure 4.14 : Comparison of transient viscosity of recycled PET and their chain extended samples.

4.2.2 Structure analysis of chain extended R-PET

4.2.2.1 FTIR analysis

As explained earlier, the epoxy functional groups available in Joncryl is able to react both hydroxyl and carboxyl end groups of the PET structure. Reactions that occur between PET's hydroxyl end groups and epoxy are defined as etherification reactions while the ones between carboxyl end groups and epoxy functionalities are defined as esterification reactions. Possible reaction between Joncryl and PET is given in Figure 4.15. As a natural result of the epoxide ring opening reaction, new secondary hydroxyl moieties are formed in the main structure of PET. If the carboxyl end groups of recycled PET react with epoxy, an increase in hydroxyl groups is expected. However, if the hydroxyl end groups of recycled PET react with epoxy, an increase in hydroxyl groups is not expected since the increase resulting from epoxide moiety is compansated by a decrease in the end-functional -OH groups. Many researchers were observed that carboxyl end groups of PET are more likely to carry out an esterification reaction with electrophilic epoxy groups. For this reason, a more observable change is expected in the both stetching and bending vibrations of -OH functionalities in -COOH end groups.

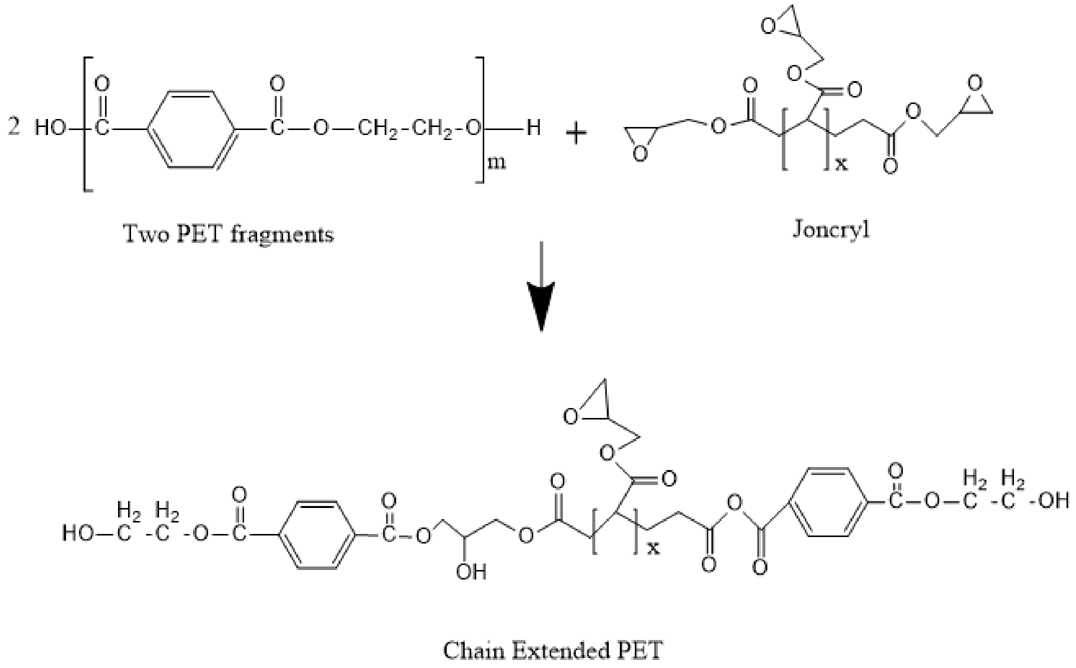

Figure 4.15 : Reaction mechanism between R-PET and Joncryl.

FTIR spectrum of R-PET and their chain extended samples is given in Figure 4.16. The most sharp peak visible in the FTIR spectrum which is the carbonyl peak of carboxylic acid at 1712 cm^{-1} was normalized. Since the chain extension reaction mostly takes place between -COOH and Joncryl's epoxide functionalities, a decrease in the intensity of the -OH streching in -COOH is observed at at 3086 cm^{-1}.

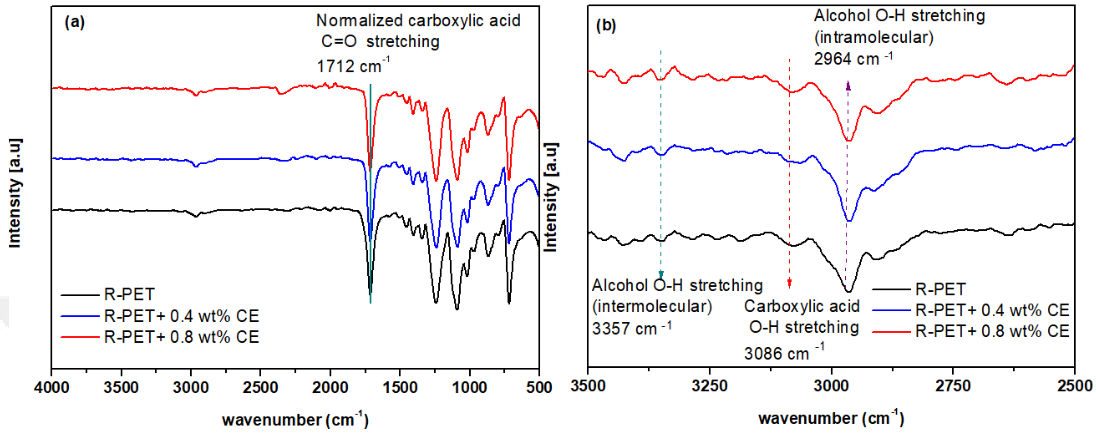

Figure 4.16 : FTIR Spectrum of R-PET and chain extended R-PET between (a) 4000-500, (b) 2500-3500.

When the corresponding peaks of -OH functionality in the main structure are analyzed, it was observed that the intensity of the intramolecular hydrogen bonded -OH peak at 2941 cm^{-1} displayed a decrease while there exists an increase in the intermolecular hydrogen bonded -OH peak at 3357 cm^{-1}. The newly formed secondary -OH groups as a result of epoxide ring opening reaction might be responsible for the increase in the intermolecular hydrogen bonding. Changes in the structure of chain extended R-PET as a result of dynamic rheological measurements at 270°C, and 285°C were examined by FTIR analysis and presented in Figure 4.17 and Figure 4.18. Dynamic rheological measurements were made for prepared R-PET 0.4wt% CE and R-PET 0.8wt% CE samples. As a result of these measurements, an increase in viscosity was observed. Reaction were expected between unreacted groups epoxide functionalites of chain extenders and -COOH and -OH end groups of R-PET. It was assigned as the C-O stretching of the primary alcohol at the end of the ethylene glycol in the structure of the recycled PET at 1010 cm^{-1} peak. Decreases were observed at this peak after dynamic rheological measurements. This result supports the formation of a polycondensation reaction in its structure of recycled PET. The peaks at 1340 cm^{-1} was assigned as -OH bending of carboxylic acid. However, this peak in both structures confirms the reactions of both polycondensation and unreacted chain extender end groups. With the effect of temperature, it was observed that the reactions of especially unreacted end groups are about to be completed and therefore this peak is about to disappear. Therefore, the decreases in the reactive unreacted functional groups indicate that the reactions of the unreacted chain extender end groups occur under the influence of temperature during dynamic rheological measurements. This peak was not observed in samples taken as a result of measurements at 285 ℃. This result clearly shows that unreacted chain extender functional groups react with R-PET. It can also be concluded that these reactions increase with temperature. The peaks at 1420 cm^{-1} was assigned as OH bending vibrations of alcohol groups. Reductions were observed as a result of the polyetherification reaction between R-PET and Joncryl's unreacted hydroxyl end groups in this peak. With the increase in temperature, a decrease was observed in peak at 2960 cm-1 which corresponds to OH strecthing peak of carboxylic acid groups in the structure. It is an expected result that supports unreacted functional groups to react with r-PET. Reductions are clearly seen when compared to R-PET. It is supported that polycondensation reactions existed during dynamic rheological measurements.

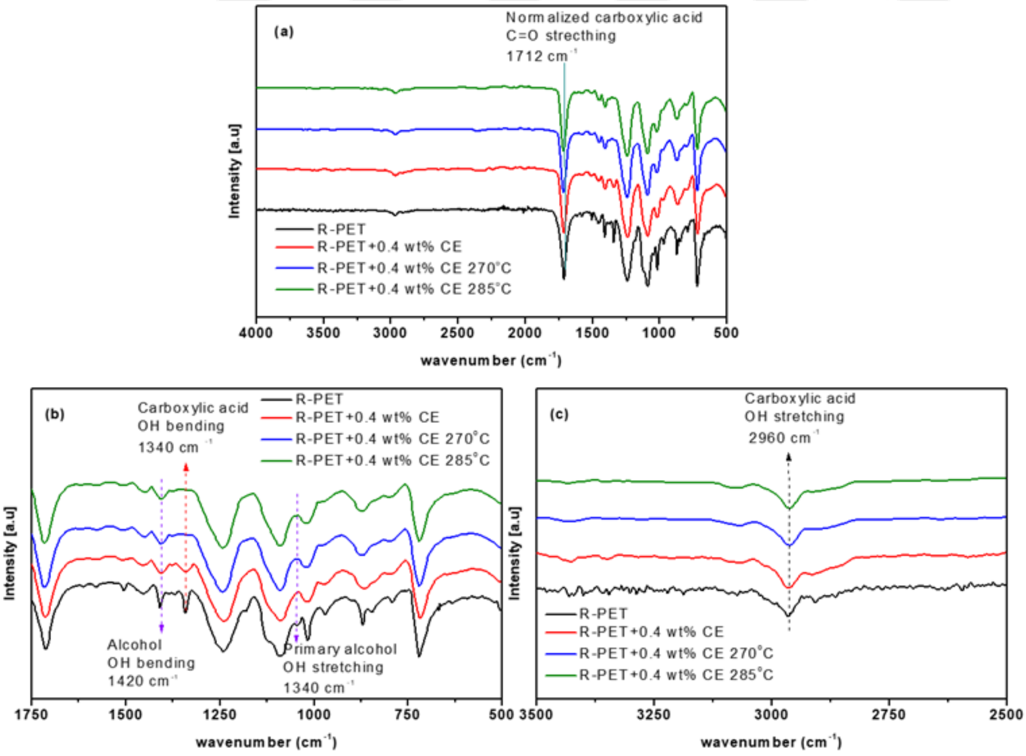

Figure 4.17 : FTIR Spectrum of R-PET and 0.4 wt% chain extended R-PET between (a) 4000-500, (b) 500-1700 and, (c) 2500-3500.

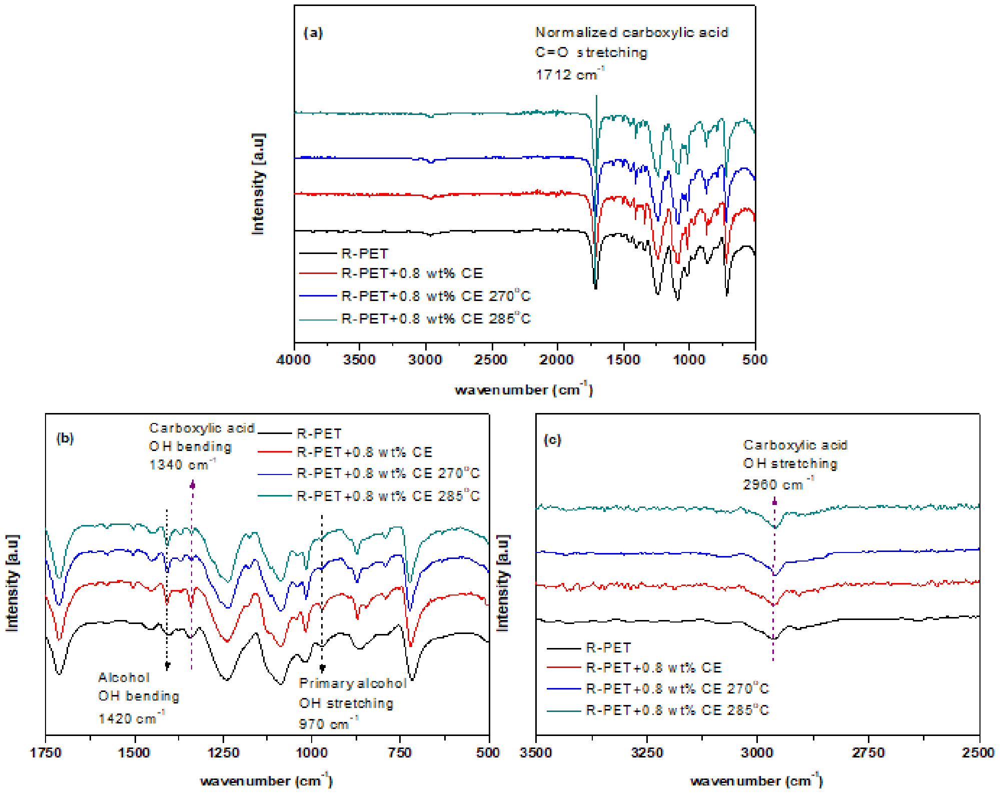

Figure 4.18 : FTIR Spectrum of R-PET and 0.8 wt% chain extended R-PET between (a) 4000-500, (b) 500-1700 and, (c) 2500-3500.

In Figure 4.218, It was assigned as the C-O stretching of the primary alcohol at the end of the ethylene glycol in the structure of the recycled PET at 1010 cm^{-1} peak. Decreases were observed at this peak after dynamic rheological measurements. This result supports the formation of a polycondensation reaction in its structure of recycled PET. The peaks at 1340 cm^{-1} was assigned as OH bending of carboxylic acid. With the effect of temperature, it was observed that the reactions of especially unreacted end groups are about to be completed and therefore this peak is about to disappear. This peak gradually decreased in samples taken as a result of dynamic rheological measurements. This indicates that unreacted end groups in the structure of epoxy react. No exhaustion was observed in the peaks compared to CE 0.4 wt%. This result is still a sign of the presence of unreacted ends in the structure. This result clearly shows that unreacted chain extender functional end groups react with R-PET. It can also be concluded that these reactions increase with temperature. It was assigned as the O-H stretching of the primary alcohol at the end of the ethylene glycol in the structure of the recycled PET at 970 cm^{-1}. It can also be concluded that these reactions increase with temperature. The peaks at 1420 cm^{-1} was assigned as OH bending vibrations of alcohol groups. Reductions were observed as a result of the polyetherification reaction between R-PET and Joncryl's unreacted hydroxyl end groups in this peak. With the increase in temperature, a decrease was observed in peak at 2960 cm^{-1} which corresponds to OH strecthing peak of carboxylic acid groups in the structure. It is an expected result that supports unreacted end groups to react with r-PET. Reductions are clearly seen when compared to R-PET. It is supported that polycondensation reactions existed during dynamic rheological measurements.

4.3 R-PET/PBT blends

4.3.1 Rheological properties of R-PET/PBT blends with/without chain extender

4.3.1.1 Thermal stability analysis

To the increase in processability of recycled PET, PET / PBT polymer blends were prepared in different ratios with twin screw extruder.

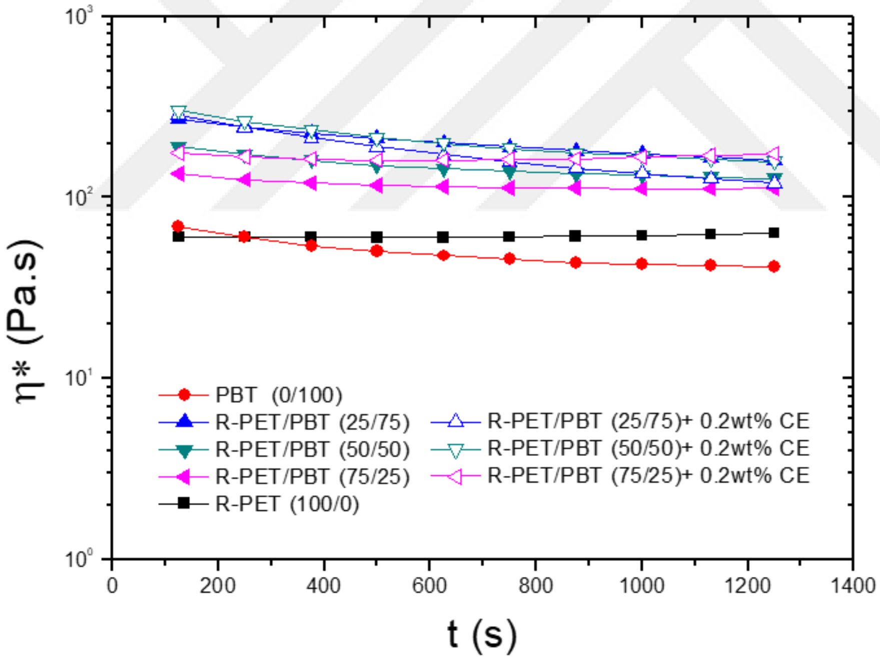

Figure 4.19 : Effects of blends and chain extended blends on thermal stability.

To observe how to change thermal stability of recycled PET with preperation of these polymer blends time sweep test was applied at 270°C that is chosen optimum temperature for both materials. Considering the time sweep test results of PBT and recycled PET, PBT degrades at high temperatures and recycled PET does not melt at low temperatures. Time sweep test was applied to polymer blends and chain extended polymer blends samples at 270°C. In addition, the change of thermal stability of R-PET and PBT was examined. The complex viscosity graphs of R-PET / PBT polymer blends is shown in Figure 4.19. Chain extender 0.2 wt% was added into the polymer blends. Molecular weight, which is one of the biggest problems for recycled materials, was developed with both blends samples and chain extended blends samples. When chain extenders are added, the thermal stability of the blend is improved. it was clearly seen that thermal stability increases and degradation is prevented by both preparing polymer blends and adding chain extender.

4.3.1.2 Frequency sweep test

The Frequency sweep test was carried out for R-PET / PBT blends in different ratios at 270 ℃. Frequency sweep test results are given in Figure 4.20. The dynamic complex viscosities $\eta*$ measured at 270 °C for R-PET/ PBT blends and their chain extended samples as a function of frequency are represented in Figure 4.12. Newtonian behavior was observed for R-PET and polycondensation reactions has been observed at low frequencies. However, this is not a desired result. It does not mean that it is thermally stable. Blends prepared at different ratios compensated the low viscosity of R-PET and the viscosity increased. it is expected that the structure of PBT will degrade at low frequencies from the time sweep test results given in Figure 4.4. With the addition of 25 wt% PBT, a decrease or increase in complex viscosity at low frequencies was not observed. This shows that even with the addition of a small amount of PBT, thermal stability can be improved. The increase in the viscosity of PET was balanced by degredation in the structure of PBT. When the PBT ratio increased to 75 wt%, r-PET was unable to compensate of degredation of PBT, and complex viscosity decreases were observed at low frequencies.

For a given frequency, the complex viscosity ($\eta*$) value for R-PET/PBT (25/75) was found to be higher than R-PET/PBT (75/25). The $\eta*$ values for the R-PET/PBT (75/25) + 0.2 wt% CE blend was found to be higher, only the value for the R-PET/PBT (25/75) + 0.2 wt% CE sample was lower for a given frequency. The unexpected result for R-PET/PBT (25/75) + 0.2 wt% CE of $\eta*$ is about increased high density entanglement in specific blend [111]. Although the amount of chain extender used is 0.2%, thermal stability can be compensated. This can be explained by the polycondensation and unreacted chain extender reactions between R-PET and chain extender. In addition, the highest viscosity increases observed in the R-PET / PBT + 0.2wt%. R-PET is high in weight show that it is more reactive than PBT. This shows that R-PET is more reactive to chain extender than PBT. Shear thinning behavior was observed at high frequencies and thermal stability were increased at low frequencies. This is a clear indication that processability has increased for R-PET / PBT + 0.2wt%

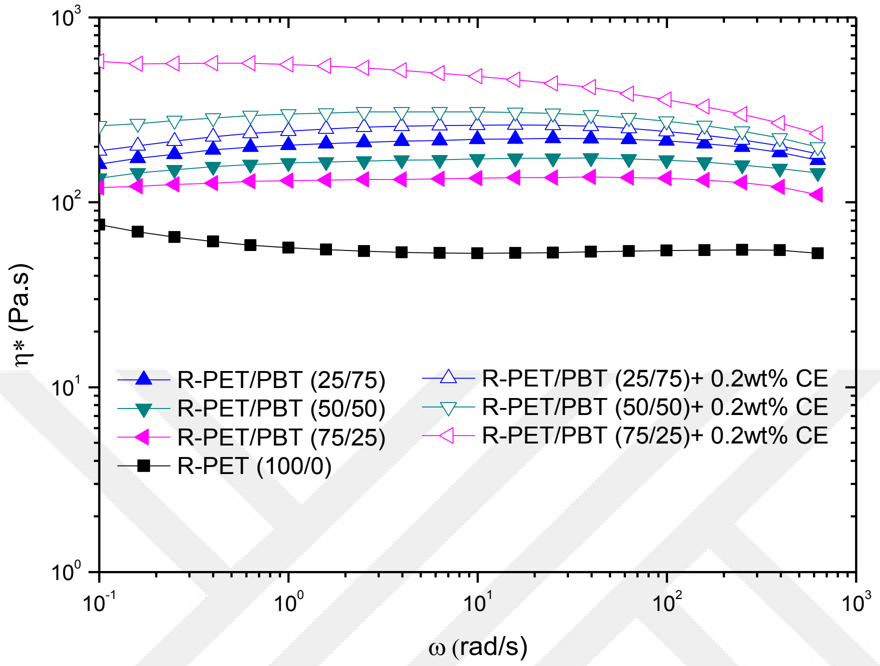

Figure 4.20 : Comparison of R-PET and their blends at 270℃ frequency sweep test.

4.3.2 Structure analysis of R-PET/PBT blends with/without chain extender

4.3.2.1 FTIR analysis

In order to increase thermal stability and processability, R-PET/PBT belnds in different ratios were prepared. FTIR analysis was performed to observe the changes occurring during rheological dynamical measurements. Viscosity increases were observed in the structure of R-PET/ PBT 75/25 +0.2 wt% CE. It is thought that these increases occured as a result of transesterification reactions between R-PET and PBT. In the process of the formation of the PET/PBT blend system, an ester exchange reaction may occur as shown in Figure 4.21.

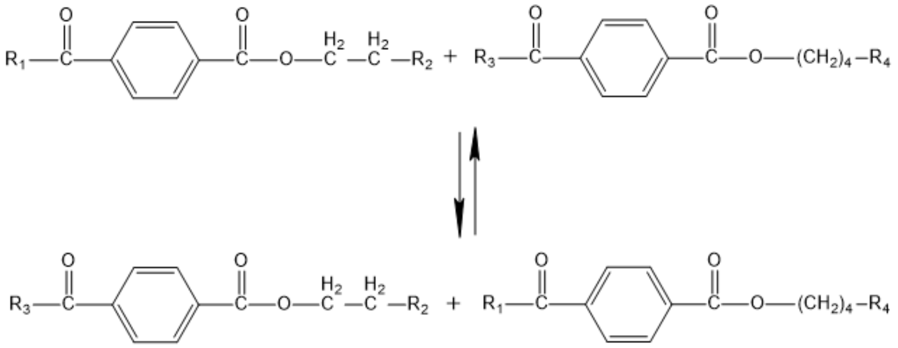

Figure 4.21 : Possible transesterification reaction mechanism between PET and PBT.

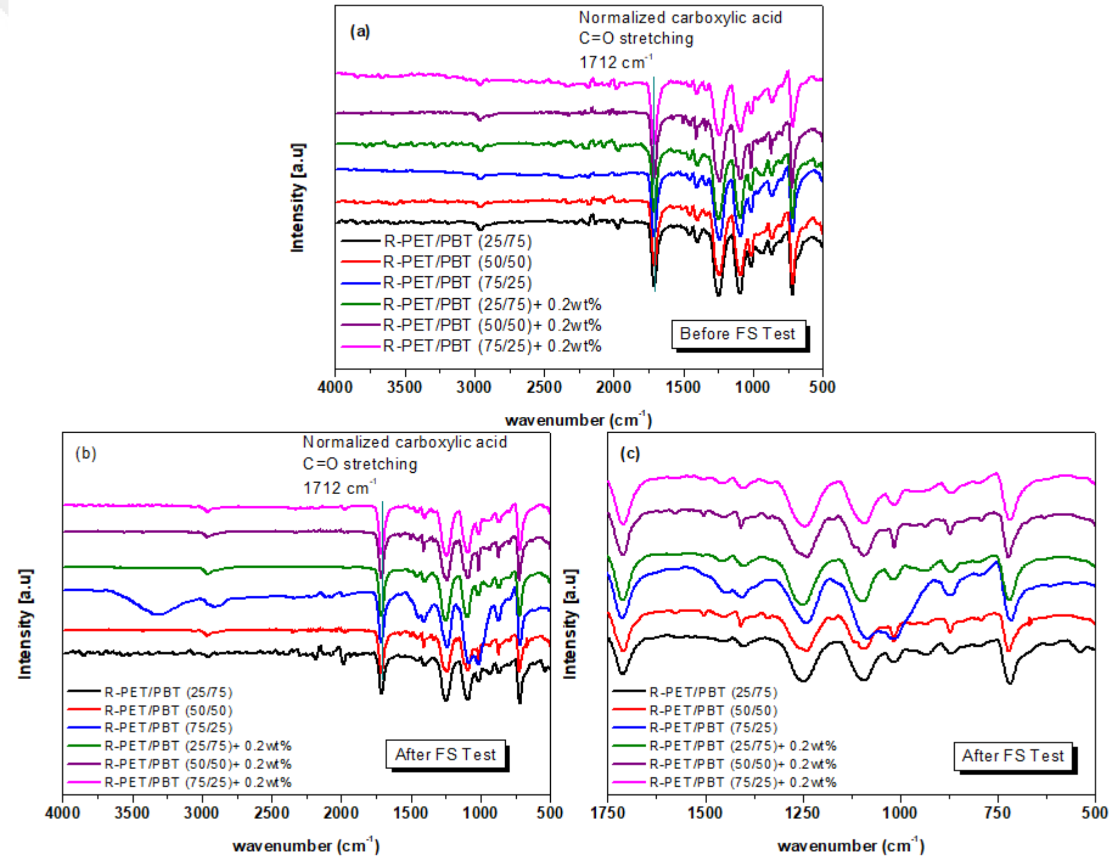

Figure 4.22 : FTIR spectrum of R-PET/PBT blends in different ratios and their chain extender samples (a) Before frequency sweep test (b)-(c) After frequency sweep test.

According to the results of FTIR analysis, as seen in Figure 4.22, many changes have been observed before and after frequency sweep test. PET and PBT are both polyester and their chemical structure is very similar. Thus, the peaks to be observed by FTIR analysis are almost similar and it will be difficult to determine whether these peaks belong to R-PET or PBT. During the frequency tsweep test, viscosity increases were observed and these increases are thought to be the result of the transesterification reaction of polyester-based polymers R-PET and PBT. However, there are many possibilities in transesterification reactions. Determining which ester group is changing requires a more detailed analysis. It can also perform R-PET or a polyesterification reaction in itself. Also, unreacted chain extender end groups in the structure may have reacted with R-PET or PBT. As can be understood from these results, there are many possibilities to explain the viscosity increases. The peaks can overlap because the two structures are similar. Therefore, it is not possible to explain the reactions occurring in the structure with a certain expression.

5. CONCLUSION

In this study, two methods have been investigated to improve the thermal properties of R-PET obtained by recycling process. After the recycling process, major disadvantages were observed in the structure of R-PET. In particular, molecular weight loss affects many properties of R-PET. Mechanical properties, processability and thermal properties significantly dcrease. Chain extender with a trade name of Joncryl ADR 4468® was used to improve thermal stability and prevent the degraded properties of R-PET. Addition of chain extender was carried out with all together mixing method. Thermal stability and rheological behavior were investigated by dynamic rheological measurements. R-PET/PBT binary blends at different ratios were investigated. The effects of R-PET / PBT blends prepared in different ratios on the thermal stability of neat R-PET were reported. In addition, the effect of chain extender added on neat R-PET was investigated and compared with R-PET / PBT blends. Complex viscosity of R-PET gradually increased when the amount of chain extender increased from 0.4 wt% to 0.8 wt% during dynamic rheological measurements. With the increase of the chain extender, thermal stability increases were also not observed. The reason for these viscosity increases was explained by the polycondensation reactions and unreacted chain extender reactions that occurred during dynamic rheological measurements. These reactions were supported by FTIR analysis results. With the addition of 25 wt% PBT in R-PET, a slightly decrease in complex viscosity at low frequencies was observed. R-PET could not compansate the degradation of PBT, but it reduced and polycondensation reactions were preveted with the addition of small amount of PBT. This shows that even with the addition of a small amount of PBT, thermal stability can be improved. Although the amount of chain extender used is 0.2%, thermal stability can be compensated. In addition, the highest viscosity increases observed in the R-PET / PBT + 0.2wt%. R-PET is high in weight show that it is more reactive than PBT. This shows that R-PET is more reactive to chain extender than PBT. Shear thinning behavior was observed at high frequencies and thermal stability were increased at low frequencies. This is a clear indication that processability has increased for R-PET / PBT + 0.2wt% R-PET / PBT (75/25) +0.2 wt% CE showed the most successful thermal stability for optimum design to reuse of PET wastes. This improvement has been achieved with high ratio R-PET and low ratio of PBT and chain extenders .

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- **B.Sc.** (2015-2019): Istanbul University, Faculty of Engineering, Civil Engineering Department
- **B.Sc.** (2012-2017): Istanbul University, Faculty of Engineering, Chemical Engineering Department

PROFESSIONAL EXPERIENCE AND REWARDS:

- 2019 Charles University- Graduate Researcher
- 2018 BASF Turkey Automotive Coatings Solutions- Technical Sales Trainee
- 2016, TÜPRAŞ- Production Intern
- 2015, Sapro Cleaning Products- R&D Intern