## ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

### THERMAL, MECHANICAL AND PHYSICAL PROPERTIES OF CHAIN EXTENDED RECYCLED POLYAMIDE 6 VIA REACTIVE EXTRUSION

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**Department of Polymer Science and Technology** 

**Polymer Science and Technology Programme** 

MAY 2019



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Ph.D. THESIS

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## REAKTİF EKSTRÜZYON YÖNTEMİ İLE ZİNCİRLERİ UZATILMIŞ GERİ DÖNÜŞTÜRÜLMÜŞ POLİAMİD 6'NIN TERMAL, MEKANİK VE FİZİKSEL ÖZELLİKLERİ

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**MAYIS 2019** 



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.....

Date of Submission: 3 April 2019Date of Defense: 17 May 2019



To my spouse and daughters,



#### FOREWORD

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My precious husband, I can accomplish anything as long as you're with me.

May 2019

Selin ÖZMEN (R&D Project Manager)



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## **ABBREVIATIONS**

EMA	: Alternating copolymer of ethylene and maleic anhydride
DTDI	: Dimeric 2,4-toluene diisocyanate
CW	: Polyester wax with reactive caprolactam groups
EPO	: Multi-functional epoxy-based oligomeric chain extender
rPA6	: Recycled polyamide6
DSC	: Differential scanning calorimetry
HDT	: Heat deflection temperature
VST	: Vicat softening temperature
PA6	: Polyamide 6
РЕТ	: Poly(ethylene terephthalate)
SMA	: Maleinated polystyrene
MAH	: Maleic Anhydride
ROP	: Ring opening polymerization
PBO-1	: 1,3-phenylene bis(2-oxazoline-2)
PBO-2	: 1,4-phenylene bis(2-oxazoline-2)
BOZ	: Bis-(2-oxazoline)
TBC	: Terephthaloyl-biscaprolactam
BGPPO	: Phenylphosphine oxide
PVC	: Polyvinyl chloride
TDI	: 2,4-toluene diisocyanate
ISO	: International organization for standardization
ASTM	: American standard test method
CONH	: Amide
CO <sub>2</sub>	: Carbondioxide
H <sub>2</sub> O	: Water



# SYMBOLS

: Relative crystallinity degree
: Degree Celcius
: Specific melting enthalpy of fully crystalline PA6
: Specific melting enthalpy of the polymer
: Elastic modulus or Young's Modulus
: Stress at yield
: Elongation at break
: Glass transition temperature
: Melting temperature
: Crystallization temperature
: Heat of fusion of polymers
: Elastic strain
: Change in length
: Initial gauge length
: Original cross sectional area
: Stress
: Force
: Crystallization onset temperature
: Relative viscosity
: Percentage



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#### THERMAL, MECHANICAL AND PHYSICAL PROPERTIES OF CHAIN EXTENDED RECYCLED POLYAMIDE 6 VIA REACTIVE EXTRUSION

#### SUMMARY

Polyamides (PAs), also known as Nylon, are one of the most important commercial engineering plastics. Polyamide 6 (PA6) is a linear condensation polymer, synthesized by the ring opening polymerization of caprolactam with an amide (-CONH-) repeating units. PA6's are widely used versatile engineering plastics due to its competitive price, excellent strength and stiffness, low friction coefficient, high dimensional stability, chemical and wear resistance properties. This combination of properties has resulted in them becoming one of the most used types of polyamide worldwide.

In the last decade plastic recycling has become one of the most important issues, due to the increasing worldwide consumption of plastic materials and environmental pollution [1, 2]. The global plastic recycling market was valued at US\$ 34.80 Bn in 2017 and one of the most important and valuable recycled plastic is Polyamide 6. Among the recycling processes the physical recycling of Polyamide 6 (PA6) by melt reprocessing is the most preferred since it is relatively simple process, needs low investments and more environmentally friendly [3-5]. However during recycling process PA6 expose to high heat and mechanical forces that causes degradation of polymer chains. Reduction in molar mass of PA6 leads to loss of mechanical and thermal properties and limits the application areas of recycled PA6 (rPA6).

Chain extension reactions via compounding process are a simple and inexpensive way to increase the molecular weight of condensation polymers [3–20]. Chain extenders can be low molecular weight monomeric chemicals or polymeric materials that can increase the molecular weight of polymers in a fast reaction. Chain extenders can react with either amine or carboxyl end groups of polyamides and link polymer chains to increase the molecular weight [3, 4].

Effective usage of chain extenders is important as choosing the optimal chain extender depending on the processing technology. It is known that viscosity of polyamides increase with chain extender amount and during extrusion process PA degradation is likely to proceed simultaneously with the chain extension reactions. In order to overcome degradation it is important to adjust process parameters.

This study focused on effect of chain extender types, screw temperature and residence time on thermal, mechanical and physical properties of chain extended recycled Polyamide 6 via reactive extrusion. In the part which the effect of chain extender types were studied, we report for the first time alternating copolymer of ethylene and maleic anhydride (EMA), polyester wax with reactive caprolactam groups (CW) and dimeric 2,4-toluene diisocyanate (DTDI) as chain extenders for the improvement of recycled polyamide6 (rPA6). In this study, chain extenders with different molecular structures were melt compounded with rPA6 in varying amounts. The effectiveness of the chain extenders was evaluated through: relative viscosity,

differential scanning calorimetry (DSC), HDT, VST measurements, and mechanical tests including tensile and impact tests of the chain extended products. A comparison between the mechanical properties of the chain extended products and neat rPA6 was also carried out to highlight the influence of optimal chain extender selection on rPA6. It is demonstrated that DTDI, which is generally used for polyurethanes, can be a viable option for rPA6.

The results showed that mechanical properties were improved by all chain extenders, however the highest improvement was achieved with EMA. Relative viscosities of chain extended products increased with increasing chain extender amounts for all chain extenders due to the increase in molecular weight of resultant materials. Between 2%-41% increase in relative viscosity of rPA6 was achieved by the incorporation of chain extenders which makes chain extenders powerful tool for industrial applications to adjust viscosity of rPA6.

While e-modulus was not significantly affected by chain extenders incorporation, elongation at break was noticeably improved. Elongation at break and notched izod impact strength increased with an increase of chain extender amount for all types of chain extenders which are also consistent with the viscosity values. Elongation at break and notched izod impact strength were increased by 6.3 times and 26% respectively with 1 wt% of EMA incorporation. Unnotched impact strength values improved from 31kj to no break data for all chain extenders in all contents. Brittle neat rPA6 became ductile after chain extension and its toughness was increased.

Chain extenders increased the molecular weight of rPA6 which increase entanglement and restrict the mobility of chains and thus lead to between 5.2%-12.4% increase in HDT of rPA6. Among the chain extenders used in this study EMA showed a higher effect in comparison to the other chain extenders as observed from relative viscosity and mechanical test results. DTDI improved the molecular weight of rPA6 better than EPO and CW. Therefore, addition of both chain extenders to commercial rPA6 through melt compounding could be an efficient way to increase molecular weight of rPA6 and leads to up-graded products with improved elongation at break and izod impact strength. In this study DTDI which is generally used for polyurethane applications, was used as chain extender for rPA6 for the first time and showed great chain extension performance according to relative viscosity, elongation at break, yield strength and izod impact strength. DTDI can be used as a chain extender for rPA6 for industrial applications.

In the part that effect of screw temperature and residence time were studied, EMA and DTDI were added at two different concentrations (0.5% and 1%) to rPA6, and effect of screw temperature and residence time on chain extension behavior were investigated through the relative viscosity measurements, DSC and mechanical tests including tensile and impact tests of the resulting materials. A comparison between physical, mechanical and thermal properties of chain extended products and neat rPA6 were also carried out to highlight the influence of optimal screw temperature and residence time selection for rPA6 chain extension.

Temperature dependent improvements of chain extended products with EMA and DTDI showed different tendencies. While chain extension reaction of EMA more effective at medium screw temperature profile, chain extended products with DTDI showed similar results at all screw temperature profiles.

According to numerical results by adjusting screw temperature at least 9.1% higher viscosity, 1.3 times higher elongation at break and 10.6% higher impact strength were obtained with EMA.

Time dependent improvements of chain extended products with EMA and DTDI also showed different tendencies. Longer residence time promoted chain extension reaction of EMA. On the other hand DTDI chain extension reaction was not significantly affected from residence time due to high reactivity of isocyanate.

Even low residence times were enough for efficient chain extension reaction. According to numerical results by adjusting residence time 41.2% higher viscosity, 1.4 times higher elongation at break and 11.8% higher impact strength were obtained with EMA.



#### REAKTİF EKSTRÜZYON YÖNTEMİ İLE ZİNCİRLERİ UZATILMIŞ GERİ DÖNÜŞTÜRÜLMÜŞ POLİAMİD 6'NIN TERMAL, MEKANİK VE FİZİKSEL ÖZELLİKLERİ

### ÖZET

Naylon olarak da bilien Poliamid'ler (PA), en önemli ticari mühendislik plastiklerin biridir. Doğrusal yoğunlaşma polimeri olan Poliamid 6 (PA6), amid (-CONH-) tekrarlanan birimli kaprolaktamın halka açılım polimerizasyonu ile sentezlenir. PA6 rekabetçi fiyatı, mükemmel kuvveti ve sertliği, düşük sürtünme katsayısı, yüksek boyutsal kararlığı, yüksek kimyasal ve aşınma direnci nedeniyle çok kullanılan çok yönlü mühendislik plastiğidir. Bu özelliklerin kombinasyonu onların dünya genelinde en çok kullanılan poliamid çeşidi haline gelmesini sağlamaktadır.

Son on yılda, plastik malzemelerin tüketiminin dünya çapında artması ve çevre kirliliği nedeniyle plastik geri dönüşümü en önemli konulardan biri haline gelmiştir [1, 2]. Küresel plastik geri dönüşüm piyasası 2017 yılında 34.80 milyar ABD Doları değerine ulaşmıştır ve en önemli ve değerli geri dönüşümlü plastiklerden biri Polyamide 6'dır. Nispeten daha basit bir süreç olması, düşük yatırım gerektirmesi ve daha çevre dostu olması nedeniyle geri dönüşüm süreçleri arasında Polyamide 6'nın (PA6) eriyik yeniden işleme ile fiziksel geri dönüşümü en çok tercih edilenidir [3-5]. Fakat, geri dönüşüm işlemi sırasında PA6, polimer zincirlerinin bozulmasına neden olan yüksek ısıya ve mekanik kuvvetlere maruz kalmaktadır. PA6'nın molar kütlesindeki azalma, mekanik ve termal özelliklerin kaybına neden olmakta ve geri dönüştürülmüş PA6 (rPA6) uygulama alanlarını kısıtlamaktadır.

Kompounding yöntemiyle zincir uzatma reaksiyonları, kondanzasyon polimerlerinin moleküler ağırlıklarını arttırmanın basit ve ucuz bir yoludur [3-20]. Zincir uzatıcılar polimerlerin molekül ağırlığını hızlı bir reaksiyonda artırabilen düşük molekül ağırlıklı monomerik kimyasallar veya polimerik malzemeler olabilirler. Zincir uzatıcılar, amin veya karboksil uç gruplu poliamidlerle reaksiyona girebilirler ve moleküler ağırlığı arttırmak için polimer zincirlerini bağlarlar [3, 4].

Zincir uzatıcıların etkin kullanımı, işleme teknolojisine bağlı olarak en uygun zincir genişleticinin seçilmesi kadar önemlidir. Polyamidlerin viskozitesinin, zincir uzatıcı miktarı ile birlikte arttığını ve ekstrüzyon işlemi sırasında PA bozulmasının zincir uzatma reaksiyonları ile aynı anda ilerleyebileceği bilinmektedir. Bozulmanın engellenebilmesi için proses parametrelerini ayarlamak önemlidir.

Bu çalışma; zincir uzatma tiplerinin, vida sıcaklığının ve alıkonma zamanının, reaktif ekstrüzyon yöntemiyle zincirleri uzatılmış geri dönüştürülmüş Polyamid 6'nın termal, mekanik ve fiziksel özellikleri üzerindeki etkisine odaklanmıştır. Zincir uzatma tiplerinin etkisinin incelendiği bölümde, rPA6'nın geliştirilmesi için zincir uzatıcılar olarak etilen ve maleik anhidrit alternatif kopolimeri (EMA), reaktif kaprolaktam grupları içeren poliester wax (CW) ve dimerik 2,4-tolüen diizosiyanat (DTDI) literatürde ilk defa raporlandı. Bu çalışmada, farklı moleküler yapılara sahip zincir uzatıcılar, değişen miktarlarda rPA6 ile kompound edildi. Zincir uzatıcıların etkinliği, zincirleri uzatılmış ürünlerin nispi viskozite, diferansiyel taramalı kalorimetre (DSC), HDT, VST ölçümleri ve çekme ve darbe testlerini içeren mekanik testler yoluyla değerlendirildi. Optimum zincir uzatıcı seçiminin rPA6 üzerindeki etkisini vurgulamak için zincirleri uzatılmış ürünlerin ve düz rPA6'nın mekanik özelliklerinin karşılaştırılması yapıldı. Genellikle poliüretanlar için kullanılan DTDI'nın rPA6 için uygun bir seçenek olabileceği gösterildi.

Sonuçlar, mekanik özelliklerin tüm zincir uzatıcılar tarafından geliştirildiğini, ancak en fazla iyileşmenin EMA ile sağlandığını gösterdi. Zincirleri uzatılmış ürünlerin nispi viskoziteleri, elde edilen malzemelerin moleküler ağırlığındaki artıştan dolayı tüm zincir uzatıcılar için artan zincir uzatma miktarları ile arttı. Zincir uzatıcıların eklenmesiyle rPA6'nın nispi viskozitesinde % 2 ila % 41 arasında bir artış sağlandı, bu da zincir uzatıcıları endüstriyel uygulamalarda, rPA6'nın viskozitesini ayarlamak için güçlü bir araç haline getirmiştir.

E-modül, zincir uzatmaların dahil edilmesinden önemli ölçüde etkilenmese de, kopma uzamaları belirgin şekilde iyileştirilmiştir. Kopma uzaması ve çentikli izod darbe dayanımı, bütün zincir uzatacı tipleri için zincir uzatıcı miktarının artmasıyla artmıştır bu sonuçlar viskozite değerleriyle de tutarlı çıkmıştır. Kopma uzaması ve çentikli izod darbe dayanımı, ağırlıkça % 1 EMA katılımıyla sırasıyla % 6,3 ve % 26 artmıştır. Çentiksiz darbe dayanımı değerleri, bütün zincir uzatıcı tiplerinin bütün katkılanma oranlarında 31 kJ'den kırılmazlık seviyesine iyileştirilmiştir. Kırılgan düz rPA6, zincir uzatma reaksiyonları sonrasında sünek hale gelmiştir ve tokluğu artmıştır.

Zincir uzatıcılar, dolaşıklaşıklığı artmasına ve zincirlerin hareketliliğinin kısıtlanmasına yol açan molekül ağırlığında artış sağlamıştır ve böylece rPA6'nın HDT'sinde % 5.2 ila % 12.4 arasında bir artışa neden olmuştur. Bu çalışmada kullanılan zincir uzatıcılar arasında EMA, nispi viskozite ve mekanik test sonuçlarından gözlemlendiği üzere diğer zincir uzatıcılara kıyasla daha yüksek bir etki göstermiştir. DTDI, rPA6'nın moleküler ağırlığını EPO ve CW'den daha iyi arttırmıştır. Bu nedenle, kullanılan bütün zincir uzatıcıların kompounding yöntemiyle ticari rPA6'ya eklenmesi, rPA6'nın molekül ağırlığını arttırmak için etkili bir yol olarak düşünülebilir ve kopma uzaması ve Izod darbe dayanımı iyileştirilmiş ürünler elde etmeyi sağlayabilir.

Bu çalışmada, genel olarak poliüretan uygulamaları için kullanılan DTDI, ilk kez rPA6 için zincir uzatıcı olarak kullanılmış ve bağıl viskozite, kopma uzaması, akma dayanımı ve Izod darbe dayanımı sonuçarına göre yüksek zincir uzatma performansı göstermiştir. DTDI, endüstriyel uygulamalarda rPA6 için zincir uzatıcı olarak kullanılabilir.

Vida sıcaklığının ve alıkonma zamanının etkisinin incelendiği bölümde, rPA6'ya iki farklı konsantrasyonda (% 0,5 ve % 1) EMA ve DTDI eklenmiş ve vida sıcaklığının ve alıkonma zamanının zincir uzatma davranışı üzerindeki etkisi, elde edilen malzemelerin viskozite ölçümleri, DSC, çekme ve darbe testlerini içeren mekanik testler yoluyla incelenmiştir. Optimum vida sıcaklığının ve tutma süresi seçiminin rPA6 zincir uzatma reaksiyonları üzerindeki etkisini vurgulamak için, zincirleri uzatılmış ürünler ile düz rPA6'nın fiziksel, mekanik ve ısıl özelliklerinin karşılaştırma yapılmıştır.

EMA ve DTDI ile zincirleri uzatılmış ürünlerin sıcaklığa bağlı gelişmeleri farklı eğilimler göstermiştir. EMA'nın zincir uzatma reaksiyonu orta vida sıcaklık profilinde daha etkiliyken, DTDI ile zincirleri uzatılmış ürünler tüm vida sıcaklık profillerinde benzer sonuçlar göstermiştir. Sayısal sonuçlara göre vida sıcaklığının ayarlanmasıyla, EMA ile en az %9.1 daha yüksek vizkozite, 1.3 kat daha yüksek kopma uzaması ve %10.6 daha yüksek darbe dayanımı elde edilmiştir.

EMA ve DTDI ile zincirleri uzatılmış ürünlerin zamana bağlı gelişmeleri de farklı eğilimler göstermiştir. Uzun alıkonma süresi, EMA'nın zincir uzatma reaksiyonunu arttırken, diğer taraftan, DTDI zincir uzatma reaksiyonu, yüksek izosiyanat reaktivitesine bağlı olarak alıkonma süresinden önemli ölçüde etkilenmemiştir.

Sayısal sonuçlara göre vidada alıkonma süresi ayarlanarak, EMA ile %41.2 daha yüksek vizkozite, 1.4 kat daha yüksek kopma uzaması ve %11.8 daha yüksek darbe dayanımı elde edildi.



#### **1. INTRODUCTION**

Polyamides (PAs), also known as Nylon, are one of the most important commercial engineering plastics [21]. Polyamide 6 (PA6) is a linear condensation polymer, synthesized by the ring opening polymerization of caprolactam with an amide (- CONH-) repeating units. PA6's are widely used versatile engineering plastics due to its competitive price, excellent strength and stiffness, low friction coefficient, high dimensional stability, chemical and wear resistance properties. This combination of properties has resulted in them becoming one of the most used types of polyamide worldwide.

In the last decade plastic recycling has become one of the most important global issues, due to the increasing worldwide consumption of plastic materials and environmental pollution [1, 2]. The global plastic recycling market was valued at US\$ 34.80 Bn in 2017 and one of the most important and valuable recycled plastic is Polyamide 6. Recycling processes are growing in importance as they are regarded as one of the best ways to economically reduce plastic materials waste. There are four main methods used for the plastic waste recycling: energy recovery (incineration), landfilling, chemical processing (de-polymerization) and material recycling [3]. While recycling polymers can be very complex due to the different sources of polymer, it is still more economic and environmental friendly than landfilling, incineration [22, 23] and chemical processing [24].

Melt reprocessing is the most widely used method for recycling of thermoplastics due to its low investment requirements and relatively simple processing with established equipment [4, 5, 25]. However, during the melt reprocessing, the high heat and mechanical forces that polymers are exposed to cause chemical changes and degradations in polymer structure, such as a decrease in molar mass. Ultimately those changes affect the thermal and mechanical properties of the polymer, which may limit their application areas.

Chain extension during compounding of recycled plastics is relatively simple and inexpensive way in comparison to other recycling methods to increase the molecular weight of condensation polymers [4–20, 25]. Chain extenders can be either low molecular weight monomeric chemicals or polymeric materials that increase the molecular weight of polymers in a fast reaction. Chain extenders can react with either amine or carboxyl end groups of polyamides and can link polymer chains to increase the molecular weight [4, 25]. It is important to choose the optimal chain extender depending on the processing technology. For injection molding processes chain extenders that have two or more functionalities are useful, as they cause partial curing and consequently increase the elastic properties of the resulting materials. For fiber production chain extenders with a linear structure are convenient, because they promote chain alignment and crystallization of drawn fibers.

Effective usage of chain extenders is important as choosing the optimal chain extender depending on the processing technology. It is known that viscosity of polyamides increase with chain extender amount and during extrusion process PA degradation is likely to proceed simultaneously with the chain extension reactions. In order to overcome degradation it is important to adjust process parameters.

Despite their simple processing and advantages, only few publications of chain extension for rPA can be found in literature [6, 7] and with none of them reporting the effect of chain extenders on heat deflection temperature (HDT) or vicat softening temperature (VST). Most studies on chain extension focus on either recycled poly(ethylene terephthalate) (PET), neat PET and neat polyamides. Chain extenders studies for PET are mainly: different phosphides [8], bisoxazolinones [9], bisoxazolines [10-12], bisoxazines [13], bisepoxides [14], epoxidic multifunctional oligomer [15] and isocyanate [16, 17]. However to date PA has been limited to bisoxazolines [18-20, 26, 27], biscaprolactam molecules [28, 29] and their combination [30, 31]. It is reported that while bis(2-oxazoline) systems reacted with carboxy-terminated PA's, biscaprolactam systems had more reactivity with amino end groups. However, the chain extension effectiveness of chain extenders having different molecular structures has not yet been fully evaluated.

In this study we focused on effect of chain extender types, screw temperature and residence time on thermal, mechanical and physical properties of chain extended recycled Polyamide 6 via reactive extrusion.

#### 2. BACKGROUND INFORMATION

#### 2.1 Polyamide 6

Polyamides are versatile engineering polymers that can be used in fiber, film, packaging and molding applications. Because of its good processability, excellent mechanical properties, and desirable chemical resistance polyamides constitudes an important part of the world engineering polymers market [32]. The main consumer is the transportation manufacturing industry which covers the 35% of the polyamide (PA) consumption [33].

Polyamide, which is also known as Nylon, was invented by the American chemist Wallace Hume Carothers who was working for Du Pont (an American chemical industry) as a group leader in 1935. There are many legends about the Nylon's acronym etymology and one of these was driven by the Japanese silk monopoly in the late 30's and it is "Now You've Lost, Old Nippon".

Polyamide is a condensation polymer that contain amide group (-CONH-) in the polymer chain [34]. Polyamide can be categorized into two, namely aromatic and aliphatic. Nylons are named by the number of carbon atoms present in its monomer. Nylons are generally made up of two monomers which are a diamine and a diacid monomers. The numbers that differentiate the nylons specifies the number of carbon in the diamine and the number of carbon in the diacid. In the case that acid and amine groups are in the same monomer, the name is defined by a single digit number. For instance polyamide 6 and polyamide 11.

Polyamides can be synthesized in different ways such as bulk polyamidation (polycondensation), anionic polymerization, polyamidation in solution [35]. Polyamide 6 (Nylon 6) is mainly polymerized by hydrolytic ring opening polymerization (ROP) of caprolactam at 250-270 <sup>o</sup>C. Process begins with the hydrolysis of caprolactam which forms aminocaproic acid. The addition of ROP of caprolactam to the amine end group of a growing chain is followed. High molecular

weight product occurs by the reaction between the amine and carboxylic acid end groups and during this polycondensation water is released. Nylon 6 synthesis process involes both the ROP and the polycondensation reaction and both reactions occur simultaneously.

Polyamide 6 is very important polymer due to its properties. Some of these properties are; it is semi-crystalline polymer and it has high yield stres. Crystallinity is an important property because it provides strength, stiffness, and temperature stability. PA6 has high yield stress due to the hydrogen bonds formed between chains. The hydrogen bonds are formed between amide and carbonyl groups and they are stronger than Van Der Waals interactions but weaker than covalent bonds. The chains of polyamide are oriented in a way to have maximum the hydrogen bonding which also provides high regularity [36,37].

Due to the polar character of PA6's monomer, interactions between chains and surroundings occurs. In an humid environment, some of the H-bonds between chains are broken and connect with the water molecules [38-40]. The absorbed water amount is important to define the polar character of PA6 which dependents on the temperature and surrouding relative humidity. The amount also proportional to the amorphous fraction [41]. Mobility of chains enhanced with the decrease in H-bonds between chains. Consequently decreases the glass transition temperature of PA6 [42]. The phenomenon which also deteriorates the mechanical properties is called "plasticization" [43-45]. Moreover, the decrease in Tg by induced-hydration can results in material morphology changes [46].

#### 2.2 Recycling Polymer

Recycling has attracted great interest in recent years due to its economical and environmental effects. Each year millions of tones of plastic scraps are collected in landfills which cause ecological threats. The economic potential of waste plastic products increase the interest on the recycling technologies.

Recycling processes are valuable because by this processes the collected materials are transformed into raw materials. This raw materilas can be used to manufacture new products.
Recycling processes can be classified into three major categories: Physical recycling, chemical recycling and thermal recycling.

Physical recycling process is melt-blending of polymers to be reused. This method gives an opportunity to modify polymers. In physical recycling process chemical structure of polymer does not change only the appearance of the material changes. Physical recycling process involves removing contaminants, changing size and shape of the materials, and blending with additives. Compounding is an example of physical recycling process.

Chemical recycling process or depolymerization involves breaking down the chemical structure of polymers by using chemicals into their chemical constituents (its monomers) and converts them into useful products like basic chemicals and/or polymers. These monomers can be re-polymerized and of a quality equivalent to that of the "virgin" polymer. Recycled materials by chemical recycling process become raw materials for producing new polymer. Glycolysis is an example of chemical recycling. Condensation polymers such as PET, PA are more common for this technique than polyolefins or PS. Polyamide 6 can be depolymerized to its monomer (caprolactam) by acidolysis, hydrolysis, aminolysis or catalyzed-de-polymerization in vaccum.

Thermal recycling process also involves breaking down the chemical structure of polymers; however, heat is used as the driving force for reactions instead of chemical reactions. Pyrolysis is an example of thermal recycling process. In this process the waste polymer is subjected to high temperatures in the absence of sufficient oxygen for combustion. Thermal recycling can be applied to all types of polymers. If the materials to be recycled are reasonably pure compound, they can be used as raw materials. But if materials are a complex mixture, recycled products are often used as fuel [47].

Separation of waste plastics is a very important issue for polymer recycling because the contaminants and solid particles affect the physical performance of polymer matrix and consequently lower the quality of final recycled product.

Recycling can be a good option when the structures of the components are preserved and no significant degradation occurs during recycling. The high heat and mechanical forces that polymers are exposed to cause chemical changes and degradations in polymer structure, such as a decrease in molar mass. Ultimately those changes affect the thermal and mechanical properties of the polymer, which may limit their application areas and reduce their value.

The most important part of plastic recycling is avoiding degradation. This is possible with the correct selection of processing conditions and by addition of stabilizers and other additives like chain extenders before melt compounding [48].

### 2.3 Chain Extenders

Chain extenders are low molecular weight compounds that can be monomeric, oligomeric, difuctional or multifunctional. They can be added either in polymerization process or during reactive extrusion processes. The right choice of chain type depending on inwhich processing technology they will utilize is very important. It is important to choose the optimal chain extender depending on the processing technology. For injection molding processes chain extenders that have two or more functionalities are useful, as they cause partial curing and consequently increase the elastic properties of the resulting materials. For fiber production chain extenders with a linear structure are convenient, because they promote chain alignment and crystallization of drawn fibers. Concentration of chain extender, the residence time of the polymer in the extruder and the temperature profile of extruder are three main parameters that effect the effectiveness of chain extenders in reactive extrusion process [49].

PA's have reactive amino and carboxyl groups. Chain extenders can react with either amine or carboxyl end groups of polyamides and can link polymer chains to increase the molecular weight [3, 4].

Thus, all the difunctional or multifunctional compounds, that can react with amino and/or carboxyl groups can be chain extenders for PA's. These are phosphides [50], bisoxazolinones [51], bisoxazolines [52–54], bisoxazines [55], and bisepoxides [56]. There are two types of chain extension reactions for PA's chain extension. These are condensation type or addition type reactions. In condensation type reactions by products are generated on the other hand in the addition-type chain extension reactions no by products are generated.

In recent years, several chain extension studies have been performed to modify polyamides [57]. Loontjens et al. [31] used 1,3-phenylene bis(2-oxazoline-2) (PBO-1) and isophthaloyl biscaprolactamate for poly(ethylene terephthalate) and PA6. They revealed that when they used only one type of chain extender, increase in viscosity of resultant material was modest but when they used two types of chain extender increase in molecular weight of resultant material was strong.

Schacker et al. [58] investigated the difference between linear chain extension with bisoxazoline and chain bundling by grafting onto the maleinated polystyrene (SMA) of the PA. They revealed that increase in melt vicosity of PA was strong by grafting onto the SMA. They conclude that chain bundling by grafting onto SMA was better linear chain extension with bisoxazoline. Qian et al. [59,60] performed a detailed study on the chain extension of PA1010 by using 2,2'-bis-(2-oxazoline) (BOZ) and 1,4-phenylene bis(2-oxazoline-2) (PBO-2) as chain extenders. Their investigations showed that the BOZ's chain extension effect was better than that of PBO-2 due to its higher reactivity and diffusivity. Jakisch et al. [61] worked on chain extension of PA with a new difunctional chain extender that had one oxazoline group and one oxazinone group. Their results suggested that the reactions of oxazoline and oxazinone groups with carboxyl and amino groups, respectively, acted independently with each other and acted high selectively. This difunctional chain extender increased the molecular weight of PA strongly. Buccella et al. [29, 62, 63] investigated the effects of using 1,1'-carbonyl-bis-caprolactam and PBO-1 individually and in combination on the chain extension behavior and thermomechanical properties of the resultant PA6 materials. Lu et al. [64-66] investigate the chain extension of PA6 using BOZ, PBO, and terephthaloyl-biscaprolactam (TBC) individually and in combination. There was an optimal dosage for only one of the chain extenders used. When less amount of chain extender was used chain extension was incomplete and when an excess amount of chain extender was used it caused to more blocked reactions. The improvement of the molecular weight was greater when two types of chain extenders were used. The epoxide group showed a relatively high reactivity with both the amino and carboxyl end-groups of the PA6 [67]. A styrene-acrylic oligomeric polyepoxide Joncryl-ADR-4368 has been used as a chain extender in engineering plastics. A small amount of Joncryl-ADR-4368 increases the PA6's tensile strength and melt viscosity [68]. Likewise, Alvianto et al.

[69] found that chain extension of PA6 with 1.5 wt% bis(glycidyloxy) phenylphosphine oxide (BGPPO) increased the melt torque about seven times than that of the unmodified PA6. BGPPO involves two epoxide groups and a phosphorus-oxygen double bond, as a forceful electronwithdrawing group to bind PA6 [70]. Moreover, due to the low molecular weight (270 g mol-1) of BGPPO might have easily diffused in high viscosity polymer melt.

### 2.4 Polymer Processing

Polymer Processing is the manufacturing activity of converting polymeric raw materials into value-added products of desirable shape and properties by means of shaping compounding and modifications. Extrusion, injection molding, calendaring, fiber spinning, film blowing, blow molding are the commen types of processing methods [71].

### 2.4.1 Polymer extrusion

Polymer extrusion is a manufacturing process that is used to obtain polymeric materials in film, sheet and profile forms. Extrusion is also used to produce compounds which are later used by all the other plastics manufacturing processes. Compounding is a process of melt blending plastics with fillers, colorants, and other additives.

The extruder consists of control panel, feeders, screw, barrel and die. The control panel has indicators to control the die pressure, temperature and torque of process and to adjust the temperature, screw speed and feeding rate. Plastic raw material and other additives are put into a hopper (feeder) which the materials fed into the extrution screw through a hole. The screw molten the materials and mix them by heating. It turns inside the extruder barrel and moves the molten plastic mixture to die. The polymer mixture is shaped in the die zone. The polymer melt is forced through the die by means of the die-head pressure [72]. There are numereous die design and applications such as compounding, sheet, film, coatings, pipe, and rod.

Screw extruders are divided into single screw and multi screw extruders. Single screw extruders are generally used for shaping and multi screw extruders are generally used for mixing (compounding).

### 2.4.1.1 Twin screw extruders

Twin-screw extruders are utulized for difficult compounding applications, devolatilization, chemical reaction and profile extrusion of thermally sensitive materials in the polymer processing industry [72]. Twin-screw extruders can have a conical or parallel design. The two screws can be counter-rotating or co-rotating, intermeshing or nonintermeshing. Also, the configurations of the screws can be varied using different conveying and mixing elements. Figure 2.1 shows intermeshing co-rotating and counter-rotating twin screws.



Figure 2.1 : Intermeshing twin screw extruder (a) Co-rotating. (b) Counterrotating.

Counterrotating twin-screw extruders are used mainly for processing polyvinylchloride (PVC) products, such as pipe, profile, sheet, pellets and film. The co-rotating units are used for compounding materials where thorough mixing is important. Co-rotating twin-screw extruders usually have modular configurations, which makes the equipment quite flexible for adapting to changing applications and material properties.

### 2.5 Experimental Techniques for Material Characterization

The experimental techniques used to characterize neat rPA6 and chain extended products investigated in this dissertation are discussed here.

#### **2.5.1 Flow characteristics**

#### 2.5.1.1 Relative viscosity measurements

Relative viscosity is an essential parameter, which defines the relation between molar mass and viscosity. It is essential for non-Newtonian fluids, especially for polymers. Higher molar mass leads to higher viscosity in the polymer. In order to determine molar mass of polymer, its viscosity can be measured because most of the polymers show a different relation between molar mass and viscosity. As the viscosity of polymer solutions increases molar mass increases. Although most of the polymer solutions are shear-dependent (i.e. non-Newtonian) in a range of sufficiently low shear rates, they behave as they are Newtonian. Relative viscosity calculated by dividing the viscosity of the polymer solution ( $\eta$ ) by the viscosity of pure solvent ( $\eta$ o) having dimensionless unit (equation 2.1).

$$\eta_{\rm rel} = \eta / \eta o \tag{2.1}$$



Figure 2.2 : Viscometer

### 2.5.2 Mechanical properties

Mechanical properties are related to evaluation of load deformation or stress-strain relationship. The forces applied can be in the form of tension, shear, torsion, compression and bending. Composition, structure and interactions at molecular and supermolecular levels affetes the mechanical behavior of polimeric matrials.

Structures are mainly determined by primary chemical bonding (mostly covalent) within the chains and secondary bonding (hydrogen bonding, van der Waals, induction and electrostatic) forces between chains. Stress-strain curve structure, stress relaxation or impact behavior are decisive factors for applications and limitations of polymers [73].

### 2.5.2.1 Tensile test

Tensile tests are performed according to standard test methods, by using specimens of a specified shape (typically dog bone shape) and dimensions. Tensile test specimen has reduced cross section at the midlength, which is called the gauge section, to prevent fracture occurs at the holding grips [74].

The test is performed with gradually increasing load applied to a sample at a predetermined strain rate. The applied strain is determined with respect to the response of the material against the load and generally chosen at the intervals of 1-100 %/min. In general up to  $10^6$  %/min when the strain rate increases, tensile strength and e-modulus increase whereas elongation at break decreases [75].

In order to determine tensile properties, stress versus strain graph is plotted. *Stress* (nominal) which is is  $\sigma$  (MPa), shows the status of a sample against applied load. Stress is calculated by dividing the load at a time by the original cross sectional area (Ao (mm2)) (equation 2.2).

$$\sigma = F/A_0 \tag{2.2}$$

The load symbolized with F (N) and it is the applied force measured at the fixed end as a function of elongation [74]. Figure 2.3 represents the stress-strain behavior of a typical polymeric material across strain range.



Figure 2.3 : Stress-strain behavior of a typical polymeric material across strain range [76].

*Strength* is the capacity of a sample to resist load without fracture and calculated at a specific load. By tensile test three different strength can be determined which are; yield, ultimate, and fracture [74].

*Elastic strain* ( $\epsilon$ ) means elongation and it is calculated as the change in length ( $\Delta$ L) divided by the length of the central section of the specimen namely the initial gauge length (L<sub>0</sub>) (equation 2.3).

$$\varepsilon = \Delta L/L_0$$
 (2.3)

$$\sigma = E \epsilon$$
 (2.4)

Young's Modulus or modulus of elasticity (E) means the material's resistance to deformation and it is calculated as the ratio of stress to corresponding strain during elastic deformation (equation 2.4)[73].

Elastic deformation is the recoverable strain which occurs in the elastic region of the stress strain curve. When the load removed, stressed chains return to their orginal state without permanent deformation [75].

Young's Modulus is calculated by dividing stress over strain from the straight line of the stress-strain curve. It is also known as the proportionality constant in Ho oke's Law which relates stress to strain for uniaxial deformation of the ideal elastic isotropic solid as represented in equation 2.3 [73, 74]. The unit of the Young's Modulus is expressed in MPa, and hard and rigid materials have high Young's Modulus. Tensile test also gives information about the stress-strain behavior of the material and typical behaviors of polymers under load are shown in Figure 2.4.



**Figure 2.4 :** Stress–strain curves at increasing temperatures from a to e: (a) low extensibility followed by brittle fracture at the lowest temperature. (b) localized yielding followed by fracture. (c) necking and cold drawing. (d) homogeneous deformation with indistinct yield. (e) rubber-like behavior [73].

### 2.5.2.2 Impact test

Impact tests measure the energy required for failure of a standard specimen when applied a sudden stress load. Impact resistance of material depends on both intrinsic factors such as mechanical properties of the material and extrinsic factors such as geometry, mode of loading, environment [73].

The impact strength of a polymer can be measured by two types of impact test instruments: pendulum type instruments and falling-weight impact instruments. Izod and Charpy impact tests (Figure 2.5) are measured by pendulum type machines that are standardized according to ISO and ASTM designations. Specimens can be unnotched or notched. An arm which rotates about a pivot point is attached to the end of the machine when the arm is released it swings and strikes the specimen and the energy-to-break is determined from the loss in the kinetic energy of the arm. In this study, Izod impact test was applied to the samples in order to determine their notched and unnotched impact strengths.



Toughness and impact resistance are correlated properties. While the impact resistance is a response of the specimen to a high and sudden load, fracture toughness is determined at low strain rate testing conditions. Toughness can be calculated from the area under the curve of the stress-strain diagram and can be improved by the incorporation of a soft, elastomeric phase into the rigid polymer matrix. Enhancements of the toughness improve impact strength [73].

# 2.5.3 Thermal analysis

Thermal analysis is concerned with the properties of materials as they change with temperature. There are several methods commonly used depending on the measured property.

### 2.5.3.1 Differential scanning calorimetry

In DSC analysis, heat energy requirement per unit time of a small amount of sample of polymer (1-15 mg) in a sealed aluminum pan is measured referenced to an empty pan. A typical DSC run involves heating/cooling the sample at a previously programmed rate, and monitoring the heat flow to characterize the phase transitions and/or cure reactions as a function of temperature (Figure 2.6) [77]. When the polymer undergoes a thermal transition, their temperatures are kept constant by adjusting the power given to heaters, signals proportional to the power variation are plotted on the axis of the recorder [78].



Figure 2.6 : Differential scanning calorimeter [29].

DSC analysis is used to measure glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), heat of fusion of polymers ( $\Delta H_f$ ), crystallization, specific heat capacity, oxidation behavior, and thermal stability. By using DSC analysis degree of crystanilinty can also be measured. Crystalinity degree calculated by the conversion of measured heat of fusion (area under the curve) if the heat of fusion for the 100% crystalline polymer is known [77]. Schematic representation of typical DSC curves is given in Figure 2.7.



- Important characteristics:  $\rm T_g$  ,  $\rm T_m$  , heat of fusion on heating;  $\rm \ T_c\,$  on cooling

Figure 2.7 : Typical DSC curves [77].

Due to heat requirement upon glass transition and melting,  $T_g$  and  $T_m$  appear on the endothermic plane of the DSC diagram. Since the heat is evolved during the formation of crystals  $T_c$  appears on the the exothermic side of the DSC diagram.

In glass transition point ( $T_g$ ), the temperature of the polymer sample is reduced compared to the reference and consequently heat capacity is increased. Relatively large amounts of heats are required to melt the crystals in the polymer at constant temperature, therefore compared to the smooth dip of  $T_g$ , a sharper dip is observed at  $T_m$  [79].

### 2.5.3.2 Heat deflection temperature

Heat deflection test is used to measure the short-term heat resistance of the selected material. However, the data obtained cannot be used to know the behavior of polymers at high temperatures. As shown in Figure 2.8. The bending temperature test under load includes an oil bath enclosure to provide an increase in temperature. The temperature increase or decrease of this housing is carried out by automatic heat control devices. The test sample is placed on two supports with a distance of 100 mm. A device with a dial indicator is used to measure the appropriate bending. Temperature is measured in ° C by digital thermometer. A pressure of 0.45 MPa or 1.8 MPa is applied to the middle of the test specimen. The temperature of the oil bath casing is increased from room temperature to 2 ° C / min. The center temperature of the test specimen is 0.254 mm (0.01 inch).



Figure 2.8 : Schematic representation of HDT equipment.

### 2.5.3.3 Vicat softening temperature

The principle of the experiment is as follows; While the temperature is uniformly increased, the temperature at which one of the given loads reaches 1mm<sup>2</sup> of the submerged surface area with 1mm<sup>2</sup> of penetration tip into the plastic test sample is determined and is read in ° C. This temperature is expressed as the Vicat softening temperature. The tip used in the test is 3 mm long, round section, preferably hardened steel. The bottom surface of the submerged tip should be flat, smooth and parallel. Schematic representation of VST equipment is shown in Figure 2.9.



Figure 2.9 : Schematic representation of VST equipment.



### **3. EXPERIMENTAL**

### **3.1 Materials**

#### 3.1.1 Effect of chain extender type

The matrix material, rPA6 (Betamid BT2PA6GRNS) is a commercial product produced with 2 wt% black masterbatch and was supplied in granule form from Beta Polimer, Turkey. Chain extenders, EMA (Zemac E-60) from Vertellus, United States of America, EPO (Joncryl ADR4468) from BASF, Germany, CW (Addimer 980R) from Ceronas, Germany and DTDI (Addolink TT) from Lanxess Chemicals, Turkey, were all received in powder form. rPA6 was dried at 90 °C for 12 hrs in an industrial dryer before used. Other materials were used as received.

### **3.1.2 Effect of screw temperature**

The matrix material, rPA6-1 (Betamid BT1PA6GRNS) is a commercial product produced with 2 wt% black masterbatch and was supplied in granule form from Beta Polimer, Turkey. Chain extenders, EMA (Zemac E-60) from Vertellus, United States of America and DTDI (Addolink TT) from Lanxess Chemicals, Turkey were received in powder form. rPA6-1 was dried at 90 °C for 12 hrs in an industrial dryer before used. Chain extenders were used as received.

# **3.1.3 Effect of residence time**

The matrix material, rPA6-2 (Betamid BT2PA6GRNS) is a commercial product produced with 2 wt% black masterbatch and was supplied in granule form from Beta Polimer, Turkey. Chain extenders, EMA (Zemac E-60) from Vertellus, United States of America and DTDI (Addolink TT) from Lanxess Chemicals, Turkey were received in powder form. rPA6-2 was dried at 90 °C for 12 hrs in an industrial dryer before used. Chain extenders were used as received.

#### **3.2 Sample Preparation**

#### 3.2.1 Effect of chain extender type

The matrix material, BT2PA6GRNS, was chosen as reference material and melt compounded with different types and amounts of chain extenders, in order to compare the thermal and mechanical properties of the chain extended products and reference material. EMA, EPO, CW and DTDI were melt compounded with rPA6 in varying amounts (0.3, 0.5, 0.7 and 1 wt%) in a twin screw extruder. The extruder has a screw diameter of 26 mm and a L/D ratio 44. Extrusion parameters were given in Table 3.1.

**Table 3.1 :** Extrusion parameters.

Screw Temperature Profile	200/215/215/220/225/230/235/240/240/245 °C
Extruder Rotation Speed	450 rpm
Throughput Rate	15 kg/h
Torque	65-70 bar

The extrudate was then cooled in a water bath and granulized. These granules were used for relative viscosity measurements and for DSC tests.

The granules were then injection molded through a Haitian MA 2000E 700e machine to prepare dumbbell specimens with dimensions 170x20x4 mm for tensile tests according to ISO 527-2/1A and rectangular bars with the dimensions 80x10x4mm for Izod impact tests according to ISO 180/A and ISO 180/U. Process parameters were given in Table 3.2.

Screw Temperature Profile	255/260/265/270/275 °C
Nozzle Temperature	275 °C
Mold Temperature	80 °C
Cycle Time	12 sec
Injection Pressure	70 bar

 Table 3.2 : Injection parameters.

In order to compare chain extended products with neat rPA6, whole tests were also performed for neat rPA6 prepared with the same procedure. From here on reference material BT2PA6GRNS is denoted as rPA6, and the chain extended products are designated indicating the matrix (rPA6), the chain extender and its content. As an example, rPA-EMA-1 indicates the rPA6 chain extended with 1wt% of EMA.

#### **3.2.2 Effect of screw temperature**

The matrix material, BT1PA6GRNS was chosen as reference material and melt compounded with DTDI and EMA via twin screw extruder. The extruder has a screw diameter of 26 mm and a L/D ratio 44. Chosen temperature profiles and process parameters are given at Table 3.3.

	-	Process Parameters			
Sample	Screw Temperature Profile	Rotational Speed (rpm)	Throughput Rate (kg/h)	Torque (%)	Residenc e Time (sec)
T1	180/195/195/200/205/210/215/220/220/225 °C	450	15	65-70	30 sec
T2	200/215/215/220/225/230/235/240/240/245 °C	450	15	65-70	30 sec
T3	220/235/235/240/245/250/255/260/260/265 °C	450	15	65-70	30 sec

**Table 3.3 :** Extrusion parameters.

The extrudate was then cooled in a water bath and granulized. These granules were used for relative viscosity measurements and for DSC tests.

The granules were then injection molded through a Haitian MA 2000E 700e machine to prepare dumbbell specimens with dimensions 170x20x4 mm for tensile tests according to ISO 527-2/1A and rectangular bars with the dimensions 80x10x4 mm for Izod impact tests according to ISO 180/A and ISO 180/U. Process parameters were given in Table 3.4.

**Table 3.4 :** Injection parameters.

Screw Temperature Profile	255/260/265/270/275 °C
Nozzle Temperature	275 °C
Mold Temperature	80 °C
Cycle Time	12 sec
Injection Pressure	70 bar

Experiments done to investigate the effect of screw temperature were conducted at 0.5 and 1 wt% of DTDI and EMA concentrations at a constant residence time, corresponding to the production speed of 15 kg/h. During the experiments, the extruder screw rotation speed was maintained constant (450 rpm) for each test run.

From here on, reference material BT1PA6GRNS is denoted as rPA6-1, and the chain extended products are designated indicating the matrix (rPA6-1), the chain extender and its content and temperature profile (T1, T2, T3). As an example, rPA6-1-EMA-0.5-T3 indicates the rPA6-1 chain extended with 0.5 wt% of EMA in highest screw

temperature (Figure 3.1). Similarly rPA6-1-DTDI-1-T1 indicates the rPA6-1 chain extended with 1 wt% of DTDI in longest screw temperature.



Figure 3.1 : Representation of sample naming.

# **3.2.3 Effect of residence time**

The matrix material, BT1PA6GRNS was chosen as reference material and melt compounded with DTDI and EMA via twin screw extruder. The extruder has a screw diameter of 26 mm and a L/D ratio 44. Screw design of the extruder is shown in Figure 3.2. Chosen temperature profiles and process parameters are given at Table 3.5.



Figure 3.2 : Screw design of the extruder utilized in this study.

		Process Parameters			
Sample	Screw Temperature Profile	Rotational Speed (rpm)	Throughput Rate (kg/h)	Torque (%)	Residenc e Time (sec)
t1	200/215/215/220/225/230/235/240/240/245 °C	600	20	65-70	23 sec
t2	200/215/215/220/225/230/235/240/240/245 °C	450	15	65-70	30 sec
t3	200/215/215/220/225/230/235/240/240/245 °C	350	10	65-70	43 sec
t4	200/215/215/220/225/230/235/240/240/245 °C	120	5	65-70	82 sec

 Table 3.5 : Extrusion parameters.

The extrudate was then cooled in a water bath and granulized. These granules were used for relative viscosity measurements and for DSC tests.

The granules were then injection molded through a Haitian MA 2000E 700e machine to prepare dumbbell specimens with dimensions 170x20x4 mm for tensile tests according to ISO 527-2/1A and rectangular bars with the dimensions 80x10x4mm

for Izod impact tests according to ISO 180/A and ISO 180/U. Process parameters were given in Table 3.6.

Screw Temperature Profile	255/260/265/270/275 °C
Nozzle Temperature	275 °C
Mold Temperature	80 °C
Cycle Time	12 sec
Injection Pressure	70 bar

Table 3.6 : Injection parameters.

Experiments done to investigate the effect of residence time were conducted at 0.5 and 1 wt% of DTDI and EMA concentrations at residence times of 82, 43, 30, 23 seconds corresponding to a extruder production speed of 5, 10, 15, 20 kg/h respectively. During the experiments, the extruder screw rotation speeds were 120, 350, 450, 600 rpm.

From here on, reference material BT1PA6GRNS is denoted as rPA6-2, and the chain extended products are designated indicating the matrix (rPA6-2), the chain extender and its content and residence time (t1, t2, t3, t4). As an example, rPA6-2-EMA-0.5-t4 indicates the rPA6-2 chain extended with 0.5 wt% of EMA in shortest residence. Similarly rPA6-2-DTDI-1-t1 indicates the rPA6-2 chain extended with 1 wt% of DTDI in longest residence time.

# 3.3 Characterization

# **3.3.1 Flow characteristics**

# 3.3.1.1 Relative viscosity measurements

Relative viscosity tests were performed according to ISO 307 by using an Ubbelohde viscometer. 0.4 g of samples were dissolved in sulfuric acid (purity 95.7 %) at 50 °C, at a concentration of 10 g  $l^{-1}$ . The solution was then conditioned in a 25 °C water bath for 20 min. Test was performed at 25 °C.

# 3.3.2 Mechanical tests

# 3.3.2.1 Tensile test

Tensile tests were performed according to ISO 527-2 by using a Zwick Roell Z020 tensile test measuring equipment at 25 °C. Test machine has a load cell of 20 kN, at a

crosshead speed of 50 mm min<sup>-1</sup>. The average results were obtained from at least six samples. In order to evaluate the elastic modulus (E), the stress at yield ( $\sigma_y$ ) and the elongation at break ( $\epsilon_b$ ) of the materials ISO 527-2/1A dumbbell specimens with dimensions 170x20x4 mm were used.

### 3.3.2.2 Izod impact test

Izod impact resistance test at 25 °C were carried out through Zwick Roell HIT5.5T impact test machine according to ISO 180/ A. The specimen dimensions 80 x 10 x 2.7 mm. A single-edge 458 V-shaped notch (tip radius 0.25 mm, depth 2 mm) was milled in the middle of the bars. A Ceast Automatic Notchvis Plus was used to perform the notching following the requirements of ISO 2818:1994. The impact tester used a manual clamping vice with a specimen adapter for ISO geometry. The sample was correctly positioned in the vice with a centering device adapted for notched specimens and, finally, blocked by turning a hand wheel clockwise. A screw in the middle of the hand wheel controlled the clamping torque that was applied with working torque ranges from 1 to 25Nm. The impact strength was calculated by dividing the absorbed energy by the initial cross-sectional area behind the notch. The average values were calculated from 10 runs for each sample.

### **3.3.3** Thermal property characterizations

# 3.3.3.1 Differential scanning calorimetry

DSC tests were performed according to ISO 11357 by using a TA Instrument DSC Q20 calorimeter equipment with a heating range 0 °C to 260 °C and heating rate of 20 °C min<sup>-1</sup>. Samples then cooled down from 260 °C to 0 °C with the same rate. 10 mg of samples were tested under a nitrogen flow of 100 ml min<sup>-1</sup>. The melting (T<sub>m</sub>) and crystallization temperature (T<sub>c</sub>) of the samples were determined from the resulting curves. The relative crystallinity degree ( $\chi$ ) was calculated by the equation 3.1; (the specific melting enthalpy of the polymer ( $\Delta H_m$ ), the specific melting enthalpy of fully crystalline PA6 ( $\Delta H_0$ ) which is taken as 190 J g<sup>-1</sup> [80])

$$\chi = \Delta H_m / \Delta H_0 . \ 100 \tag{3.1}$$

### **3.3.3.2** Heat deflection temperature

HDT measurements were performed according to ISO 75-2 by using a Ceast 3 Junior HDT machine. In order to determine HDT A and B type measurements, bars with dimensions 130x13x4 mm were heated in an oil bath room temperature up to  $300 \,^{\circ}C$  at a constant rate of  $120 \,^{0}C$ /h after conditioning for 5 min. A stress of 0.45 MPa and 1.82 MPa were used to bend the samples for HDT B and A respectively. The average results were obtained from six samples.

### **3.3.3.3 Vicat softening temperature**

VST measurements were performed according to ISO 306 by using a Ceast 3 Junior Vicat measuring equipment. In order to determine Vicat A type measurements, bars with dimensions 80x10x4 mm were heated from room temperature up to 300 °C in an oil bath at a constant rate of 120 °C/h. A needle with a surface area of 1 mm<sup>2</sup> was set to penetrate the bar with a downward force of 10 N until the needle penetrated the bar by 1 mm. The average results were obtained from six samples.



### 4. RESULTS AND DISCUSSIONS

#### 4.1 Effect of Chain Extender Type

### 4.1.1 Possible reactions between rPA6 and chain extenders

Figure 4.1 represents the chain extension mechanisms of rPA6 with DTDI. In the first step DTDI splits up in to two molecules of TDI at above 140  $^{0}$ C which doubles its functional isocyanate groups as a chain extender. The reaction of TDI with the amminic end of rPA6 is faster than its reaction with carboxylic end. The former provides the formation of a stable carbamate (1 in Figure 4.1 a), whereas the latter results in unstable O-acylcarbamates (3 in Figure 4.1 b) and consequently decompose to amides with loss of CO<sub>2</sub>. At higher concentrations of isocyanates, the allophanates (2 in Figure 4.1 a) and ureas (5 in Figure 4.1 b) are formed in a branched structure [16].

Chain extension mechanism of rPA6 with EMA is shown in Figure 4.2. The chain extension reaction with amminic end group involves maleic anhydride ring-opening and leads to the formation of unstable acid (1 in Figure 4.2), resulting in a ring closing reaction to form stable amide (2 in Figure 4.2) with loss of  $H_2O$  [81].

Epoxy ring-opening chain extension mechanism of EPO with carboxyl end group (Figure 4.3 a) and amminic end group (Figure 4.3 b) are shown in Figure 4.3. The chain extension reaction leads to formation of covalent bonds due to amine side groups [58].

Figure 4.4 represents the chain extension mechanism of rPA6 with caprolactam reactive groups. According to the literature references [31], caprolactam molecules react mainly with the amminic end groups of PA by nucleophilic substitution reaction (Figure 4.4 a) or by a ring opening reaction (Figure 4.4 b). The first mechanism leads to the formation of a caprolactam molecule as a by-product which can only be eliminated at low temperature (i.e. below 200  $^{0}$ C).



**Figure 4.1 :** Chain extension mechanism of DTDI with (a) amine end group. (b) carboxyl end group.



Figure 4.2 : Chain extension mechanism of EMA.



Figure 4.3 : Chain extension mechanism of EPO with (a) carboxyl end group. (b) amine end group.



**Figure 4.4 :** Chain extension mechanism of CW (a) nucleophilic substitution with caprolactam formation. (b) ring-opening reaction.

### 4.1.2 Relative viscosity measurements

Relative viscosity measurements were carried out for four different types of chain extenders at four different wt%. Relative viscosity values increased with an increase of chain extender amount for both types of chain extenders, which can be attributed to the increase in the molecular weight of rPA6 (Figure 4.5). The trend of increasing

relative viscosities suggests the increasing chain extension capability of both materials for rPA6 during reactive extrusion. Between 2%-41% increase in relative viscosity of rPA6 was achieved by the incorporation of chain extenders, making chain extenders powerful tool for industrial applications to adjust viscosity of rPA6.

rPA6-EMA-1 showed highest relative viscosity of all the chain extended products. Between 20%-41% increase in relative viscosity of rPA6 was achieved with EMA. Improvement of the relative viscosity of chain extended product with EMA can be explained with the structural differences. Due to the brush like structure of resultant materials formed from the reaction of rPA6 with EMA, chain extended products with EMA had higher molecular weights than that of chain extended products with DTDI, which leads to linear structured resultant products (Figure 4.6). A similar result was obtained by Schacker et al. [58] when they investigated the difference between linear chain extension with bisoxazoline and chain bundling by grafting onto the maleinated polystyrene (SMA) of the PA. In that study they also concluded that chain extension by chain bundling (grafting onto the SMA) improved the PAs melt viscosity greater than linear chain extension with bisoxazoline.

rPA6-DTDI-1 showed a 22% increase in relative viscosity of rPA6. Higher relative viscosities of chain extended products with DTDI than that of EPO can be attributed to higher reactivity of isocynates with amine groups than epoxides.



Figure 4.5 : Relative viscosity vs wt% of chain extenders.



**Figure 4.6 :** Increasing the molecular weight of oligomers (a) by linear chain extension. (b) by grafting onto a functionalized backbone chain.

# 4.1.3 Mechanical tests

# 4.1.3.1 Tensile tests

In order to investigate the effect of chain extenders on tensile behavior, tensile tests were performed. Table 4.1 summarizes the tensile properties of neat rPA6 and chain extended products. While e-modulus was not significantly affected by chain extenders incorporation, elongation at break was noticeably improved. Elongation at break increases as the chain extender content increases for all chain extenders. The incorporation of chain extenders offset thermal degradation and limits the chain mobility and thus increased the yield strength of rPA6. Higher yield strength was achieved with DTDI which can be explained by the rigid structure of DTDI.

The elongation at break noticeably increased with chain extender incorporation since chain extension decreased the degree of crystallinity. Even at 0.3 wt% chain extender content, elongation at break was increased at least by 4.4 times. In Table 4.1 it is shown that of all chain extenders, EMA shows higher elongation at break compared to the other investigated chain extenders. The highest elongation at break was achieved with 1 wt% of EMA incorporation, which increased the elongation at break by 6.3 times (Figure 4.7). By comparison, DTDI increased elongation at break by 6.1 times. Elongations at break results are consistent with relative viscosity results, because molecular weight is closely related to elongation at break and relative viscosity. Long branches cause an increase in chain entanglement and chain straightening prior to break. High molecular weight chains can be stretched and straightened.

In Figure 4.8 representative tensile test diagram and related images of deformation of neat rPA6 and chain extended products are shown. It is shown that brittle neat rPA6 did not deform plastically or exhibited a negligible amount of plastic deformation prior to fracture. While chain extended products became ductile and undergo plastic deformation before fracture. After chain extension, neat rPA6 absorbed energy in the plastic range and its toughness was increased. It is also shown that chain extended products showed necking, except the one that chain extended with CW.

Sample	Elastic modulus (MPa)	Yield Strength (MPa)	Elongation at break (%)
rPA6	$2788 \pm 211$	$60.0\pm0.7$	$7\pm2$
rPA6-EMA-0.3	$2810\pm65$	$63.9\pm0.5$	$38 \pm 3$
rPA6-EMA-0.5	$2908 \pm 112$	$62.4\pm0.6$	$41 \pm 2$
rPA6-EMA-0.7	$2871 \pm 156$	$62.2\pm0.5$	$42 \pm 1$
rPA6-EMA-1	$2850\pm119$	$61.7\pm0.8$	$44 \pm 1$
rPA6-CW-0.3	$2718 \pm 111$	$62.5\pm0.4$	$33 \pm 2$
rPA6-CW-0.5	$2727\pm76$	$62.7\pm0.5$	$34 \pm 2$
rPA6-CW-0.7	$2563\pm81$	$60.6\pm0.4$	$35 \pm 3$
rPA6-CW-1	$2650\pm61$	$60.6\pm1.3$	$36 \pm 2$
rPA6-EPO-0.3	$2700\pm89$	$63.1 \pm 1.7$	$31 \pm 1$
rPA6-EPO-0.5	$2784 \pm 141$	$62.2\pm0.8$	$34 \pm 3$
rPA6-EPO-0.7	$2712 \pm 157$	$61.4 \pm 1.2$	$37 \pm 2$
rPA6-EPO-1	$2648 \pm 105$	$60.7\pm0.5$	$37 \pm 2$
rPA6-DTDI-0.3	$2878 \pm 274$	$63.7\pm0.4$	$33 \pm 2$
rPA6-DTDI-0.5	$2805\pm106$	$64.1\pm0.5$	$36 \pm 2$
rPA6-DTDI-0.7	$2710 \pm 111$	$64.2\pm0.4$	$40 \pm 3$
rPA6-DTDI-1	$2729\pm79$	$63.4\pm0.4$	$43 \pm 1$

**Table 4.1 :** Tensile properties of neat rPA6 and chain extended products.



Figure 4.7 : Elongation at break vs wt% of chain extenders.



**Figure 4.8 :** Representative tensile test diagram and related images of deformation of neat rPA6 and chain extended specimens after tensile test.

### 4.1.3.2 Notched Izod impact test

In order to observe the effect of chain extenders impact strengths impact tests were performed on both notched and unnotched samples.For both chain extenders notched Izod impact strengths were increased as the chain extender contents increased. As shown in Figure 4.9 chain extender effects on notched impact strength was similar to their effect on elongation at break. The impact strength results showed a 7.5% to 26% increase. EMA showed the highest impact strength because of its higher molecular weight, built up by chain extension. The decrease in crystallinity can also explain the improvement of impact resistance, whereby the cracks can propagate more readily in crystallite. As the degree of crystallinity decreased the polymer became less rigid. The impact strength results are consistent with the viscosity measurements and the corresponding molecular weight because increase in molecular weight tends to increase toughness.



Figure 4.9 : Notched Izod impact strength vs wt% of chain extenders.

# 4.1.3.3 Unnotched Izod impact test

Due to the notch sensitive structure of PA6 it was possible to observe the differences in the notched Izod impact strengths of chain extended materials for related contents. In the unnotched impact strength tests it was only possible to observe the improvement of unnotched impact strength from 48.63 kJ/m<sup>2</sup> to no break (71.33 kJ/m<sup>2</sup>) for all chain extenders in all contents (Figure 4.10).



Figure 4.10 : Unnotched Izod impact strength vs wt% of chain extenders.

#### **4.1.4 Thermal property measurements**

### 4.1.4.1 Differential scanning calorimetry

The effect of chain extenders on the melting and crystallization behaviors of rPA6 was investigated through DSC studies. DSC cooling thermograms obtained from the first heating for rPA6, 0.5 wt% and 1 wt% chain extended products are shown in Figure 4.11 and Figure 4.12. DSC heating thermograms obtained from the first heating for rPA6, 0.5 wt% and 1 wt% chain extended products are shown in Figure 4.13 and Figure 4.14. Table 4.2 shows the results from DSC tests performed on neat rPA6, 0.5 wt% and 1 wt% of chain extended products. Melting temperature (T<sub>m</sub>) and crystallization onset temperature (T<sub>c.onset</sub>) were slightly reduced upon EMA and DTDI incorporation and crystallization temperature  $(T_c)$ , melting enthalpy  $(\Delta H_m)$  and degree of crystallinity  $(\chi)$  were reduced upon all chain extender incorporation. This is a clear indication that the crystallization of rPA6 is partially hindered by chain extension reaction. Increase in the molecular weight of chain extended products causes a decrease in the crystallinity and hinders the arrangement of the polymer chain in a crystalline structure. Besides the increase in molecular weight, there are also structural reasons that consequently disrupted the chain regularity. Those are: the incorporation of carbamide (or urethane groups) to the rPA6 main chains (Figure 4.2) in DTDI case, formation of free caprolactam by products (Figure 4.4) in CW case and formation of brush-like structured resultant products in EMA (Figure 4.1) and EPO (Figure 4.3) cases. Similar results were obtained by Lu et al. in PA chain extension studies [20, 26, 28] and Fambri et al. [29, 30, 62, 63]. In those studies, they explained the decrease in crystallinity by the increase in the molecular weight of PA6, incorporation of ester amide groups to main chain and formation of free caprolactam by products.

Lower crystallinity of chain extended product with EMA than that of chain extended product with DTDI can be explained with brush like structure of resultant product. This is a result of the linear structure of the product chain extended with DTDI having more chain regularity. At 0.5 wt% and 1 wt% of chain extended products, crystallization was initiated at lower temperatures (Table 4.2). Owing to the higher molecular weight of chain extended products there would not be sufficient time for

arrangement of polymer chains. At neat rPA6 however, polymer chains had enough mobility to grow in to a crystalline structure.



**Figure 4.11 :** DSC cooling thermograms obtained from the first heating for rPA6 and 0.5 wt% chain extended products.



**Figure 4.12 :** DSC cooling thermograms obtained from the first heating for rPA6 and 1 wt% chain extended products.



**Figure 4.13 :** DSC heating thermograms obtained from the first heating for rPA6 and 0.5 wt% chain extended products.



**Figure 4.14 :** DSC heating thermograms obtained from the first heating for rPA6 and 1 wt% chain extended products.

	Heating		-	Cooling			
Sample	$T_m$ (°C)	$\Delta H_m (J.g^{-1})$	)	$T_{c}$ (°C)	$T_{c,onset}$ (°C )	$\Delta H_{c} \left(J.g^{-1}\right)$	χ(%)
rPA6	229.3	67.8		187.1	195.1	48.3	35.7
rPA6-EMA-0.5	226.9	50.8		185.4	192.9	48.5	26.7
rPA6-EMA-1	228.5	46.7		184.4	192.8	51.1	24.6
rPA6-DTDI-0.5	225.5	51.8		186.8	194.4	49.1	27.2
rPA6-DTDI-1	226.8	48.8		185.0	193.6	51.2	25.7
rPA6-EPO-0.5	229.3	49.9		185.7	193.9	44.6	26.3
rPA6-EPO-1	231.6	47.7		186.1	194.9	47.2	25.1
rPA6-CW-0.5	230.4	54.7		186.5	195.1	52.4	28.8
rPA6-CW-1	229.8	51.3		187.4	195.4	52.3	27.0

**Table 4.2 :** Results of DSC tests on rPA6, 0.5 wt% and 1 wt% chain extendedproducts.

#### 4.1.4.2 Heat deflection temperature and vicat softening temperature

Table 4.3 shows the results from HDT and VST tests performed on neat rPA6 and 1 wt% of chain extended products. Compared with rPA6, the thermal dimensional stability of chain extended products exhibited a substantially higher value, thus allowing an application of these chain extended products at significantly higher temperature. The results demonstrate that the addition of chain extenders significantly improves the thermal performance of rPA6.

As a general expression HDT is as a measure of the stiffness of the material as the temperature increases. Hardness/stiffness is mainly ability of the polymer chains to move when a load is applied. In hard materials the polymer chains are more tightly crosslinked and so more restricted than in soft materials, where they can move more easily. Chain extenders increase the molecular weight of rPA6, which increase entanglement and restrict the mobility of chains and leading to an increase in HDT of rPA6. VST of rPA6 was increased by the addition of chain extenders due to higher molecular weight of resultant material causing increased polymer resistance, at higher temperature. On the other hand wide molecular weight distribution can facilitate the landslide between polymer chains and consequently can reduce the VST as it is also mentioned in the study of Costa et al [14]. Increasing trend of HDT and VST is similar to relative viscosity trend of related products. Between 5.2%-12.4% increase in HDT and very slight increase in VST of rPA6 was achieved by the incorporation of chain extenders.

Sample	HDT (°C) 0.45 MPa	HDT (°C) 1.8MPa	VST (°C) 10N
rPA6	$52.3\pm0.6$	$42.4\pm0.5$	$203.0\pm0.4$
rPA6-(EMA)-1	$58.8\pm0.3$	$46.7\pm0.2$	$205.7\pm0.3$
rPA6-(DTDI)-1	$57.6\pm0.3$	$45.6\pm0.4$	$205.5\pm0.4$
rPA6-(EPO)-1	$55.3\pm0.2$	$44.9\pm0.2$	$204.9\pm0.3$
rPA6-(CW)-1	$55.0 \pm 0.3$	$44.7\pm0.3$	$204.4\pm0.2$

Table 4.3 : HDT and VST of rPA6 and 1% wt chain extended products.

#### **4.1.5 Die pressure measurements**

Another important parameter in the reactive extrusion process to investigate the chain extension behavior is die pressure of extruder [82]. According to Janssen's interaction diagram for reactive extrusion [83], the die pressure is affected by the flow rate and viscosity of a polymer. Figure 4.15 shows the extruder die pressure readings with respect to variable chain extender concentrations. The results show that the die pressure increased with increasing chain extender concentration. This is a result of the increase in melt viscosity of chain extended materials, causing flow to become more difficult and the high viscosity material applying more pressure to the extruder die.



Figure 4.15 : Die pressure vs wt% of chain extenders.

### 4.2 Effect of Screw Temperature

### 4.2.1 Relative viscosity measurements

Relative viscosity measurements were carried out for two different chain extenders at three different screw temperature profiles. In our previous study [84] it was observed
that relative viscosity increases with an increase of chain extender amount and EMA leads to highest relative viscosity among used chain extenders due to brush like structure of resultant product. The effect of screw temperature on chain extension reactions is dual while an increase in temperature leads to an increase in reaction rate, also causes an increase in degradation side reactions, leading to chain scission and consequently to a decrease of the molar mass. Relative viscosities  $(\eta_{rel})$  of chain extended products at different screw temperature profiles were given in Figure 3. According to results of chain extended product with EMA, as temperature profile increased from T1 to T2 relative viscosity increased. This can be explained as the chain extension reaction is favored at higher reaction temperature than T1 and with a concern that low operation temperature leads to low efficiency to well mix the polymer and chain extender. When temperature profile increased from T2 to T3, relative viscosity values slightly decrease which can be explained as at higher temperature than T2 rPA6 went through more thermal degradation. It was evidenced how relative viscosity of polyamides increased with the chain extender amount, and how during the up-grading process PA degradation is likely to proceed simultaneously with the chain extension reactions.

According to numerical values; 28.2%, 47.4% and 41.4% increase in relative viscosity were obtained at T1, T2 and T3, respectively, which showed that by adjusting screw temperature at least 6.8% higher viscosity was obtained for rPA6-1-EMA-0.5. Likewise, 41.4%, 54.9% and 45.9% increase in relative viscosity were obtained at T1, T2 and T3 respectively which showed that by adjusting screw temperature at least 9.1% higher viscosity was obtained for rPA6-1-EMA-1.

Relative viscosity measurement results of chain extended products with DTDI were similar at all temperature profiles. This is because isocyanate has high reactivity even at low temperature and at high temperatures fast reaction rate of isocyanate with rPA6 prevents reduction of molecular weight resulted from thermal degradation.



Figure 4.16 : Relative viscosity vs screw temperature profiles.

## **4.2.2 Mechanical tests**

#### 4.2.2.1 Tensile tests

In order to evaluate the effect of screw temperature on tensile behavior of chain extended products, tensile tests were performed. Table 4.4 summarizes the most important tensile properties with respect to different screw temperatures. It was not able to observe a regular effect of screw temperature on e-modulus or tensile strength. Figure 4.17 shows the relation between elongation at break values with the corresponding screw temperature profile for chain extended products with EMA and DTDI. According to results as screw temperatures increased from T1 to T2, elongation at break values increased for both concentrations of EMA. This can be explained as the chain extension reaction was favored at the higher reaction temperature which resulted in higher molecular weight. When screw temperatures increased from T2 to T3, elongation at break values slightly decreased for both concentrations which can be explained as the thermal degradation of rPA6 chains at higher temperatures. In the case of DTDI it was shown that elongation at break was similar at all screw temperature profiles. This is because the reactivity of DTDI is high even at low temperature. Effect of screw temperature was more obvious for chain extension with EMA. 1 wt% EMA introduction at T2 increased elongation at break by 4.1 times while at T1 and T3 increased by 2.6 and 3.4 respectively which showed the temperature dependency of chain extension behavior of EMA. On the

other hand similar elongation at break results of chain extended products with DTDI due to high reactivity of DTDI showed that chain extension behavior of DTDI was independent from temperature changes. Elongation at break results were consistent with relative viscosity results, since molecular weight is closely related to elongation at break and relative viscosity.

According to numerical results; elongation at break were increased by 1.8, 2.9 and 2.2 times at T1, T2 and T3 respectively which showed that by adjusting screw temperature at least 1.3 times higher elongation at break was obtained for rPA6-1-EMA-0.5. Likewise, elongation at break were increased by 2.1, 3.3 and 2.7 times at T1, T2 and T3 respectively which showed that by adjusting screw temperature at least 1.3 times higher elongation at break was obtained for rPA6-1-EMA-0.5. Likewise, elongation at break were increased by 2.1, 3.4 mm and 2.7 times at T1, T2 and T3 respectively which showed that by adjusting screw temperature at least 1.3 times higher elongation at break was obtained for rPA6-1-EMA-1.

Sample	Elastic modulus (MPa)	Yield strenght (MPa)	Elongation at break (%)
rPA6-1	$2648 \pm 49$	$67.6 \pm 0.7$	$27 \pm 2$
rPA6-1-EMA-0.5-T1	$2766\pm82$	$66.9\pm0.9$	$51 \pm 3$
rPA6-1-EMA-0.5-T2	$2558 \pm 124$	$59.8\pm0.4$	$81 \pm 3$
rPA6-1-EMA-0.5-T3	$2700\pm100$	$63.6\pm0.9$	$62 \pm 4$
rPA6-1-EMA-1-T1	$2691 \pm 163$	$65.5\pm0.8$	$57 \pm 4$
rPA6-1-EMA-1-T2	$2563\pm59$	$59.4\pm0.7$	$90\pm8$
rPA6-1-EMA-1-T3	$2712\pm78$	$64.4\pm0.9$	$74\pm8$
rPA6-1-DTDI-0.5-T1	$2518\pm21$	$64.3\pm0.4$	$38 \pm 5$
rPA6-1-DTDI-0.5-T2	$2654 \pm 129$	$68.0\pm0.7$	$36 \pm 5$
rPA6-1-DTDI-0.5-T3	$2623\pm61$	$66.9 \pm 1.0$	$34 \pm 6$
rPA6-1-DTDI-1-T1	$2618\pm91$	$64.7\pm0.7$	$44 \pm 3$
rPA6-1-DTDI-1-T2	$2616\pm73$	$65.1\pm0.6$	$44 \pm 3$
rPA6-1-DTDI-1-T3	$2616\pm39$	$65.2\pm0.6$	$43 \pm 2$

**Table 4.4 :** Tensile properties of rPA6 and chain extended products at different screw temperatures.



Figure 4.17 : Elongation at break vs screw temperature profiles.

## 4.2.2.2 Notched Izod impact test

In order to observe the effect of screw temperatures on notched and unnotched impact strengths of chain extended products impact tests were performed. For all screw temperature profiles notched Izod impact strengths were slightly increased as the incorporation of chain extenders. As it is shown in Figure 4.18 effect of screw temperature on notched impact strengths were in similar trend with their effect on elongation at break.

EMA showed the highest impact strength at T2 because of its higher molecular weight built up by chain extension. The decrease in crystallinity also explained the improvement of impact resistance because the cracks can propagate more readily in crystallite. As the degree of crystallinity decreased polymer became less rigid. The impact strength results were consistent with the viscosity measurements and the corresponding molecular weight because increase in molecular weight tends to increase toughness. DTDI showed similar notched Izod impact strengths at all screw temperature profiles depending on molecular weight of resultant products.

According to numerical results; 13.8%, 22.5% and 19% increase in impact strength were obtained at T1, T2 and T3 respectively which showed that by adjusting screw temperature at least 3.3% higher impact strength was obtained for rPA6-1-EMA-0.5. Likewise, 18.4%, 32.4% and 21.8% increase in impact strength were obtained at T1,

T2 and T3 respectively which showed that by adjusting screw temperature at least 10.6% higher impact strength was obtained for rPA6-1-EMA-1.



Figure 4.18 : Notched Izod impact strength vs screw temperature profiles.

## 4.2.2.3 Unnotched Izod impact test

Due to the notch sensitive structure of PA6 it was possible to observe the differences in the notched Izod impact strengths of chain extended materials. In the unnotched impact strength tests it was only possible to observe the improvement of unnotched impact strength from 44.08 kJ/m<sup>2</sup> (rPA6-1) to no break (70.96 kJ/m<sup>2</sup>) for all screw temperature profiles in all contents (Figure 4.19).



Figure 4.19 : Unnotched Izod impact strength vs screw temperature profiles.

#### **4.2.3 Thermal property measurements**

#### 4.2.3.1 Differential scanning calorimetry

The effect of screw temperature on the melting and crystallization behaviors of chain extended rPA6 were analyzed through DSC measurements. DSC cooling thermograms obtained from the first heating for rPA6-1 and 0.5 wt% chain extended products with EMA at different screw temperature profiles is shown in Figure 4.20. DSC cooling thermograms obtained from the first heating for rPA6-1 and 0.5 wt% chain extended products with DTDI at different screw temperature profiles is shown in Figure 4.21. DSC cooling thermograms obtained from the first heating for rPA6-1 and 1 wt% chain extended products with EMA at different screw temperature profiles is shown in Figure 4.22. DSC cooling thermograms obtained from the first heating for rPA6-1 and 1 wt% chain extended products with DTDI at different screw temperature profiles is shown in Figure 4.23. DSC heating thermograms obtained from the first heating for rPA6-1 and 0.5 wt% chain extended products with EMA at different screw temperature profiles is shown in Figure 4.24. DSC heating thermograms obtained from the first heating for rPA6-1 and 0.5 wt% chain extended products with DTDI at different screw temperature profiles is shown in Figure 4.25. DSC heating thermograms obtained from the first heating for rPA6-1 and 1 wt% chain extended products with EMA at different screw temperature profiles is shown in Figure 4.26. DSC heating thermograms obtained from the first heating for rPA6-1 and 1 wt% chain extended products with DTDI at different screw temperature profiles is shown in Figure 4.27. Table 4.5 shows the results from DSC measurements performed on neat rPA6 and chain extended products at different temperature profiles. Melting temperature (T<sub>m</sub>), crystallization temperature (T<sub>c</sub>), melting enthalpy ( $\Delta H_m$ ), crystallization enthalpy ( $\Delta H_c$ ) and crystallinity degree were reduced with the incorporation of chain extenders in any conditions. According to temperature studies with EMA;  $T_m$ ,  $T_c$ ,  $\Delta H_m$  and degree of crystallinity were reduced when screw temperature increased from T1 to T2 for both concentrations of chain extender. This can be explained as the chain extension reaction was favored at higher reaction temperature which leads to higher molecular weight and hinders the arrangement of the polymer chain in a crystalline structure. In addition, the presence of the chain extender in the polymer structure also negatively affects the regularity of the chains that limits the crystallizability. When temperature profile increased from

T2 to T3, thermal degradation promoted and prevents the increase in molecular weight of resultant materials. Consequently leads to higher crystallinity than it is at T2.

Results from the screw temperature studies with DTDI showed different tendency. There was not a significant change observed in crystallinity degree of chain extended product at T1 and T2, due to high reactivity of isocyanate even at low temperature. Similar crystallinity degree at T3 can also be explained with the high reactivity of isocyanate, because thermal degradation and chain extension reaction were proceed simultaneously and fast reaction rate of isocyanate with rPA6 prevented decrease in molecular weight resulted from thermal degradation.



**Figure 4.20 :** DSC cooling thermograms obtained from the first heating for rPA6-1 and 0.5 wt% chain extended products with EMA at different screw temperature profiles.



**Figure 4.21 :** DSC cooling thermograms obtained from the first heating for rPA6-1 and 0.5 wt% chain extended products with DTDI at different screw temperature profiles.



**Figure 4.22 :** DSC cooling thermograms obtained from the first heating for rPA6-1 and 1 wt% chain extended products with EMA at different screw temperature profiles.



**Figure 4.23 :** DSC cooling thermograms obtained from the first heating for rPA6-1 and 1 wt% chain extended products with DTDI at different screw temperature profiles.



**Figure 4.24 :** DSC heating thermograms obtained from the first heating for rPA6-1 and 0.5 wt% chain extended products with EMA at different screw temperature profiles.



**Figure 4.25 :** DSC heating thermograms obtained from the first heating for rPA6-1 and 0.5 wt% chain extended products with DTDI at different screw temperature profiles.



**Figure 4.26 :** DSC heating thermograms obtained from the first heating for rPA6-1 and 1 wt% chain extended products with EMA at different screw temperature profiles.



**Figure 4.27 :** DSC heating thermograms obtained from the first heating for rPA6-1 and 1 wt% chain extended products with DTDI at different screw temperature profiles.

	Heating			Cooling	
Sample	$T_m$ (°C)	$\Delta H_m (J.g^{-1})$	$T_{c}(^{\circ}C)$	$\Delta H_{c} \left(J.g^{-1}\right)$	χ(%)
rPA6-1	220	67.53	187	60.03	35.55
rPA6-1-EMA-0.5-T1	218	42.24	185	52.64	22.24
rPA6-1-EMA-0.5-T2	217	34.03	186	37.76	17.91
rPA6-1-EMA-0.5-T3	217	47.31	185	57.10	24.90
rPA6-1-EMA-1-T1	217	49.35	185	55.75	25.97
rPA6-1-EMA-1-T2	217	42.85	184	54.07	22.55
rPA6-1-EMA-1-T3	214	43.84	184	57.48	23.07
rPA6-1-DTDI-0.5-T1	217	48.80	186	56.58	25.68
rPA6-1-DTDI-0.5-T2	218	48.10	187	43.37	25.32
rPA6-1-DTDI-0.5-T3	218	48.98	186	53.38	25.78
rPA6-1-DTDI-1-T1	217	49.82	186	52.24	26.23
rPA6-1-DTDI-1-T2	217	53.07	186	60.50	27.94
rPA6-1-DTDI-1-T3	217	53.83	186	59.04	28.34

**Table 4.5 :** Results of DSC tests on rPA6 and chain extended products at different screw temperature profiles.

## 4.2.4 Die pressure measurements

Die pressure of extruder is an important parameter in the reactive extrusion process to investigate the chain extension behavior [82]. According to Janssen's interaction diagram for reactive extrusion [83], the die pressure is affected by the flow rate and viscosity of a polymer. Figure 4.28 shows the extruder die pressure readings with respect to screw temperature profiles. The results show that the die pressure increased with increasing chain extender concentration and showed similar tendencies with relative viscosity results of related screw temperature profiles. The increase in melt viscosity of chain extended materials causes flow to become more difficult and consequently the high viscosity material applies more pressure to the extruder die.



Figure 4.28 : Die pressure vs screw temperature profiles.

## 4.3 Effect of Residence Time

## 4.3.1 Relative viscosity measurements

Relative viscosity measurements were carried out for two different chain extenders at at four different residence times. Relative viscosity measurements of residence time studies were given in Figure 4.29.

Results of chain extended product with EMA showed that longer residence time promoted chain extension and thus resulted in higher viscosity rPA6. It was observed that at longer residence times than t3 acceleration of increase in relative viscosity slowed down depending on the reduction of unreacted MAH.

According to numerical results 27.2%, 37.9%, 59.7% and 67.5% increase in relative viscosity were obtained at t1, t2, t3 and t4 respectively which showed that by

adjusting residence time 41.2% higher viscosity was obtained for rPA6-2-EMA-0.5. Likewise, 33.8%, 46.5%, 61.4% and 74.9% increase in relative viscosity were obtained at t1, t2, t3 and t4 respectively which showed that by adjusting residence time at least 41.2% higher viscosity was obtained for rPA6-2-EMA-1.

According to results of chain extended product with DTDI residence time did not have significant effect on relative viscosity as it was also observed from temperature effect studies. Slight increase in relative viscosity was obtained with an increase in residence time. It can be explained with same reason; isocyanate is highly reactive product that even low residence time was enough for the chain extension reaction hence most of the DTDI was consumed in a short time.



Figure 4.29 : Relative viscosity vs residence times.

## 4.3.2 Mechanical tests

## 4.3.2.1 Tensile tests

In order to evaluate the effect of residence time on tensile behavior of chain extended products, tensile tests were performed. Table 4.6 summarizes the most important tensile properties with respect to different residence time. It was not able to observe a regular effect of residence time on e-modulus or tensile strength.

Figure 4.30 shows the relation between elongation at break values with the corresponding residence times for chain extended products with EMA and DTDI, respectively. According to results of chain extended products with EMA, elongation at break increased with an increase in residence times due to the increase in

molecular weight and brush-like structure of resultant products. It was also observed that at longer residence times than t3 acceleration of increase in elongation at break slowed down depending on the reduction of unreacted MAH.

According to numerical results; elongation at break were increased by 2, 2.4, 2.7 and 2.8 times at t1, t2, t3 and t4 respectively which showed that by adjusting retention time 1.4 times higher elongation at break was obtained for rPA6-2-EMA-0.5. Likewise, elongation at break were increased by 2.6, 2.7, 3.3 and 3.4 times at t1, t2, t3 and t4 respectively which showed that by adjusting retention time 1.4 times higher elongation at break was obtained for rPA6-2-EMA-0.5.

Almost similar elongation at break results were obtained with chain extended products with DTDI at different residence times due to the high reactivity of isocyanates.

Sample	Elastic modulus (MPa)	Yield strenght (MPa)	Elongation at break (%)
rPA6-2	$2630\pm103$	$64.7 \pm 1.0$	$22 \pm 1$
rPA6-2-EMA-0.5-t1	$2747\pm83$	$68.2\pm0.4$	$43 \pm 4$
rPA6-2-EMA-0.5-t2	$2438 \pm 190$	$60.4\pm0.8$	$51 \pm 4$
rPA6-2-EMA-0.5-t3	$2710\pm116$	$64.9\pm0.5$	$58 \pm 1$
rPA6-2-EMA-0.5-t4	$2576\pm78$	$66.4 \pm 1.0$	$60 \pm 2$
rPA6-2-EMA-1-t3	$2724\pm83$	$66.3\pm0.8$	$56 \pm 2$
rPA6-2-EMA-1-t1	$2688\pm67$	$66.8 \pm 1.0$	$59\pm5$
rPA6-2-EMA-1-t4	$2636\pm74$	$65.9\pm0.6$	$72 \pm 3$
rPA6-2-EMA-1-t2	$2626 \pm 148$	$62.7\pm0.5$	$74 \pm 2$
rPA6-2-DTDI-0.5-t1	$2730\pm51$	$64.2\pm0.1$	$27 \pm 4$
rPA6-2-DTDI-0.5-t2	$2810\pm91$	$71.7\pm0.4$	$27 \pm 4$
rPA6-2-DTDI-0.5-t3	$2747\pm37$	$71.9\pm0.4$	$29 \pm 4$
rPA6-2-DTDI-0.5-t4	$2845 \pm 176$	$63.0\pm0.2$	$31 \pm 3$
rPA6-2-DTDI-1-t3	$2850\pm88$	$63.4\pm0.3$	$32 \pm 1$
rPA6-2-DTDI-1-t1	$2878 \pm 118$	$72.2\pm0.6$	$32 \pm 3$
rPA6-2-DTDI-1-t4	$2802\pm100$	$71.8\pm0.6$	$33 \pm 2$
rPA6-2-DTDI-1-t2	$2916\pm61$	$63.7\pm0.6$	$34 \pm 2$

**Table 4.6 :** Tensile properties of rPA6 and chain extended products at different residence times.



Figure 4.30 : Elongation at break vs residence times.

#### 4.3.2.2 Notched Izod impact test

In order to observe the effect of residence time on notched and unnotched impact strengths of chain extended products impact tests were performed. For all residence times notched Izod impact strengths were slightly increased as the incorporation of chain extenders. As it is shown in Figure 4.31 effect of residence time on notched impact strengths were in similar trend with their effect on elongation at break.

Effect of residence time on impact properties were also observed in similar trend with relative viscosities and elongation at break for EMA and DTDI. As the molecular weight increased with an increase in residence time, notched Izod impact strength increased. Likewise, close molecular weights obtained from the chain extension with DTDI despite longer residence times resulted in similar impact strengths.

According to numerical results 5.5%, 7.5%, 12.3% and 15.1% increase in impact strength were obtained at t1, t2, t3 and t4 respectively which showed that by adjusting residence time 9.6% higher impact strength was obtained for rPA6-2-EMA-0.5. Likewise, 8.8%, 12.7%, 17.4% and 20.5% increase in impact strength were obtained at t1, t2, t3 and t4 respectively which showed that by adjusting residence at least 11.8% higher impact strength was obtained for rPA6-2-EMA-1.



Figure 4.31 : Notched Izod impact strength vs residence times.

## 4.3.2.3 Unnotched Izod impact test

Due to the notch sensitive structure of PA6 it was possible to observe the differences in the notched Izod impact strengths of chain extended materials. In the unnotched impact strength tests it was only possible to observe the improvement of unnotched impact strength from 40.75 kj/m<sup>2</sup> (rPA6-2) to no break (70.96 kJ/m<sup>2</sup>) for all residence times in all contents (Figure 4.32).



Figure 4.32 : Unnotched Izod impact strength vs residence times.

#### **4.3.3** Thermal property measurements

#### **4.3.3.1** Differential scanning calorimetry

The effect of residence time on the melting and crystallization behaviors of chain extended rPA6 were analyzed through DSC measurements. DSC cooling thermograms obtained from the first heating for rPA6-2 and 0.5 wt% chain extended products with EMA at different residence times is shown in Figure 4.33. DSC cooling thermograms obtained from the first heating for rPA6-2 and 0.5 wt% chain extended products with DTDI at different residence times is shown in Figure 4.34. DSC cooling thermograms obtained from the first heating for rPA6-2 and 1 wt% chain extended products with EMA at different residence times is shown in Figure 4.35. DSC cooling thermograms obtained from the first heating for rPA6-2 and 1 wt% chain extended products with DTDI at different residence times is shown in Figure 4.36. DSC heating thermograms obtained from the first heating for rPA6-2 and 0.5 wt% chain extended products with EMA at different residence times is shown in Figure 4.37. DSC heating thermograms obtained from the first heating for rPA6-2 and 0.5 wt% chain extended products with DTDI at different residence times is shown in Figure 4.38. DSC heating thermograms obtained from the first heating for rPA6-2 and 1 wt% chain extended products with EMA at different residence times is shown in Figure 4.39. DSC heating thermograms obtained from the first heating for rPA6-2 and 1 wt% chain extended products with DTDI at different residence times is shown in Figure 4.40. Table 4.7 shows the results from DSC measurements performed on neat rPA6 and chain extended products at different residence times. Melting temperature  $(T_m)$ , crystallization temperature  $(T_c)$ , melting enthalpy ( $\Delta H_m$ ), crystallization enthalpy ( $\Delta H_c$ ) and crystallinity degree were reduced with the incorporation of chain extenders in any conditions.

According to residence time studies (Table 4.7) with EMA longer residence time promotes chain extension and thus resulted in higher molecular weight and disrupted the chain regularity. Due to the higher molecular weight of chain extended products there was not sufficient time for arrangement of polymer chains and consequently crystallinity degree decreased upon increasing residence time.

According to results of chain extended product with DTDI residence time did not have significant effect on crystallinity, slight decrease in crystallinity were obtained upon longer residence times due to high reactivity of isocyanate, even low residence time was enough for the chain extension reaction. Relative viscosity measurements are also support these results.



**Figure 4.33 :** DSC cooling thermograms obtained from the first heating for rPA6-2 and 0.5 wt% chain extended products with EMA at different residence times.



**Figure 4.34 :** DSC cooling thermograms obtained from the first heating for rPA6-2 and 0.5 wt% chain extended products with DTDI at different residence times.



**Figure 4.35 :** DSC cooling thermograms obtained from the first heating for rPA6-2 and 1 wt% chain extended products with EMA at different residence times.



**Figure 4.36 :** DSC cooling thermograms obtained from the first heating for rPA6-2 and 1 wt% chain extended products with DTDI at different residence times.



**Figure 4.37 :** DSC heating thermograms obtained from the first heating for rPA6-2 and 0.5 wt% chain extended products with EMA at different residence times.



**Figure 4.38 :** DSC heating thermograms obtained from the first heating for rPA6-2 and 0.5 wt% chain extended products with DTDI at different residence times.



**Figure 4.39 :** DSC heating thermograms obtained from the first heating for rPA6-2 and 1 wt% chain extended products with EMA at different residence times.



**Figure 4.40 :** DSC heating thermograms obtained from the first heating for rPA6-2 and 1 wt% chain extended products with DTDI at different residence times.

	Heating			Cooling	
Sample	$T_m$ (°C)	$\Delta H_m \left(J.g^{\text{-}1}\right)$	T <sub>c</sub> (°C)	$\Delta H_c \ (J.g^{\text{-1}})$	χ(%)
rPA6-2	221	71.09	186	60.68	37.42
rPA6-2-EMA-0.5-t1	219	56.33	186	57.14	29.65
rPA6-2-EMA-0.5-t2	218	54.61	186	53.77	28.74
rPA6-2-EMA-0.5-t3	218	53.23	184	56.11	28.02
rPA6-2-EMA-0.5-t4	216	48.40	183	47.64	25.47
rPA6-2-EMA-1-t1	219	52.18	186	49.25	27.47
rPA6-2-EMA-1-t2	218	51.93	186	50.91	27.34
rPA6-2-EMA-1-t3	217	44.99	185	54.38	23.68
rPA6-2-EMA-1-t4	216	43.73	185	52.20	23.02
rPA6-2-DTDI-0.5-t1	218	64.44	186	61.01	33.91
rPA6-2-DTDI-0.5-t2	218	62.06	187	56.79	32.66
rPA6-2-DTDI-0.5-t3	217	60.73	187	60.28	31.97
rPA6-2-DTDI-0.5-t4	218	57.56	186	60.55	30.29
rPA6-2-DTDI-1-t1	219	60.56	186	59.94	31.87
rPA6-2-DTDI-1-t2	218	56.96	187	57.38	29.98
rPA6-2-DTDI-1-t3	219	55.99	186	55.90	29.47
rPA6-2-DTDI-1-t4	215	51.80	186	55.73	27.27

**Table 4.7 :** Results of DSC tests on rPA6 and chain extended products at different residence times.

## 5. CONCLUSIONS

## **5.1 Effect of Chain Extender Type**

Different amounts of four different chain extenders were melt compounded with rPA6 via twin screw extruder. The chain extension behavior of the resulting products was investigated through relative viscosity, DSC, HDT, VST measurements, tensile and impact tests.

Relative viscosities of chain extended products increase with increasing chain extender amounts for all chain extenders due to the increase in molecular weight of resultant materials. Between 2%-41% increase in relative viscosity of rPA6 was achieved by the incorporation of chain extenders which makes chain extenders powerful tool for industrial applications to adjust viscosity of rPA6.

While e-modulus was not significantly affected by chain extenders incorporation, elongation at break was noticeably improved. Elongation at break and notched izod impact strength increased with an increase of chain extender amount for both types of chain extenders which are also consistent with the viscosity values. Elongation at break and notched izod impact strength were increased by 6.3 times and 26% respectively with 1 wt% of EMA incorporation. Unnotched impact strength values improved from 31kj to no break data for all chain extenders in all contents. Brittle neat rPA6 became ductile after chain extension and its toughness was increased.

Chain extenders increase the molecular weight of rPA6 which increase entanglement and restrict the mobility of chains and thus lead to between 5.2%-12.4% increase in HDT of rPA6.

Among the chain extenders used in this study EMA showed a higher effect in comparison to the other chain extenders as observed from relative viscosity and mechanical test results. DTDI improved the molecular weight of rPA6 better than EPO and CW.

Therefore, addition of both chain extenders to commercial rPA6 through melt compounding could be an efficient way to increase molecular weight of rPA6 and leads to up-graded products with improved elongation at break and izod impact strength.

In this study DTDI which is generally used for polyurethane applications, is used as chain extender for rPA6 for the first time and showed great chain extension performance according to relative viscosity, elongation at break, yield strength and izod impact strength. DTDI can be used as a chain extender for rPA6 for industrial applications.

#### 5.2 Effect of Screw Temperature

Two different types of chain extenders were melt compounded with rPA6 by using twin screw extruder at three different screw temperature profile in order to investigate temperature dependence of chain extension reactions. The chain extension behaviors were investigated through relative viscosity measurements, DSC measurements, tensile and impact tests. When all the data keep in consideration chain extension reaction of EMA was observed to be temperature dependent. It was seen that screw temperature should be adjusted for the reaction of EMA. When the screw temperature was below the optimum, it was not enough to well mix the polymer and chain extender, consequently chain extension efficiency was low. When the screw temperature was higher than optimum, PA degradation was likely to proceed simultaneously with the chain extension reactions thus leaded to low efficiency. On the other hand DTDI chain extension reaction was not significantly affected from screw temperature due to high reactivity of isocyanate. Even low screw temperatures were enough for efficient chain extension reaction. According to numerical results by adjusting screw temperature at least 9.1% higher viscosity, 1.3 times higher elongation at break and 10.6% higher impact strength were obtained with EMA.

## 5.3 Effect of Residence Time

Two different types of chain extenders were melt compounded with rPA6 by using twin screw extruder at four different residence times in order to investigate residence time dependence of chain extension reactions. The chain extension behaviors were investigated through relative viscosity measurements, DSC measurements, tensile and impact tests. When all the data keep in consideration chain extension reaction of EMA was observed to be residence time dependent. It was seen that longer residence time promoted chain extension reaction of EMA and resulted in higher molecular weight. On the other hand DTDI chain extension reaction was not significantly affected from residence time due to high reactivity of isocyanate. Even low residence times were enough for efficient chain extension reaction. According to numerical results by adjusting residence time 41.2% higher viscosity, 1.4 times higher elongation at break and 11.8% higher impact strength were obtained with EMA.





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# PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

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