ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

EFFECTS OF ANTI-SCRATCH ADDITIVES ON THE PROPERTIES OF POLYPROPYLENES

M.Sc. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**ÇİZİLMEZLİK KATKILARININ
POLİPROPİLENİN ÖZELLİKLERİNE
ETKİSİ**

YÜKSEK LİSANS TEZİ

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MAYIS 2014

Hilal Güneysu, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID 515121013, successfully defended the **thesis** entitled "**EFFECTS OF ANTI-SCRATCH ADDITIVES ON THE PROPERTIES OF POLYPROPYLENES**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below

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Date of Submission : 05 May 2014
Date of Defense   : 27 May 2014

To my mother and father,

FOREWORD

May 2014   Hilal GÜNEYSU

                                                             (Chemical Engineer)

x

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ABBREVIATIONS

ABS   **:** Acrylonitrile-butyldiene-styrene
ASTM   **:** American Society for Testing and Materials
COF   **:** Coefficient of friction
DIM   **:** Diiodomethane
DSC   **:** Differential Scanning Calorimeter
EG   **:** Ethylene glycol
FTIR-ATR **:** Fourier Transform Infrared Spectroscopy Attenuated Total Reflection
Tg   **:** Glass Transition Temperature
HDPE   **:** High Density Polyethylene
ISO   **:** International Organization for Standardization
L/D   **:** Length to diameter ratios
LLDPE   **:** Linear low density polyethylene
MPa   **:** Mega Pascal
MFR   **:** Melt Flow Rate
MWD   **:** Molecular weight distribution
MW   **:** Molecular Weight
nPP   **:** Neat polypropylene
PDMS   **:** Poly(dimethyl siloxane)
PP   **:** Polypropylene
PO   **:** Polyolefin
Rpm   **:** Revolutions per minute
SEM   **:** Scanning Electron Microscope
Tp   **:** Significant Melting Peak Temperature
tPP   **:** Talc reinforced polypropylene
UV   **:** Ultra Violet
W   **:** Water

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EFFECTS OF ANTI-SCRATCH ADDITIVES ON THE PROPERTIES OF POLYPROPYLENES

SUMMARY

Polypropylene (PP) is one of the most widely used thermoplastic. It is used in many applications such as components of automobiles, large and small appliances, packaging, textiles and medical devices. The use of polypropylene has increased significantly especially in automotive sector over the past decades due to a good price to performance ratio, weight reduction, recyclability and design opportunities for vehicle production.

A wide variety of unfilled polypropylene and talc filled polypropylene can be found in the vehicle's interior, exterior parts including bumper fascias, instrumental panels and door trims. Usage of talc brings about several modifications of polypropylene properties, which increase the industrial interest for this particular. On the other hand, scratch resistance is an important parameter for automotive applications but polypropylene has poor scratch resistance. Therefore, it is desirable to improve scratch resistance and reduce scratch visibility from the aesthetic point of view. Generally, improvement in scratch resistance can be achieved by increasing crystallinity, compounding with scratch resistant polymers, and adding silicone-based additives. Additive approaches include the use of lubricating migratory amide slip agents, polysiloxane (silicone oil), lubricants (such as PDMS), grafted polymer agents and special fillers such as talc, wollastonite and nanoclays. Silicones are macromolecules that consist of a backbone of alternating silicon and oxygen atoms. They act as a slipping agent on the surface of polymer to decrease coefficient of friction at the surface as a result of that improved scratch resistance of polymer. Polydimethylsiloxanes (PDMS) have very low solubility parameters, and are thus highly immiscible with many other organic monomers and solvents. It is sometimes fairly difficult to properly react siloxanes with conventional organic monomers or oligomers due to immiscibility problems. During the modification of network structures, where the reactions are conducted in bulk, miscibility is even a more serious problem. The versatility of (Si--R--X) terminated siloxane oligomers provides and important solution under these circumstances. By proper choice and design of the (R) groups, it is possible to enhance the miscibility and as a result, the copolymerizability between reactive siloxanes and other organic monomer.

The aim of this work is to improve scratch resistance of neat PP (nPP) and talc reinforced PP (tPP) by using different commercially available anti-scratch additives which are a mixture of modified polyolefin-silicone block copolymer, siloxane copolyester, and organically modified siloxane, by using as 1 and 3 wt-% both in nPP and in tPP. The samples were prepared by melt blending extrusion. The extruder was a 25 mm diameter single screw extruder with L/D ratio of 25 consisted of three heating zones surrounding the screw, a static mixer after the third heating zone and a strand die with four holes. The 3-stage single screw with compression ratio of 2.05

was equipped with dispersive mixing elements in the metering zone. An optimization study was carried out to determine the optimum temperature profile; 190/ 195/ 195/ 200/ 200 ºC for heating zones, static mixer and die, respectively. The samples were prepared for each test differently. Strands types of specimens prepared for the mechanical measurement tests. Compression molding at 210ºC temperature and 100 bar pressure was used to prepare the 10cm×10cm×2mm samples for other tests.

Structural analyses of the additives and samples were determined by Fourier transform infrared spectroscopy (FTIR-ATR) to observe chemical composition of additives and the behaviour of additive on the surface.

Tensile strength, elastic modulus and elongation at break values were determined by tensile tests. Mechanical properties of polypropylene depended on filler, additive types and additive content. Hardness of samples was evaluated by Shore-D hardness tests which resulted that additives decreased the hardness of samples but talc as a rigid filler increased the hardness of samples. Thermal properties of the samples were analyzed by differential scanning calorimetry (DSC) analysis. Percent of crystallinity of the samples was calculated which resulted that talc increased % crystallinity of the samples.

The scratch resistance of the samples was examined by using Erichsen scratch tester. Scratch marks were applied to the test surface that was prepared by using hot press. A series of parallel scratch marks were applied with 20 cuts (10 in one direction and 10 perpendicular to those) at a distance of 2 mm under 20 N stress loads for all samples. Tribological investigation were done to determine the scratch resistance of the samples. Width (μm) of the scratches was measured by optical microscopy. Exposed talc particles on the surface of talc reinforced PP are found to be responsible for the increased light scattering, leading to greatly increased visibility. Talc reinforced polypropylene always showed higher scratch width which means that the samples with talc exhibit lowered scratch resistance and lowered scratch hardness as well. PDMS containing additives acted as slipping agent on the surface of polymer and decrease scratch width and visibility, improve the scratch resistance both in nPP and tPP. When they were used as 3 %, the visibility of scratch was seen only in one direction for nPP based samples by optical microscope.

Surface properties were investigated by contact angle measurements and by using these data the surface free energy of samples were calculated. It was shown that siloxane containing additives increased water contact angle value and made the surface more hydrophobic. Samples with PDMS containing additives had low surface free energy due to the fact that the methyl groups of PDMS have virtually no interactions with each other.

Melt flow rate was also measured for all of the samples which showed that PDMS containing additives increase processability by increasing MFR value. tPP based samples had lower MFR value due to lack of contribution of the talc to the flow.

The density values of additives and samples were measured to show that samples with PDMS containing additives lowered density of samples depend on their density value. On the other hand, talc increased density of PP.

ÇİZİLMEZLİK KATKILARININ POLİPROPİLENİN ÖZELLİKLERİNE ETKİSİ

ÖZET

Polipropilen (PP) en yaygın kullanılan termoplastiklerden biridir. PP'nin, büyük ve küçük ev aletleri, otomobil bileşenleri, ambalaj, tekstil, tıbbi cihaz parçaları gibi birçok kullanım alanı vardır. Son on yılda polipropilenin özellikle araba endüstrisinde kullanımı oldukça yaygınlaşmıştır. Bunun nedenleri arasında performasına göre fiyatının uygunluğu, hafifiliği, ultraviole ışınlarına dayanımı ve kolaylıkla değişik tasarım fırsatları yaratması gösterilebilir.

Saf polipropilen ve talk dolgulu polipropilen arabaların iç ve dış aksamlarında enstrümantal panellerinde ve kapı süslerinde kullanılabilir. Talkın kullanımı polipropilenin birçok özelliğini iyileştirmektedir ve endüstriyel alanda kullanımını arttırmaktadır. Öte yandan çizilmeye karşı direnç otomotiv sektöründe önemli bir parametredir. Fakat polipropilenin çizilme direnci düşüktür. Bu nedenle çizilme direncini arttırmak, çizinirliğini düşürmek estetik açıdan önemlidir. Ayrıca çizinirliği düşürmek malzemenin ömrünün de uzamasını sağlar. Genel olarak çizilme direncini arttırmak; kristalliği arttırarak, çizilmeye karşı dayanıklı polimerlerle birleştirerek ve silikon bazlı katkı maddeleri ile takviye edilerek sağlanabilir. Bu katkı maddelerine örnek olarak; yağlama maddeleri, polidimetil siloksanlar (PDMS), polisiloksanlar (silikon yağı), graft edilmiş yağlama ajanları ve talk, nanokil gibi özel dolgu maddeleri gösterilebilir. Silikonlar, iskeletinde karbon (C) yerine ardışık olarak dizilmiş silisyum (Si) ve oksijen (O) atomları bulunan polimerlerin ortak adıdır. Silikon moleküllerinin çoğunda silisyum atomlarına bağlı metil ya da fenil grupları yer alır. Yüzeye göç ederek kayganlaşmayı sağlarlar, sürtünme katsayısını düşürür ve böylece çizinirliği düşürerek, çizilme direncini arttırırlar. Polidimetil siloksan (PDMS), polisiloksan grubunun en yaygın kullanılan üyesidir. Geniş molar hacim, kohezif enerji yoğunluğunun düşük olması ve esnekliğinin yüksek olması PDMS'nin önemli fiziksel özelliklerindendir. Bunlara ek olarak PDMS, görünür ve UV ışığına karşı saydam, ozon ve korona karşı çok dirençli, atomik oksijen ve hatta oksijen plazmalarına karşı kararlıdır. Diğer üstün özellikleri ise film şekillendirme yeteneği, çeşitli gazlara karşı yüksek geçirgenliği, su sevmeyen (hidrofob) yapıda olması, serbest hareket yeteneği, yüzey aktivitesi, kimyasal ve fiziksel etkilere karşı etkisiz (inert) olmasıdır. PDMS çok düşük çözünürlük parametrelerine sahiptir ve bir çok organik monomerler ve çözücüler ile karışmazlar. Bunedenle siloksanların organik monomer ve oligomerlerle reaksiyona girmesi çok zordur. Sonlu siloksan oligomerlerin (Si--R--X) fonksiyonlu yapısı bu durumda çözüm sağlar. R grubunun doğru seçimi ve dizaynı, karışabilirliğin artmasını sağlar. Reaktif siloksanlar ve diğer organik monomerler arasındaki kopolimerizasyonu mümkün hale getirir. Öte yandan talk $Mg_3Si_4O_{10}(OH)_2$ kimyasal formülüne sahip hidratlanmış magnezyum silikadan

oluşan bir mineraldir. Özellikle otomotiv sektöründe polipropileni kuvvetlendirmek için yaygın olarak kullanılır.

Bu çalışmanın amacı, polipropilenin ve talk dolgulu polipropilenin çizinme direncini arttırmak ve kullanılan katkıların polipropilenlerin mekanik, ısıl ve tribolojik özelliklerine etkisini incelemektir. Bu amaçla ticari olarak bulunan PDMS içeren üç farklı katkı maddesi kullanılmıştır. Bunlar: modifiye edilmiş poliolefin-silikon blok kopolimer karışımı, siloksan kopolyester ve organik olarak modifiye edilmiş siloksandır. Bu katkılar % 1 ve % 3 oranında kullanılmıştır. Örnekler eriyik karıştırma ile ekstrüderde hazırlanmıştır. Kullanılan ekstrüder, 25 mm çapında, L/D'si 25 olan, vidayı çevreleyen üç ısıtma bölgesi, üçüncü ısıtma bölgesinin devamında bir statik mikser ve kafadan oluşan tek vidalı bir ekstrüderdir. 3 basamaklı ve sıkıştırma oranı 2,05 olan vida, dispersif karıştırma elemanları ile donatılmıştır. Optimizasyon çalışması sonucunda katkı maddelerinin karışımlarının ekstrüzyonu için optimum sıcaklık profili birinci, ikinci ve üçüncü ısıtma bölgesi, statik mikser ve kafa için sırasıyla 190/ 195/ 195/ 200/ 200 ºC olarak belirlenmiştir. Pellet haline getirilen örnekler herbir karakterizasyon için farklı şekilde kalıplanmıştır. Çizinirlik testi için sıcak preste 210ºC ve 100 bar'da 10cm×10cm×2mm boyutlarında hazırlanmıştır.

Kızılötesi spektroskopisi katkıların molekül bağlarının yapısı hakkında bilgi edilmek için kullanıldı. IR ışınları molekülün titreşim hareketleri tarafından soğurulmaktadır ve dalga boyuna göre spektrumlar elde edilmektedir. Ayrıca katkıların yüzeydeki davranışını incelemek için hem örneğin yüzeyinden hem içinden analiz yapılarak aradaki fark gözlemlenmeye çalışılmıştır. Additivlerin PDMS karakteristik piklerine sahip olduğu görülmüştür. İçte ve dışta görülen katkının yüzeyde pikleri daha baskındır.

Evrensel test cihazından alınan gerilim-gerinim sonuçlarından, elastik modülü ve kopma uzaması ile çekme mukavemeti değerleri hesaplanmıştır. Farklı oranların ve farklı katkılarının mekanik özellikleri nasıl etkilediği gösterilmiştir.

Örneklerin sertlik değerleri, Shore D tipi durometre ile, ASTM D2240 standardına göre ölçülmüştür. Malzemenin sertliği, genel anlamda, metal bir çubuk, bilye ya da iğnenin batmasına karşı gösterdiği direnci ifade eder. Silikon katkılı örneklerde sertlik düşerken, talk katkısının sertliği arttırdığı gözlemlenmiştir.

Tüm karışımların ısıl özellikleri DSC analizi ile incelenmiştir. Örneklerin erime sıcaklığı oldukça yakındır. Yüzde kristallilik değerleri entalpi değerlerinden hesaplanmıştır. Yüzde kristallilik değerinin talklı örneklerde arttığı belirlenmiştir.

Çizilme direnci malzemenin tribolojik özelliklerinden biridir. Çizilme direncini tayin etmek için Erichsen çizme test cihazı kullanılmıştır. Tüm örnekler uygulanan kuvvet 20 N dur. Çiziklerden 10 tanesi birbirine paralel ve diğer 10 tanesi de bunlara dik ve kendi içinde paralel şekilde 2 mm aralıklarla uygulanmıştır. Cihazda kullanılan uç 1 mm lik ISO 1518-1 tipidir.

Çizinirliklerin genişliğini ölçmek ve görüntülemek için optik mikroskop kullanılmıştır. Bir örneğin on farklı noktasından görüntü alınmıştır. Talk dolgulu örneklerin çizinirlik genişlikleri talk dolgusu olmayan örneklere göre oldukça fazladır. Bu da talk dolgulu örneklerin çizilmeye karşı gösterdikleri direncin ve çizilme sertliğinin daha az olduğunun göstergesidir. Çünkü çizilme sertliği çizik genişliği ile ters orantılıdır. Silikon bazlı katkıların herbirinin çizilme direncini arttırdığı gözlemlenmiştir. Talk katkısı olmayan örneklerde % 3 oranında kullanılan

katkıların çizinirliği oldukça düşürdüğü hatta, çizinirliğin sadece tek yönde oluştuğu optik mikroskop ile gözlemlenmiştir.

Kontakt açı ölçümleri ile yüzey özellikleri incelenmiş ve bu veriler kullanılarak serbest yüzey enerjileri hesaplanmıştır. PDMS içeren katkılı örneklerde su ile yapılan temas açı ölçümlerinde açının arttığı gözlemlenmiş. Açının artması daha hidrofobik bir yüzey oluştuğunun göstergesidir. PDMS içeren katklı örneklerin serbest yüzey enerjileride daha düşük çıkmıştır.

Eriyik akış hızı (MFR) analizi (190ºC, 2,16 kg) tüm örnekler için hesaplanmıştır. Ölçüm sonuçlarının silikon bazlı katkıların MFR değerini arttırdığı gözlemlenmiştir. Akışkanlığın artması, daha kolay işlenebilirliği de sağlamıştır. Talk katkılı örneklerin MFR değeri azalmış, akışkanlığa gösterdiği direnç artmıştır.

Örneklerin yoğunluklarına bakıldığında PDMS içeren katkılı örneklerin yoğunluğu azalttığı gözlemlenmiştir. Talk dolgu maddesinin ise yoğunluğu arttırdığı görülmüştür. Organik olarak modifiye edilmiş siloksan en düşük yoğunluğa sahiptir. Bunedenle bu katkının kullanıldığı örnekler de en düşük yoğunluğa sahiptir. Siloksan kopolyester katkısı da en yüksek yoğunluğa sahiptir. Bunun nedeni içeriğindeki yüksek yoğunluklu polikaprolaktonlardır. Bu katkının kullanıldığı örneklerde daha yüksek yoğunluğa sahiptir.

1. INTRODUCTION

For the past decade, polypropylene (PP) has become one of the most widely used polyolefin especially for automotive industries, food packaging, fabrication of electric and electronic components and currently its utilization in building structural component for civil needs [1].

Polypropylene compounded materials are being increasingly used to produce various components in modern passenger cars due to its low cost and chemical resistance. On the other hand, aesthetical appeal and low susceptibility to mechanical damage are important parameters especially in the automotive industries. But, the major drawback of PP is the poor scratch resistance which is important for the life of materials and aesthetic of view. Many factors affected scratch behavior of polymers, such as scratch testing parameters, methods, material ductility, crystallinity, hardness, surface roughness and surface tension [2]. In general, improvement in resistance to scratch deformation of thermoplastic olefins can be achieved by increasing crystallinity, compounding with scratch resistant polymers, and by reinforcement of the polymer matrix with fillers and additives [3]. Besides those lubricants, impact modifiers, surface morphology, and the interface between the matrix/filler are important for scratch resistance performance [4]. Lubricate the surface using slip additives has been successfully employed to reduce scratch damage in polypropylene-based materials. As the coefficient of friction at the surface is reduced, the magnitude of the maximum tensile stress during scratching is also decreased, which in turn reduced brittle scratch damage such as cracking, crazing, and cavitations. Materials with higher scratch resistance are expected greater scratch hardness and lower scratch visibility [5].

The aim of this work is to investigate effects of anti-scratch additives on the properties of different types of polypropylenes. One of the used polypropylene was filled with talc which is a magnesium sheet silicate with the chemical formula $Mg_3 Si_4 O_{10} (OH)_2$. Three different commercially available additives were used to improve

scratch resistance of neat PP (nPP) and talc reinforced PP (tPP). These additives are (1) a mixture of modified polyolefin-silicone block copolymer, (2) siloxane copolyester and (3) organically modified siloxane, used as 1 and 3 wt-% both in nPP and in tPP. These additives were mixed to PPs by single screw extruder which contained dispersive and distributive elements with static mixer. Structural surface analyses of the samples and additives were determined by Fourier transform infrared spectroscopy (FTIR-ATR). The prepared samples were moulded at hot press for testing scratch resistance. A series of parallel scratch marks were applied by Erichsen scratch tester under same force to the samples. Widths (μm) of the scratches were measured by using optical microscopy. The peak temperature (Tp), the enthalpy of melting were obtained by differential scanning calorimeter (DSC) and percentage crystallinity were calculated from these data. Tensile test was performed in order to examine the effects of filler, additive type and additive content on the mechanical properties of polypropylenes. Hardness of the samples was evaluated by Shore-D hardness tests. The surface properties of the samples were investigated by means of contact angle measurements. The density of additives and samples were measured by density kits. Melt flow index of the samples were measured to investigate the effects of additives on processability.

2. THEORETICAL PART

2.1 Polypropylene (PP)

Polypropylene (PP) is a crystalline thermoplastic polyolefin resin. It belongs to the group of olefinic polymers, which can generally be described by the chemical structure in Figure 2.1.
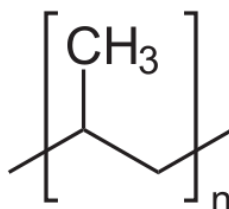
Figure 2.1 : Structure of polypropylene.

Polypropylene (PP) is readily formed by polymerizing propylene with suitable catalysts, generally aluminum alkyl and titanium tetrachloride. Polypropylene properties vary according to molecular weight, method of production, and the copolymers involved [6].

2.1.1 History of polypropylene

Propylene was first polymerized to a crystalline isotactic polymer by Giulio Natta as well as by the German chemist Karl Rehn in March 1954. This pioneering discovery led to large-scale commercial production of isotactic polypropylene by the Italian firm Montecatini from 1957 onwards. German Karl Ziegler, for his discovery of first titanium-based catalysts, and Italian Giulio Natta, for using them to prepare stereo regular polymers from olefins, were awarded the Nobel Prize in Chemistry in 1963 for their discoveries in the field of the chemistry and technology of high polymers. Ziegler–Natta catalysts have been used in the commercial manufacture of various polyolefins, such as polypropylene (PP), high density polyethylene (HDPE), linear low density polyethylene (LLDPE) etc. since 1956.

It was found that olefins can be polymerized by using coordination catalysts, but the monomers approach the reactive site, they randomly orient relative to the growing chain, creating the atactic form. It had not been possible to perform any steric control on polymerization processes until the discovery of stereospecific polymerization of PO. Polymerization of stereoregular isotactic PP by coordination catalysts was the first practical performance of steric control on the growth of a polymer chain. Besides being the starting point of PP industry, this was the first event in a long series of successful applications of coordination catalysts to other monomers, leading to stereoregular polymers of higher α-olefins, styrene and diolefins [7]. The properties of isotactic polypropylene enabled it to be utilized as a raw material for film and fiber industry as well as being a thermoplastic resin. Industrial production of PP was started in 1957. Polymerization of syndiotactic PP was also performed by using coordination catalysts; however, this product has not achieved any commercial importance and has been only of scientific interest [8].

Beside from Ziegler-Natta type catalysts, metallocene catalysts activated by MAO (methylaluminoxane) are also used in the polyolefin production as catalyst (initiator). Metallocene contains a transition metal and two cyclopentadienyl ligands coordinated in a sandwich structure. Metallocenes were developed in 1950's, beginning with the discovery of ferrocene followed shortly thereafter by synthesis of titanocene dichloride and zirconocene dichloride. Polypropylene produced by metallocene catalysts (mPP/isotactic mPP) have good impact resistance, chemical resistance better than polycarbonate and acrylics, glossy and transparent. [9].

2.1.2 Structure and property relationships

Propylene is an asymmetrical monomer so that polypropylene can be produced with different stereochemical configurations. The most common types of polypropylene, shown in Figure 2.2, are isotactic, syndiotactic, and atactic. In isotactic polypropylene, the methylgroups are placed on the same side of the backbone; in syndiotactic polypropylene, on alternating sides; and in atactic polypropylene, the methyl groups are arranged randomly along the chain.

Isotactic homopolymer polypropylene has a high degree of crystallinity thereby creating a material that is strong, with low permeability to vapor or solvents, and high chemical resistance. Atactic polypropylene is amorphous and has little

commercial value. The atactic form, due to its lack of crystallinity, has poor physical strength with lower resistance to dissolution in solvents and greater permeability to low molecular weight gases such as oxygen and water vapor. Syndiotactic polypropylene is prepared with soluble coordination catalysis and the stereoregularity attained is generally lower than that of isotactic polymers. Both isotactic and syndiotactic polypropylene are semicrystalline polymers with high melting temperatures. Isotactic polypropylene dominates the market, likely because it is easily produced with heterogeneous Ziegler–Natta and metallocene catalysts; syndiotactic polypropylene can be produced only with some metallocene catalysts and has much less widespread commercial use.
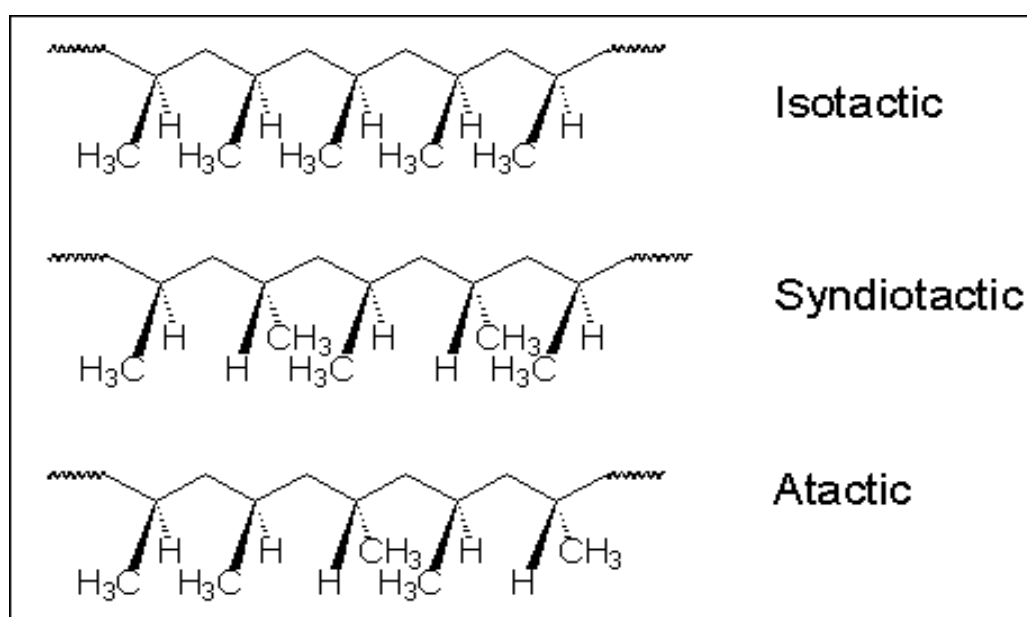
Figure 2.2 : Structure of isotactic, syndiotactic and atactic polypropylene.

2.1.3 Properties of polypropylene

The mechanical and thermal properties of polypropylene can vary based on the isotacticity, the molecular weight and its distribution and % crystallinity. Since PP is a viscoelastic material like other thermoplastics, its mechanical properties are strongly dependent on time, temperature and stress.

- **Density**

Polypropylene is the lightest among the commonly used thermoplastics and has a density of 0.9 g/cm^3.

- **Thermal properties**

Polypropylene has a glass transition temperature and a crystalline melting point of -10ºC and 160-170ºC, respectively. Moreover, it has a maximum continuous use temperature of 100ºC, which is significantly higher than those of the other commodity plastics and some other engineering plastics.

- **Mechanical properties**

The mechanical properties of isotactic PP depend on its percent crystallinity. Due to its relatively high melting temperature, the crystalline phase maintains mechanical strength up to rather high temperatures. It has high tensile strength, stiffness and hardness due to its crystallinity. However, an increase in molecular weight leads to a reduction in tensile strength, stiffness, hardness but an increase in impact strength of polypropylene.

2.1.4 Applications

Polypropylene has become one of the most widely use polyolefine especially for intensive activities in research, product development and commercialization. Polypropylene has a variety of applications in our daily life, from packaging, toys, pipes, and tools, to some promising specialty applications in the electronic, airplane, and automotive industries.

Applications of polypropylene range from injection-molded, blow-molded products, fibers and filaments to films and extrusion coatings. Extruded polypropylene fibers are utilized in products such as yarn for carpets, woven and knitted fabrics. Nonwoven polypropylene fabrics are used in applications carpet backing, liners for disposable diapers, disposable hospital fabrics, reusable towels and furniture dust covers whereas oriented polypropylene film is used as overwrap of items such as cigarettes, snacks and phonograph records [11].

2.1.4.1 Automotive applications for interior and external parts

Polypropylene has long been used for various automotive applications due to weight saving and hence fuel reduction and easy processability. Polymers can be moulded at high speeds and low costs into complexly shaped parts. A wide variety of unfilled

polypropylene and polypropylene composites can be found in the vehicle's interior, exterior, and under-the-hood.

a) Interior parts:

- Trim Components

Polypropylene is one of the most common plastics selected for trim components in automobiles today. It can often be found in molded-in-color applications for various trim items throughout the vehicle. Most pillar trim found in vehicles composed of a polypropylene copolymer. Garnish moldings are all the trim-colored body panels in the automotive interior. The more structural parts often contain talc or another mineral to improve heat capabilities and stiffness. The upper trim component of the instrument panel may contain up to 26 wt% talc-filled polypropylene. Many other interior components, such as glove box and console bins, as well as console housings, are molded-in-color polypropylene. Door trim consists of unfilled or talc-filled high-crystalline polypropylene with molded-in color.

- Functional Components

Polypropylene can be compounded to meet many different component stiffness, impact, heat resistance, and appearance requirements. In order to make automotive components having both toughness and processability, high melt flow resistance (low molecular weight) polypropylene resins are important ingredients in TPO (thermoplastic olefin) formulations. Mineral-reinforced polypropylene materials can often be found in structural parts throughout the vehicle. Armrest substrates and console substrates are often injection molded with 20-30% glass-reinforced polypropylene.

b) Exterior parts

Polypropylene is used frequently in the exterior of automobiles to air inlet panels and wheel house liners. Polypropylene offer excellent weatherability properties. Air inlet panels often require substantial weather resistance as these parts are subjected to extreme temperatures (high and low), sunlight, and rain or snow. These parts are

often polypropylene copolymer with 10-20 wt% talc to offer improved stiffness and good impact [12].

2.2 Scratch Resistance

Polymers are preferred for microelectronic packaging, coatings, aerospace, automotive, food packaging and biomedical applications due to their adequate strength, lightness, versatility, ease of processing and low cost. It is important that the products are manufactured with durable, low-gloss first surfaces and aesthetically appealing. In order to maintain a good appearance, it is required that materials exhibit minimal susceptibility to mechanically induced surface damage and stress whitening does not occur. However, polymers are more susceptible to scratches and abrasion when compared to other materials because they are relatively soft [10].

Scratch deformation of polymeric surfaces has become an important area of research in the field of materials science and mechanics. The surge of interest in the subject of scratch resistance stems from the increasing use of polymers in applications. Scratch behaviour of polymers depends on a variety of factors, which can be classified into two primary groups: (i) indenter geometry and testing conditions such as normal load temperature and sliding tip velocity and (ii) material properties such as modulus, yield stres, ductility, crystallinity, hardness, surface roughness, surface tension [2].

A scratch on the surface of a polymeric material is a large size flaw that can potentially be a stress raiser restricting the applicability during tensile, impact or fatigue loading. Moreover, surface damage induced by scratch or any mechanical deformation process detracts the user from the subjective perception of quality of the product and limits the applicability of polymeric materials.

Scratches can also decrease the mechanical strength of polymeric materials. In general, the scratch performance of polymeric materials depends on the scratch stress field associated with the indenter geometry and properties of the polymeric materials. Other factors such as lubricant, filler and additives also affect the scratch performance of thermoplastic olefins. [14]

Scratches promote crazing, wedging, ironing and debonding that drastically increases the ability of the surface to scatter light, consequently increase in scratch visibility.

Polymeric materials should be characterized by high modulus and elastic recovery in order to enhance scratch resistance. Surface texture, crystalline orientation and impact strength are the other aspects of consideration. Even small decreases in percentage crystallinity enhance stress whitening. High modulus and yield stress characteristics of highly crystalline polymers lead to their lower susceptibility to stress whitening [10].

Kody and Martin developed a sophisticated scratch testing methodology in 1996 which involves quantifying the light scattered from solid polymer or a polymer composite surface due to surface deformation. The technique involves first deforming the material in a controlled and reproducible manner. Scratch test has been developed so as to evaluate the scratch behavior of polymers. In a scratch test, an indenter with a constant penetration rate is used. The machine uses a conical diamond stylus to induce scratches into a flat piece of material mounted on a rotating stage. Furthermore, the indenter can be made of various materials such as diamond, sapphire, steel, silicone nitrite, etc. The scratch is done with a constant loading rate and constant scratch rate. A scratch tester is shown in Figure 2.3 [15].
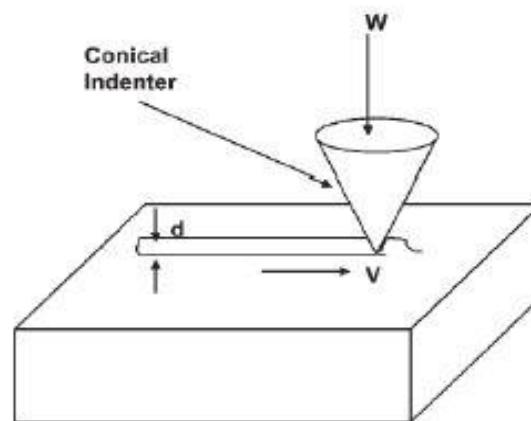
Figure 2.3: Schematic representation of the scratch test. W, V and d are normal applied load, scratching velocity and scratch width, respectively [14]

The results could then be used to compare the scratch resistance of materials. The severity of the scratch damage is evaluated by using various techniques such as atomic force microscopy, optical microscope, scanning electron microscope, laser confocal microscope, Raman spectroscope, white-light interferometer, cross profilometer, tribometer, elipsometer, etc. Stress whitening is the scattering of visible

light and the extent of scattering is a measure of the visibility of the scratch. Light will be scattered from the scratch if the plastically deformed region contains features (voids, stretched fibrils, ridges) of dimensions corresponding to the wavelength of visible light [16]. In recent study, Erichsen scratch tester is used and scratch damage is evaluated by optical microscope. The example of optical imaging that is taken after Erichsen scratch tester is shown Figure 2.4. This measurement corresponds to the difference in brightness of the cut and uncut polymer surface of scratch.
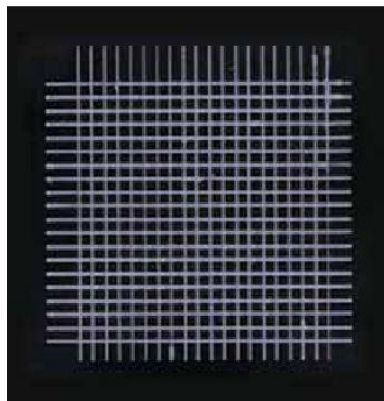
Figure 2.4 : Example of scratch marks on the samples.

2.2.1 Types of additive and filler for scratch resistance

Improving the scratch resistance and surface durability of polypropylene and TPO used for automotive interior and exterior parts continues to be a topic of interest to the industry. Over the years a number of technical approaches have been developed which provide varying degrees of improvement in scratch resistance. Examples include increasing part surface lubricity through the use of filler selection (e.g. wollastonite vs. talc), slip additives (e.g. fatty acid amides and siloxanes), improving adhesion between the polymer matrix and inorganic fillers (e.g. through surface modification and compatibilization), and increasing surface hardness (e.g. through polymer architecture as well as the use of additives such as nucleating agents to increase the crystallinity) [17].

2.2.1.1 Special fillers

Polypropylene (PP) filled with particulate fillers are of great interest in both research and industry. It is well known that polypropylene has good processability allowing to accept different types of natural and synthetic fillers. As fillers, mica, kaolin, calcium

carbonate, and talc are the most often used to reduce both the production costs and to improve the properties of the thermoplastics, such as rigidity, strength, hardness, flexural modulus, dimensional stability, crystallinity, electrical and thermal conductivity. However, fillers have a detrimental effect on other properties such as the impact property and deformability. The filler type and size, interfacial adhesion and bond strength between matrix and filler and surface characteristics of the composite can greatly influence the filled system. In a highly filled polymer system, nonuniformity of properties can exists because of poor dispersion of the filler in the matrix. A good interfacial adhesion between matrix and filler may improve the mechanical strength [17].

One of the most commonly used filler is wollastonite. It provides better scratch resistance to TPO and PP vs. talc. However, wollastonite has some limitations, e.g.,

- Higher cost vs. talc
- Difficult to incorporate during compounding due to high aspect ratio (must be fed downstream)
- Several grades of wollastonite-filled materials are available.

The other commonly used filler is based on nanoclays. It also provides improved scratch resistance vs. talc but suffers from following limitations:

- Very high cost
- Not yet a mature and commercially viable technology
- Adopted in some low volume platforms to test.

2.2.1.2 Slip additives

One particular strategy that has been successfully employed to reduce scratch damage in polypropylene-based materials is to lubricate the surface using slip additives. As the coefficient of friction at the surface is reduced, the magnitude of the maximum tensile stress during scratching is also decreased, which in turn reduced brittle scratch damage such as cracking, crazing, and cavitation. Decreasing the coefficient of friction has also been shown to reduce the yielded zone size on the surface from scratching, resulting in reduced scratch visibility.

Slip additive may be categorized as migratory or nonmigratory. Migratory slip additives must migrate from the bulk of the part to the surface in order to function as lubricants. Nonmigratory slip additives are by their nature randomly distributed

throughout the part, and must be used at relatively high concentrations in order for enough additive to be present at the surface to provide a lubricating effect.

- **Migratory Slip Additives**

Primary and secondary fatty acid amides are the most common migratory slip additives, including oleamide, erucamide, stearyl erucamide, ethylene bis (oleamide), and oleyl palmitamide. The use of these additives to reduce the coefficient of friction at polymer surface has been practiced since the 1950's, when they were first employed in polyethylene films. The products function by migrating from the polymer bulk to the part surface to form a close-packed, oriented layer. In polyethylene, a monolayer of the additive has been shown to be sufficient to reduce the coefficient of friction to a low value. In polypropylene films, migratory slip additives can provide a reduction in the coefficient of friction.

However, several disadvantages related to uncontrolled migration:

- Stickiness after aging/weathering can be an issue
- Fogging (critical for interior applications)
- Poor paintability (partial paint applications & touch up)
- Poor adhesion (parts may be attached using adhesives)
- Effect is not permanent
- Weatherability is poor

- **Nonmigratory Slip Additives**

High moleculer weight polysiloxanes are the most common nonmigratory slip additives used to enhance the scratch resistance of polypropylene-based materials. The nonmigratory slip additives have some technical advantages over their migartory counterparts. For example, they provide an immediate and somewhat more durable antiscratch effect. Also owing to their nonmigratory nature they would be expected to be evenly distributed at the surface, even in textured parts. Unlike the migratory slip additives, polysiloxane shows no decrease in performance after washing. A major disadvantage vs. migratory slip additives is inferior cost performance due to both the higher price of the additive and the higher loadings that must be used to give an effect at the part surface. It has also been reported that polysiloxanes have are prone to adsorption on talc, which necessitates the passivation of the talc filler prior

to incorporation of the polysiloxane. Many polysiloxanes are viscous liguids, which can be difficult to handle and dose in a compounding operation. For this reason more user-friendly solid forms such as masterbatches have been developed and are typically employed.

Although, these additives are less migratory than slips, but still suffers from some of the same disadvantages:

- Poor paintability (partial paint applications & touch up)
- Poor adhesion (parts may be attached using adhesives)
- Effect is not permanent. [5]

2.3 Polysiloxanes

Polysiloxanes are the most common organosilicon polymers used in polymer chemistry. They are usually known as "silicones" or "silicon elastomers", have received wide spread attention as specialty polymers since their commercial introduction in the 1940's and are by far the most important of the inorganic backbone polymers. Special interest in these systems has developed as a result of their unique properties which fulfill a wide range of needs for very diversified applications ranging from electrical insulation to biomaterials and to space research. Thermodynamic calculations and spectroscopic studies have shown that in polydimethyl siloxanes, $[(CH_3)_2SiO]_n$, the methyl groups rotate with unusual ease around the (Si-O) bonds. A large molar volume (75.5 cm^3/mole) and a low cohesive energy density (intermolecular forces) of polydimethyl siloxanes (PDMS) are consequences of the ease of rotation of the methyl groups. Low intermolecular forces and the flexibility are also responsible for many unique properties of the PDMSs such as extremely low glass transition temperature (T_g = -123 ^{o}C), low surface tension and surface energy, low solubility parameter and low dielectric constant. The reason for the surface energy being so low is that the methyl groups have virtually no interactions with each other. Another factor in the surface energy is the boiling point. Since it is low for polysiloxanes, the surface energy is low as well. The bonding is strong and so the polymer can be used as a good adhesive as well. Since it has the ability to bend and twist, there wont be as much cracking going on in the application. In addition, polydimethyl siloxanes are transparent to visible and UV light, very resistant to ozone and corona discharge, stable against atomic oxygen an even

oxygen plasmas. Despite their many outstanding properties, PDMS rubbers require extremely high molecular weights to develop useful mechanical properties. Chemical backbone structure of PDMS is given in Figure 2.5.
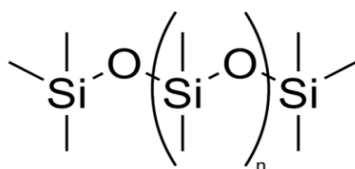

Figure 2.5 : Chemical backbone structure of PDMS.

Even at a molecular weight of 500,000 g/mole they exhibit cold flow and very weak rubbery properties. Therefore, PDMS must generally be chemically crosslinked in order to be used in an elastomer. However, unfilled PDMS vulcanizates still have very low tensile and tear strengths and elongations. Polysiloxanes are not compatible with the numerous organic polymers due to their low solubility-parameter (7.5 (Cal cm^{-3})$^{1/2}$). In addition, they have high gas permeability, chemically and physically inert and hydrophobic properties [19]. Properties of PDMS is given in Table 2.1.

Table 2.1 : Properties of PDMS [20].

Sample	Properties
Mass density	0.97 kg/m^3
Young's modulus	360-870 Kpa
Poisson ratio	0.5
Tensile or fracture strength	2.24 Mpa
Specific heat	1.46 kJ/kg K
Thermal conductivity	0.15 W/m K
Dielectric constant	2.3-2.8
Index of refraction	1.4
Electrical conductivity	4x10^{13} Ωm
Magnetic permeability	0.6x10^6 cm^3/g
Adhesion to silicon dioxide	Excellent
Biocompatibility	Noniritating to skin, no adverse effect on rabbits and mice, only mild inflammatory reaction when implanted
Hydrophobicity	Highly hydrophobic, contact angle 90-120°
Melting Point	-49.9–40°

2.3.1 Theory of contact angle

The surface tension of solids with a low surface free energy (such as polymers) cannot be measured directly because of the elastic and viscous restraints of the bulk phase. So it is needed to be measured by using of indirect methods. If we consider a liquid drop standing on a solid surface (Figure 2.6), the drop is in equilibrium by balancing three forces (the interfacial tensions between solid and liquid, *SL*; between solid and vapor, *SV*; and between liquid and vapor, *LV*). In another saying, the contact angle (*θ*), is the angle formed by a liquid drop at the three phase boundary where a liquid, gas and solid intersect, and it is included between the tangent plane to the surface of the liquid and the tangent plane to the surface of the solid, at the point of intersection. Low values of *θ* indicate a strong liquid-solid interaction such that the liquid tends to spread on the solid surface (well wetting) and high *θ* values indicate weak interaction and poor wetting (Erbil, 2006; Çağlar, 2007).
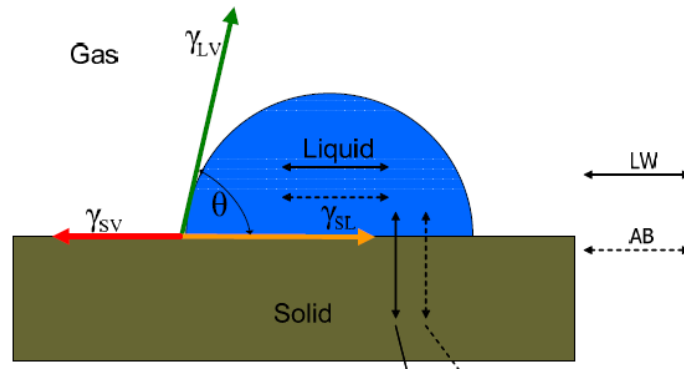
Figure 2.6: Illustration of a liquid drop on a solid surface.

Various type of liquids such as deionized water, diiodomethane and ethylene glycol can be used to measure contact angle degree of surface. After contact angle measurement with liquids, the total free energy was calculated. The total surface energy, γi^{TOT}, of a given non-metallic material (i) can be considered as being composed of two parts: the Liftshitz-van der Waals (LW), γi^{LW}, and the acid-base (AB) component, γi^{AB}. The former represents the dispersion forces, dipole-dipole and induction, and the latter represents the short range H bonding or acid-base interactions. This is written as the sum of the two components in Equation 3.1,

$$\gamma i^{TOT} = \gamma i^{LW} + \gamma i^{AB} \tag{3.1}$$

where the acid-base term is a property of one that depends on the mutual interaction of two unlike species, an acid and base. γi^{AB} is composed of two surface parameters which are independent of physical presence of another one: γi^{+} is the Lewis acid component and γi^{-} is the Lewis base component of the surface free energy. These, together, yield the acid-base component of surface free energy, γi^{AB} is given in Equation 3.2,

$$\gamma i^{AB} = 2(\gamma i^{+}\gamma i^{-})^{1/2} \tag{3.2}$$

The most characteristic feature of these Lewis acid and base components is that they are not additive although the non-polar ones are. It means that if phase (i) possesses only γi^{+} or γi^{-}, this component does not participate in the total surface free energy of the phase (i). However, it will interact with the complementary component of phase (j), contacting phase. As a result, the total surface free energy of a phase (i) is given Equation 3.3,

$$\gamma i^{TOT} = \gamma i^{LW} + \gamma i^{AB} = \gamma i^{LW} + 2(\gamma i^{+}\gamma i^{-})^{1/2} \tag{3.3}$$

The values of γi^{AB}, γi^{+} and γi^{-} can be determined by using the contact angle θ and "Complete Young Equation" is given Equation 3.4,

$$(1+\cos\theta)\gamma i^{TOT} = 2\left[(\gamma i^{LW}\gamma j^{LW})^{1/2} + (\gamma i^{+}\gamma j^{-})^{1/2} + (\gamma i^{-}\gamma j^{+})^{1/2}\right] \tag{3.4}$$

The LW component of a solid surfaces (i) can also be found from the contact angle of a non-polar liquid (j) (diiodometan for our study), where $\gamma i^{TOT}=\gamma j^{LW}$, on the solid surface. In this case Equation 3.5 reduces to,

$$(1+\cos\theta)\gamma i^{TOT} = 2(\gamma i^{LW}\gamma j^{LW})^{1/2} \tag{3.5}$$

As a result, the LW component of a solid surface can be calculated by applying the contact angle of a non-polar liquid on the solid surface in Equation (3.6). For a bipolar liquid (L) contacting with the solid (S), with surface tension γ_L, acidic and basic surface parameters γ_L^{+} and γ_L^{-}, respectively, and non-polar surface component, γ_L^{LW}, the complete equation to be considered is as follows,

$$(1+\cos\theta_L)\gamma_L^{TOT} = 2\ [(\gamma_L^{LW}\gamma_S^{LW})^{1/2} + (\gamma_L^+\gamma_S^-)^{1/2} + (\gamma_L^-\gamma_S^+)^{1/2}\ ] \tag{3.6}$$

which can be constructed to form a set of two simultaneous equation, in terms of the parameters of the solid γ_S^-, γ_S^+ and two advancing contact angles θ1 and θ2, which are measured on the solid surface. These two equations can then be simultaneously solved for γ_S-and γ_S+ provided that the γ_i^{LW}, γ_i^+ and γ_i^- for the probe liquids are known.

Providing the known surface components of the contacting phases (i.e. polymer and fiber), the work of adhesion (Wa) between phase 1 and phase 2 can be calculated from the summation of dispersive and acid/base components by using Equation 3.7, [21],

$$Wa^{TOT} = Wa^{LW} + Wa^{AB} = 2\ [(\gamma_1^{LW}\gamma_2^{LW})^{1/2} + (\gamma_1^+\gamma_2^-)^{1/2} + (\gamma_1^-\gamma_2^+)^{1/2}] \tag{3.7}$$

Surface free energy components of probe liquids were given for diiodometan (DIM) ethylene glycol (EG) and deionized water in Table 2.2.

Table 2.2: Surface free energy components of probe liquids, (mN/m) (Luner and Oh, 2001, McMohan and Ying, 1982).

Surface Tension	DIM (mN/m)	EG (mN/m)	W (mN/m)
γ_L^{TOT}	50.8	48	72.8
γ_L^{LW}	50.8	29	21.8
γ_L^-	-	47	25.5
γ_L^+	-	1.92	25.5

2.4 Polymer Processing

Polymer processing is defined as the "engineering activity concerned with operations carried out on polymeric materials or systems to increase their utility". Primarily, it deals with convertion of raw polymeric material into finish products involving not only shaping but also compounding.

2.4.1 Mixing

Mixing is a key in almost every polymer processing operation, affecting material properties, processability and cost. Various additives and reinforcing agents are mixed with polymers to improve mechanical performance and impart specific properties to the mixture. Besides achieving the desired shape, a suitable degree of homogeneity in composition and properties is required in the manufacture of products from polymeric materials.

2.4.1.1 Types of mixing

The two types of mixing occurring in the extruder are distributive and dispersive mixing. As their names describe, the distributive mixing evenly distributes particles throughout the melt, while the dispersive mixing breaks up agglomerates or large particles and disperses them evenly throughout the melt. The distributive and dispersive mixing is shown schematically in Figure 2.7.
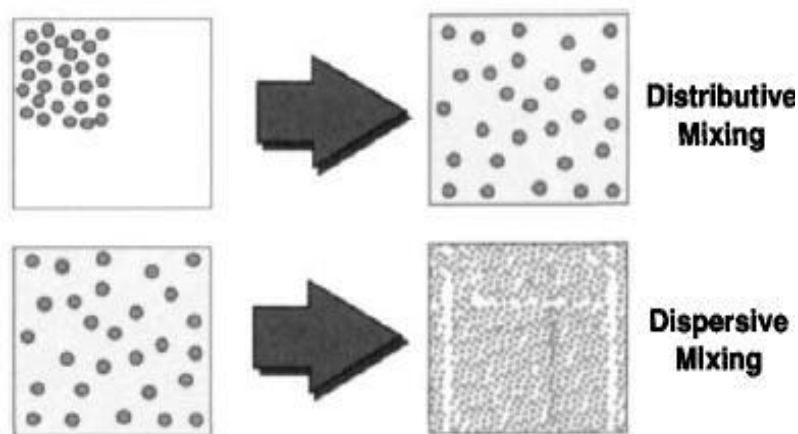

Figure 2.7 : Distributive and dispersive mixing.

The distributive mixing is used with fibers, reinforcing fillers, and shear-sensitive materials to provide a uniform melt temperature. The dispersive mixing is a high-

shear process where the molten polymer is forced through very small openings that may generate shear heating. The dispersive mixing is used in alloying different plastics, pigment dispersing, and mixing non-reinforcing fillers and additives, such as flame-retardants, impact modifiers, lubricants, and so forth [23, 10].

2.5 Extrusion Process

Extrusion is a high volume manufacturing process used to create fixed cross sectional profiles such as pipe/tubing, slot bars with several cavities, weather stripping, windows frames, adhesive tapes, and wire insulations.

2.5.1 Extrusion

The extrusion of polymeric materials to produce finished products for industrial or consumer applications is an integrated process, with the extruder comprising one component of the entire line. In some applications, the production lines are very long with numerous operations, requiring operators to communicate and work together to produce an acceptable finished product. In batch extrusion systems, the aim is only to take a desired shape product so the feed is already uniform. On the other hand, in continuous extrusion processes, the ingredients are fed together to the extruder and besides taking the shape of the die, homogeneous mixing of the ingredients is also very important.

The extrusion process is shown in Figure 2.8. Polymeric material is received, inspected, and stored. Prior to extrusion, the polymer may be blended with additives, color pigments or concentrates, flame retardants, fillers, lubricants, reinforcements, etc., to produce the desired product property profile. Some resin systems must be dried prior to extrusion to eliminate polymer degradation due to moisture. Other resins, which do not normally require drying, may have to be dried if they are stored in a cold warehouse and brought into a warm environment, causing moisture to condense on the surface of the pellets, flake, or powder.
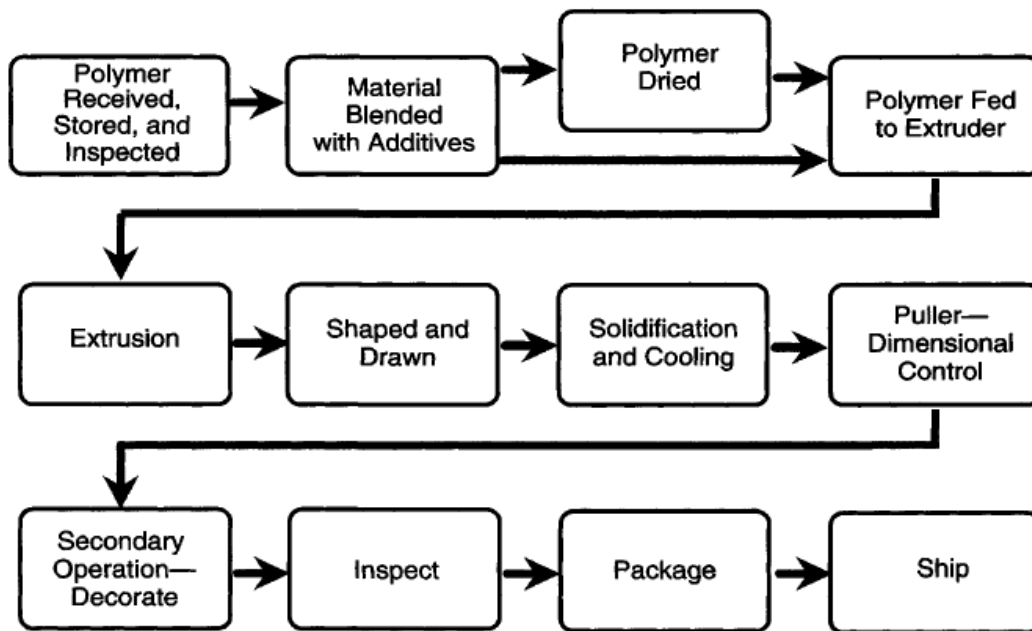
Figure 2.8 : A general scheme of extrusion process.

Once the polymer or blend is properly dried and ingredients mixed, the formulation is fed to the extruder, where it is melted, mixed, and delivered to the die to shape the extrudate. After exiting the die, the product is cooled and solidified in the desired shape and pulled away from the extruder at constant velocity to attain the appropriate cross section. Secondary operations, i.e., flame treatment, printing, cutting, annealing, etc., can be done in line after the puller. Finally, the product is inspected, packaged, and shipped.

In a screw extrusion process, polymer is fed from the hopper, and mechanically pushed forward by the rotation of the screw. The screw pushes the plastic material into the barrel, which is heated to reach the melting temperature. In most processes, the barrel has three or more controlled heating zones increasing the temperature from the rear to the front. At the front of the screw, the molten material travels through a screen or breaker plate, a metal puck having many small holes. The screen or the breaker is required to develop a backpressure and thus control the melting and proper mixing of the polymer. The material enters the die after passing the breaker. After the die gives the polymer the final product shape, the material is cooled in a water bath. It is necessary to take into consideration the flow, deformation, and temperature relationship in all parts of the production line. The product must be cooled in a

20

carefully controlled vacuum water bath to avoid collapsing. Products produced include films, sheets, profiles, pipes, tubes, rods, wire/cable coverings, coatings, filaments, blown shapes, and others [24].

Namely, there are continuous extruders with single-screws or multi screws; continuous disk or drum extruders, which use viscous drag, melt actions or elastic melt actions and discontinuous extruders, which use ram and reciprocating actions [25]. Since a single screw extruder is employed in this thesis, only this type of extruder will be mentioned from now on.

2.5.1.1 Single screw extruder components

A single screw extruder has five major equipment components: drive system, feed system, screw-barrel and heaters system, die assembly and control system as shown in Figure. 2.9 [24].
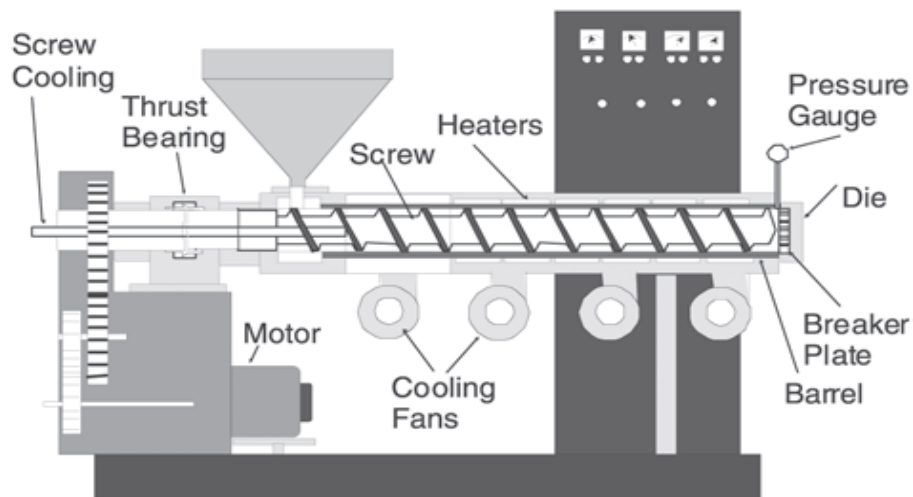

Figure 2.9 : Single screw extruder [24].

The drive system comprises the motor, gear box, bull gear, and thrust bearing assembly. The feed system is the feed hopper, feed throat, and screw feed section. The screw, barrel, and heating systems are where solid resin is conveyed forward, melted, mixed and pumped to the die. Extrudate is transported and shaped in the adapter and die, respectively. Finally, the control system controls the extruder electrical inputs and monitors the extruder feedback. Computer-designed extrusion controls not only run and monitor the extruder, but also can control the entire

extrusion process with feedback loops that automatically change feeder settings, puller speeds, screw speeds, etc., to maintain product quality.

The cooling channels takes placed around the feed section to remove frictional heat generated by the rotating screw and pellet compression into the screw channels, preventing the pellets from premature melting. The barrel and heaters help heat and melt the polymer by controlling the temperature in the different zones, preventing material from overheating and degrading.

A single screw extruder screw typically has three different sections, as shown in Figure 2.10. The feed section has deep flights to transport powder or pellets away from the feed throat. The transition section changes gradually from deep flights with unmelted pellets to shallow flights containing the melt. Resin is compressed in the transition section during the melting process. Metering is the last screw section and has the shallowest flight depths.
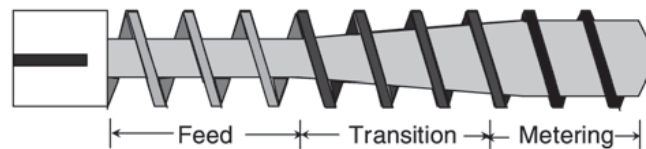

Figure 2.10 : Extruder screw stages [24].

The extruder head assembly includes breaker plate, adapter to connect the die assembly to the extruder, and die. The die is attached either directly to the extruder or to a transfer pipe or adapter that is connected to the extruder. Polymer melt temperature in the adapter must be maintained. Transfer pipes, like extruder barrels, should have heater bands covering as much area as possible to minimize hot or cold spots. Control is making a measurement, determining if something needs to be changed, making a decision, and taking action [25].

2.6 Literature Review

In this section, the studies about scratch resistance of polypropylenes will be mentioned.

Dasari et al. investigated the scratch deformation characteristics of neat and wollastonite containing polypropylenes. Electron microscopy and atomic force microscopy techniques are used to determine surface tribology of polypropylenes. Beside Neat PP, coated and coupled wollastonite containing PP, fine wollastonite containing PP, coarse wollastonite containing PP and coated wollastonite containing PP were prepared. Scratch resistance was evaluated in terms of scratch hardness, scratch depth, average scratch roughness, thickness and density of the scratch tracks. The study indicated that filled polypropylene showed plastic deformation due to debonding/detachment of wollastonite mineral particles from the polypropylene matrix. Materials with higher scratch hardness are expected to exhibit greater resistance to scratch deformation and lower scratch visibility. They observed that resistance to scratch deformation decreases with the following sequence: coated and coupled wollastonite containing PP, neat PP, fine wollastonite containing PP, coarse wollastonite containing PP and coated wollastonite containing PP [4].

Chu et al. investigated the test methods used to see effect of different mineral fillers on the scratch and mar resistance of pigmented mineral-filled polypropylene. Pigmented mineral-filled polypropylene (PP-PMF) is marketed as a potential alternative to acrylonitrile-butyldiene-styrene (ABS) for automotive interior components. But PP-PMF was more easily damaged by surface scratch. A new method was introduced to characterize the scratch visibility by image analysis. A correlation was found between scratch visibility and scratch hardness measured by interferometer. They concluded that wollastonite can reduce the scratch depth and visibility whereas talc is not very efficient for this purpose. An interface modifier and lubricant can further reduce scratch depth and whitening for wollastonite-filled PP but the additives was ineffective for talc-filled PP-PMF [26].

In a work of Shuhao and co-workers, polypropylene (PP) and talc-filled PP with various lubricants were prepared to study the effects of normal force on the scratch resistance of polymers. The effects of additives on the scratch behavior of neat and talc-filled PP systems were investigated. Differential scanning calorimetry and

optical microscopy were used to characterize crystallinity and scratch deformation mechanisms in the PP systems. It was found that the scratch hardness is related to the applied loads during the scratch process. Lower load showed higher scratch hardness due to elastic deformation of PP composites. The talc-filled impact copolymer polypropylene (ICPP) exhibited higher scratch hardness than the neat ICPP. Homo-PP exhibited superior scratch resistance and less susceptibility to scratch deformation than ICPP. The addition of lubricant and annealing treatment improved the scratch resistance of both neat and the talc-filled PP systems [27].

Thridandapani et al. investigated the surface deformation during scratching of neat polypropylene and polypropylene-clay nanocomposites. Neat PP, PP-4 wt.% clay, and PP-8 wt.% clay were used. Nanoclay has a significant effect on modulus, yield strength, elastic recovery and resistance to mechanically induced scratch damage. It was seen that there was an increase in crystallinity but the spherulite size decreases by reinforcement of polypropylene with clay. Reinforcement with nanoclay introduces an "ironing" mechanism, implying higher scratch resistance. Higher scratch resistance is directly related to lower scratch visibility [16].

Hadal and co-workers described the effect of wollastonite and talc on the scratch deformation behavior of low and high crystallinity polypropylenes. The vertical resolution of atomic force microscopy and lateral resolution of scanning electron microscopy was utilized to examine the characteristics of scratch damage. It was indicated that reinforcement of polypropylenes with wollastonite and talc increased the tensile modulus of polypropylenes, but yield strength remained unaffected. This behavior was related to the high aspect ratio of the particles that encouraged detachment of minerals from the matrix at the yield point. Scratch deformed regions in neat polypropylenes were free of voids and grooves, while reinforced-polypropylenes exhibited voids and debonding/detachment of filler particles. As a result the severity of plastic deformation was comparatively higher for talc-reinforced polypropylenes than wollastonite-reinforced polypropylenes because of the layered structure of talc that encourages delamination. Usage of coupling agents improved the resistance to scratch deformation by promoting adhesion and bonding between the reinforcement and matrix [28].

In a work of Koch and co-workers, the influence of addition of different polyethylenes to a heterophasic PP/EPR copolymer on the scratch behavior was investigated. The nano-indentor scratch tests and the Erichsen cross cutter method were used for comparison the effect of scratch test types on the scratch resistance of material. The scratch evaluation was carried out by measuring the ΔL values with a spectral photometer. It was found that the addition of PE to the PP/EPR blend leads to an improvement of scratch resistance. No strong correlation was found between micro- and macro-scratch experiments [3].

In a work of Xiang and co-workers, scratch behavior in neat and talc-filled high crystallinity polypropylene (PP) copolymers containing various additives were investigated. Differential scanning calorimetry, scanning electron microscopy and attenuated total reflectance Fourier transform infrared spectroscopy were used to characterize crystallinity, morphology and scratch mechanisms in PP systems. The influences of talc, nucleating agent and lubricant on the scratch behavior of PP were discussed. For high crystallinity PP copolymers, it was found that the scratch resistance depends mainly on the fracture features generated on the scratch surface, which was confirmed by SEM and interferometer surface analyses. They concluded that the talc filled PP copolymer exhibited high scratch visibility and scratch depth. The addition of nucleating agent or lubricant reduces scratch depth and scratch visibility of the talc-filled PP since the additives were likely to flow to the surface and reduce scratch fracture features during scratch [29].

In a work of Wong et al. surface damage of polypropylene under progressive loading was investigated. Homo polypropylene, talc filled homo polypropylene, copolymer-PP blend, talc filled copolymer-PP blend were used. The results show that for the PP systems, the magnitude of critical load to stress whitening occurs in the following order: homopolymer, talc-filled homopolymer, copolymer, talc filled copolymer. Scratch visibility increases significantly due to the massive formation of voids and exposed talc particles on the scratched surface. Exposed talc particles on the surface of talc-filled PP were found to be responsible for the increased light scattering, leading to greatly increased visibility. Even though, talc increases scratch hardness in both homopolymer and copolymer PP systems, if not properly modified, is found to have a deleterious role in terms of scratch visibility [30].

3. EXPERIMENTAL

3.1 Materials

3.1.1 Polypropylene (PP)

Neat polypropylene (nPP) which has a trade name of MH 418, was purchased from PETKIM Petrochemical Holding Inc., Izmir. Basic properties of the pelletized polypropylene are declared by the company in Table 3.1.

Table 3.1 : Basic properties of neat polypropylene.

Property	Value	Unit	Test Method
Melt flow rate (2160 g, 230ºC)	4.0 – 6.0	g/10 min	ASTM D1238
Tensile strength at yield	350	kg/cm^2	ASTM D638
Tensile strength at break	430	kg/cm^2	ASTM D638

3.1.2 Talc reinforced polypropylene (tPP)

40 wt-% talc reinforced polypropylene which has a trade name of EMOPLEN ® HP MTF 40, was the commercial polypropylene supplied from EMAS Plastic Industry and Trade Inc., Bursa. Basic properties of the pelletized talc reinforced polypropylene are declared by the company in Table 3.2.

Table 3.2 : Basic properties of talc reinforced polypropylene.

Property	Value	Unit	Test Method
Melt flow rate (2160 g, 230ºC)	1.0 – 7.0	cm^3/g	ISO 307
Tensile stress	27-37	MPa	ISO 527
Tensile strain at break	≥ 5	%	ISO 527

3.1.3 Mixture of modified polyolefin and silicone block copolymer

TEGOMER® PP-Si 401 was a mixture of modified polyolefin-silicone block copolymer obtained from EVONIK Industry. The melt flow rate (190°C/2.16 kg), silicone content [wt-% PDMS] and density are declared minimum 100 g/ 10 min, 15 and 939 kg/m^3 by the company respectively.

3.1.4 Polyester modified siloxane

TEGOMER® H-Si 6440 P was the polyester modified siloxane obtained from EVONIK Industry. The melting point and water content were declared 54°C and less than 0.1 % by the company respectively.

3.1.5 Organically modified siloxane

TEGOMER® Antiscratch 100 was organically modified siloxane obtained from EVONIK Industry. The melt flow rate (230°C/2.16 kg) is declared minimum 100 g/ 10 min by the company.

3.2 Equipments

3.2.1 Extruder

A single screw extruder with a diameter of 25 mm and L/D of 25 was used to prepare samples by melt mixing method. The scheme of the extruder is given in Figure 3.1.
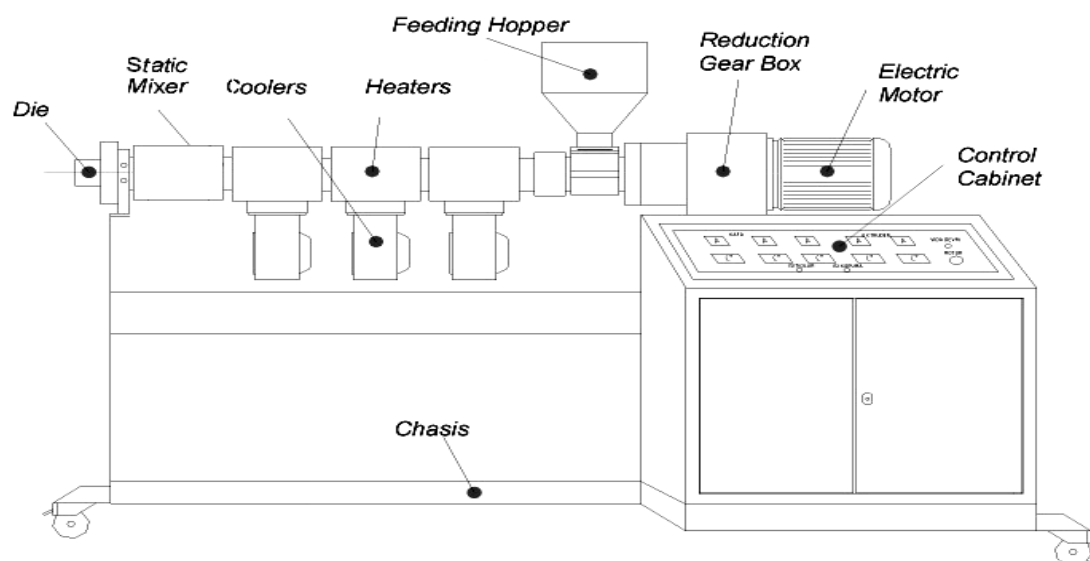

Figure 3.1 : Single screw extruder.

The extruder has 5 zones; 3 heating zones, a static mixer and a die. Temperature control is achieved by PID control of ceramic heaters. Every ceramic heater section is surrounded with a cover. All the controllers are introduced in a control board.

The screw of the extruder has 3 stages, which consists of universal single flights in the feeding and transition zones with distributive pineapple mixing elements in the metering zone. The compression ratio (ratio of metering section flight depth/feeding section flight depth) is 2.05. The screw configuration is given in Figure 3.2.
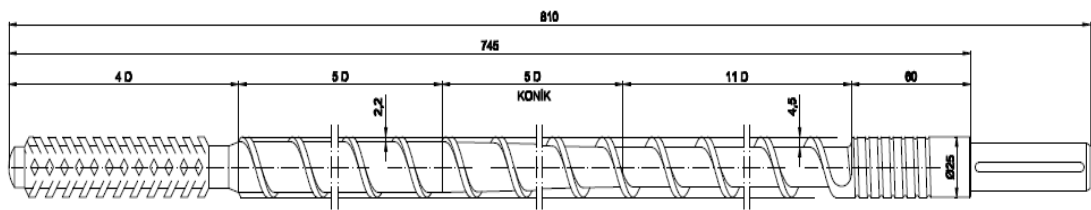
Figure 3.2 : Screw configuration.

Static mixer is placed between the barrel and die to increase the degree of mixing. The pressure before the die is monitored by the pressure gauge. This static mixer which is given in Figure 3.3 consists of eight mixing elements.
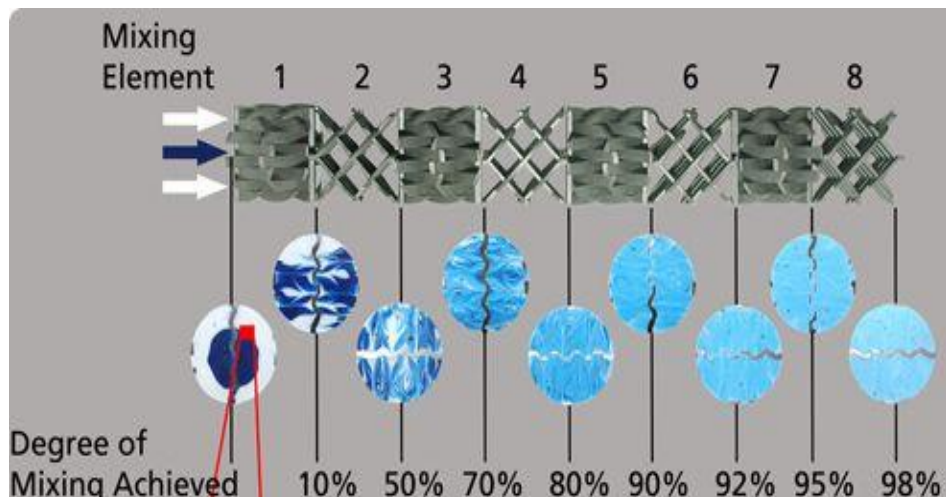

Figure 3.3 : Static mixer and degree of mixing achieved.

3.2.2 Hot press

Molding were performed on a hydraulic press for their own optimum cure times, at 210^oC and under 100 bar pressure. The conceptual view of hydraulic hot press can be seen from Figure 3.4. Samples were handled as casts with 2 mm thickness for FTIR-ATR analysis, Shore-D hardness test, contact angle measurement and anti-scratch tests.

The uncured pieces of compound placed in the mold are known variously as preforms, billets or load weights. Normally the weight of this preform will be chosen to be a few percent (from two to ten percent) above the weight of the final product, to ensure a fully formed product and to give an extra 'push' for expulsion of any residual trapped air. The preform is placed in the bottom cavity and the top mold section placed on it by hand. If a significant number of moldings are to be made, it is often advantageous to fix the two halves of the mold to their respective press platens [46].
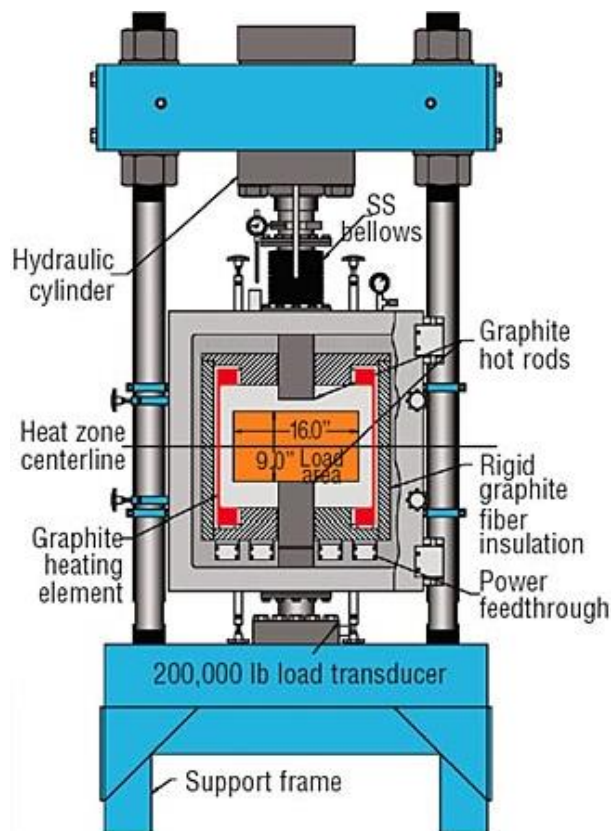

Figure 3.4 : Hydraulic hot press.

3.2.3 Fourier transform infrared spectroscopy (FTIR-ATR) test device

Perkin Elmer Spectrum 100 model FTIR apparatus with ATR (Attenuated Total Reflectance) technique was used to determine the organic components of the samples. Percent transmittance versus wavenumber graph was obtained from the apparatus.

3.2.4 Universal testing machine

A Zwick/Roel Z.05 universal testing machine was performed for the evaluation of tensile properties of the samples. The machine had 500 N capacities, sizes to 12x30 mm stainless steel Zwick pincer grips. The load cell was capable of applying 500 N force and testing samples up to 200 mm/min speed.

3.2.5 Shore-D hardness test device

Zwick Roell Shore D in accordance with ASTM D 2240 was used.

3.2.6 Differential scanning calorimetry analysis (DSC)

Thermal analyses of the samples were done with a Mettler Toledo DSC1 Differential Scanning Calorimetry equipment. The analysis were done for all samples between 25ºC and 200ºC at 10ºC/min heating rate under inert atmosphere. Melting temperatures (Tm), the peak temperature (Tp), the enthalpy of melting were obtained using a differential scanning calorimeter (DSC).

3.2.7 Scratch Tester

430 P-II Erichsen scratch tester was used for anti-scratch experiments. The motor-driven scratch hardness tester 430 P-II is a universal testing instrument designed for carrying out a wide range of tests on plastic surfaces to determine their resistance to scratches. The instrument is equipped with an ISO 1518-1 type (1 mm) edge and defined speed (normally 10 mm/s). As it can be seen Figure 3.5, one tip is used to make single cuts, parallel cuts and - by turning the specimen by 90° cross-cuts at various thicknesses.

Figure 3.5 : Erichsen scratch tester.

3.2.8 Optical microscopy

Nikon Eclipse LV100 optical microscopy was used to measure scratch widths (μm) of the samples.

3.2.9 Contact angle test device

Attension Biolin Scientific AB, ThetaLite TL101 model optical tensiometer aparatus was used to measure contact angles of the surfaces for all samples.

3.2.10 Melt flow index device (MFI)

HAAKE Melt Flow MT was used to measure melt flow rate (MFR) values of the samples. It is equipped with a standard 8 mm in length and 3 mm in diameter die, a standard 6.35 mm in length and 9.4772 mm in diameter piston, and a standard load to apply 2.16 kg force during the extrusion.

3.2.11 Density Measurement

Mettler Toledo's Density Kit was used to measure density of nPP, tPP, additives and samples with additives.

3.3 Experimental Procedure

3.3.1 Optimization

The aim of this study is to analyze the effects of additive types on mechanical, thermal, and tribological properties of nPP and tPP which are prepared by melt mixing via a single screw extruder. Firstly, an optimum temperature profile was determined. The lower limit of the processing temperatures was determined 190ºC for PP, which is higher than melting temperature of PP.

After knowing the processing limits, experiments with several temperature profiles were carried out. As a result of these experiments, the temperature profile was decided to be 190/ 195/ 195/ 200/ 200 ºC for zone 1, zone 2, zone 3, static mixer and die respectively. Then, residence time measurements at 30 rpm was done by dye detecting method with the use of blue colored PP-based masterbatches, which were found to be between 1.1 – 1.5 minutes. After the temperature profile determination, optimum additives amounts were determined. According to the literature, additives were useful between 0.5 – 4 wt-% for PPs. So, nPP and tPP were extruded with three commercially available additives by using 1 and 3 wt-% of PPs by melt mixing method.

3.3.2 Preparation of samples

In this study, different compositions of samples were extruded in order to investigate the effects of additives on mechanical, thermal, and tribological properties of nPP and tPP. Sample recipes and nomenclature were given in Table 3.3.

300 grams of polymer was prepared for each batch for melt mixing in extruder. Additives were added to the nPP and tPP as weight percent. The PP and additives pellets were premixed by shaking in a large – closed container by hand for 5 minutes before being fed to the extruder. Temperatures of the zone 1, zone 2, zone 3, static mixer and die were 190/ 195/ 195/ 200/ 200 °C respectively. The samples were extruded at 30 rpm. The strands from the die were collected on a metal plate and pelletized after complete solidification. The middle of these productions was taken as samples, because effective mixing takes place at this point.

Table 3.3 : Sample recipes and nomenclature.

Sample	PP [wt-%]	Talc reinforced PP [wt- %]	A [wt- %] TEGOMER PP-Si 401	B [wt- %] TEGOMER H-Si 6440 P	C [wt- %] TEGOMER Antiscratch 100
nPP	100				
nPP-%1 A	99		1		
nPP-%3 A	97		3		
nPP-%1 B	99			1	
nPP-%3 B	97			3	
nPP-%1 C	99				1
nPP-%3 C	97				3
tPP		100			
tPP-%1 A		99	1		
tPP-%3 A		97	3		
tPP-%1 B		99		1	
tPP-%3 B		97		3	
tPP-%1 C		99			1
tPP-%3 C		97			3

The samples were prepared for each characterization differently. Strands types of specimens prepared for the mechanical measurement tests. Hydraulic hot press was used to prepare the 10cm×10cm×2mm film samples for scratch tests via compression molding. Used mould was shown at Figure 3.6. The PP samples were preheated for 10 minutes at 210ºC and then molded for 3 minutes with a pressure of 100 bars. tPP samples were immersed in cold water after they had been removed from the press. nPP samples were put on metal plate to cool by themselves. These samples also were used for FTIR-ATR analysis, Shore-D hardness test, contact angle measurement.
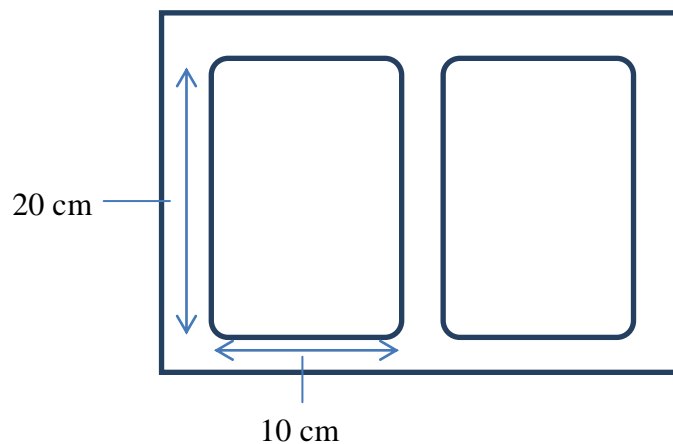
Figure 3.6 : Shape and dimensions of 2 mm thick mould.

3.3.3 Fourier transform infrared spectroscopy (FTIR-ATR)

FTIR analysis was performed over the range of 650 to 4000 cm^{-1} at room conditions. The inside and surface of hot pressed samples were measured by FTIR-ATR analysis to determine the organic components on the surface and inside of samples as it was given in Figure 3.7. It was done to see molecular behavior of additives on the surface of samples.
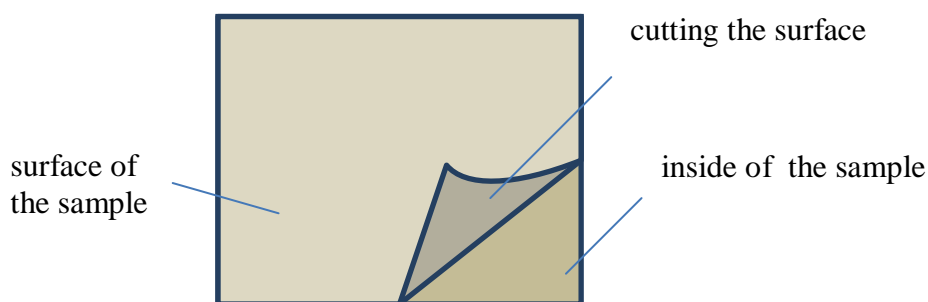

Figure 3.7 : Example of taking sample for FTIR-ATR anlaysis.

3.3.4 Mechanical property characterization

Specimens were cut with a cutter. Then dimensional measurements were taken place. Suitable specimens were placed between gauges. The tensile tests were carried out at 100 mm/min rate according to ISO 6259 (specifies a short-term tensile test method for determining the tensile properties of thermoplastics pipes) standards. From the measured stress and strain values, tensile strength, % strain and elastic modulus were calculated from the average of as 5 specimens tested.

3.3.5 Shore-D hardness test

According to standard measurement (ASTM D 2240); after 15 seconds of the beginning the measured values were recorded. For every sample, at least 3 parallel values measured and the averages of the values were calculated and recorded.

3.3.6 Thermal property characterization

The thermal properties of the samples were determined by differential scanning calorimetry (DSC). The heating scans were carried out at 10ºC/min rate in the temperature range of 25ºC - 200ºC in the DSC analysis. The enthalpy of melting

were calculated from the thermograms by evaluating the area under the melting curves.

3.3.7 Anti-scratch experiments

Erichsen scratch tester was used to scratch samples. The scratch tester has a one tip which provide single and parallel cuts and than by turning the specimen by 90° - cross-cuts was applied to test panels of various thicknesses. A series of parallel scratch marks were applied with 20 cuts at a distance of 2 mm under 20 N loads for all samples. Two samples were scratched for the same composition. After applying scratch tests, the photos were taken with optical microscope from 20 different points of scratches for the same composition. Average scratch widths (μm) of the samples were calculated by using the length of scratches.

3.3.8 Determination of surface properties by contact angle measurements

Various type of liquids such as deionized water, diiodomethane and ethylene glycol were used to measure the contact angles of all samples. Each contact angle measurement was repeated at least three times. After, average contact angle values were measured for three kind of liquids, the surface free energy was calculated by using these datas. The sessile drop method was applied in order to calculate surface free energy and determine surface behavior by using equations which was mentioned in Section 2.3.1 at theory of contact angle.

3.3.9 Melt flow rate determination

The melt flow rate (MFR) of nPP, tPP and samples with additives were measured at 190ºC with 2.16 kg load according to ASTM D1238 standard.

3.3.10 Density Measurement

Mettler Toledo's Density Kits were used to measure density of nPP, tPP, additives and samples with additives. Density Kits were mounted on balance to provide a convenient solution for determining the density of solid. The measurement was repeated as three times.

4. RESULTS AND DISCUSSION

In this study, neat PP (nPP) and talc reinforced PP (tPP) were extruded with three commercially available additives by using 1 and 3 wt-% of PPs. One of the additives was a mixture of modified polyolefine-silicone block copolymer, the other one was polyester modified siloxane and the third one was the organically modified siloxane. Thermal, mechanical and tribological properties of the prepared fourteen samples were characterized.

4.1 FTIR-ATR Results

FTIR analysis was used to examine the chemical composition and structure of materials. Additives and samples were characterized to obtain FTIR-ATR spectra. The structural and characteristic groups of materials were determined. The FTIR-ATR spectra of additives were presented in Figure 4.1.

In the FTIR-ATR spectra of PDMS containing additives the band at 2963 and 2905 cm^{-1} refer to CH stretching region of CH$_3$. The peaks from Si-O (at 1024 cm^{-1}), and Si-CH$_3$ (at 1260 and 800 cm^{-1}) are clearly seen the latter two of which are characteristic peaks for PMDS. While the bands at 1446 and 1412 cm^{-1} show CH$_3$ asymmetric deformation of Si-CH$_3$, the band at 1258 cm^{-1} shows CH$_3$ symmetric deformation of Si-CH$_3$. CH$_3$ rocking are shown at the peaks 863 and 787 cm^{-1}. These results are in aggrement with references [43, 44].

FTIR-ATR spectra of tPP, surface of tPP-C and inside of tPP-C were shown in Figure 4.2. Surface of the sample was analyzed to see the migration of additive on the surface. When the FTIR-ATR graphs were compared, it can be seen that the peak between 1800-2400 cm^{-1} disappeared for the surface of the tPP due to the fact that TEGOMER Antiscratch 100 had no peak between these values. FTIR-ATR spectra of inside of tPP-C resembled with spectra of tPP. PP samples showed PP characteristic bands with symmetric vibration of H atoms of CH$_2$ at 2853 ±5 cm^{-1}, asymmetric and symmetric deformations of C-H of CH$_3$ at 1450 ± 20cm^{-1} and 1380-

1370 cm^{-1}, respectively, [47]. Inside of tPP-C also had characteristic peak of TEGOMER Antiscratch 100 as 1260 cm^{-1} (Si-CH$_3$).
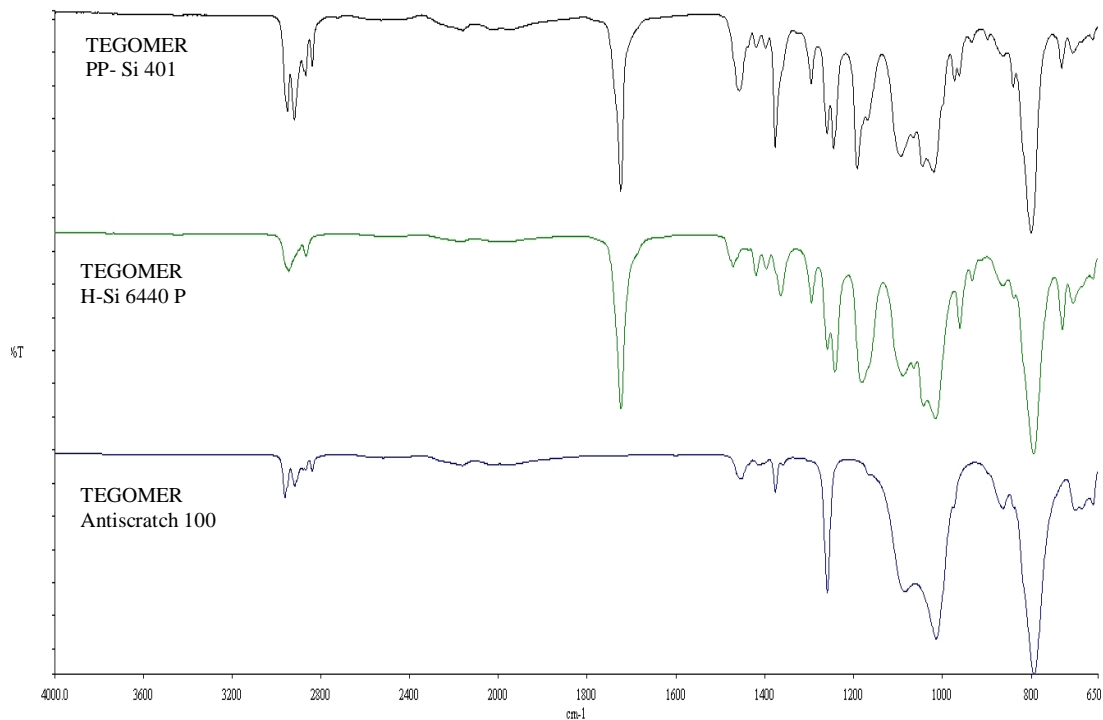

Figure 4.1 : FTIR-ATR spectra of TEGOMER PP-Si 401, TEGOMER H-Si 6440 P, TEGOMER Antiscratch 100.
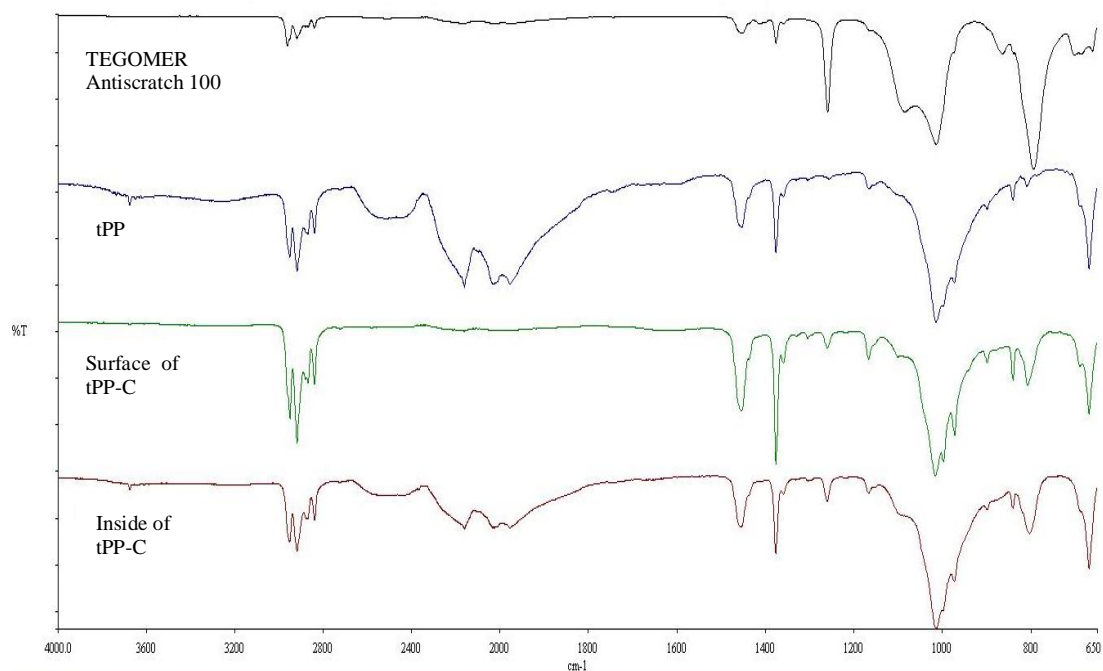

Figure 4.2 : FTIR-ATR spectra of tPP, surface of tPP-C and inside of tPP-C (3%).

The results showed that all additives has characteristic peak of PDMS in their structure. PDMS containing additives behaved as a slipping agent on the surface of samples. It was seen that the additive migrated on the surface quite higher the inside of the polymer. FTIR-ATR spectra of surface of tPP-C resembled with spectra of additive.

4.2 Tensile test result of samples

Tensile tests were performed with universal test machine at 25ºC. The values of all the mechanical parameters are calculated as 5 specimens for each composition. Tensile strengths of samples were compared in Figure 4.3. The tensile strength of nPP and tPP was found 50.0 MPa, 46.2 MPa respectively. Addition of talc (tPP) decrease the tensile strength of polypropylene (nPP). It is known that type and particle size of filler, distribution of filler are the most important factor affecting the mechanical properties of binary (PP/filler) [17]. When the additives were added 1%, an increase in tensile strength was observed due to the effect of other groups than PDMS. The tensile strength of nPP- 1% A was found 57.6 MPa whereas it was 51.0 MPa for nPP- 3% A. When the additives were added 3%, affect of PDMS can be seen more obvious than other groups that tensile strength decreased both in nPP and tPP according to error bars.
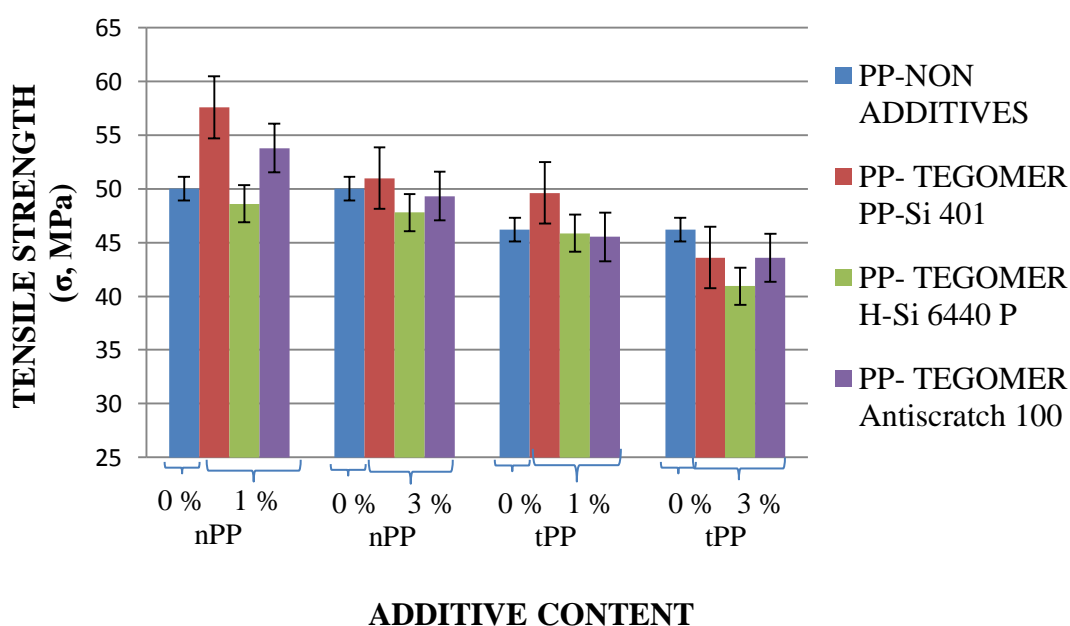
Figure 4.3 : Tensile strength of samples.

As it is given in the literature, PDMS containing additives can reduce the tensile strength of the polymer materials, but improving the toughness and surface properties [48, 49]. PP-1% TEGOMER PP-Si 401 had the highest tensile strength than other samples containing other additives for both nPP and tPP.

Modulus of elasticity equals to the ratio of the applied load per unit area of cross section to the increase in length per unit length. PP can be considered a tough material at room temperature. One of the reason for incorporating talc in plastics is to increase the stiffness (modulus of elasticity). The degree of rigidity obtained depends on the filling level, aspect ratio and fineness of the talc [42]. Modulus of elasticity of samples were compared in Figure 4.4. Addition of talc to the polypropylene increased the modulus of elasticity significantly. The modulus of elasticity was found 127.7 MPa for nPP, it was 148.7 MPa for tPP. The increase in elasticity modulus was related to the rigid filler particles that restrict the mobility. On the other hand, the additives acted as a rather softening material so that addition of additives decreased the modulus of elasticity. It was also seen that increasing amount of additives, lowered the modulus of elasticity. For each type of additives, the percent of decreasing was the same for nPP and tPP.
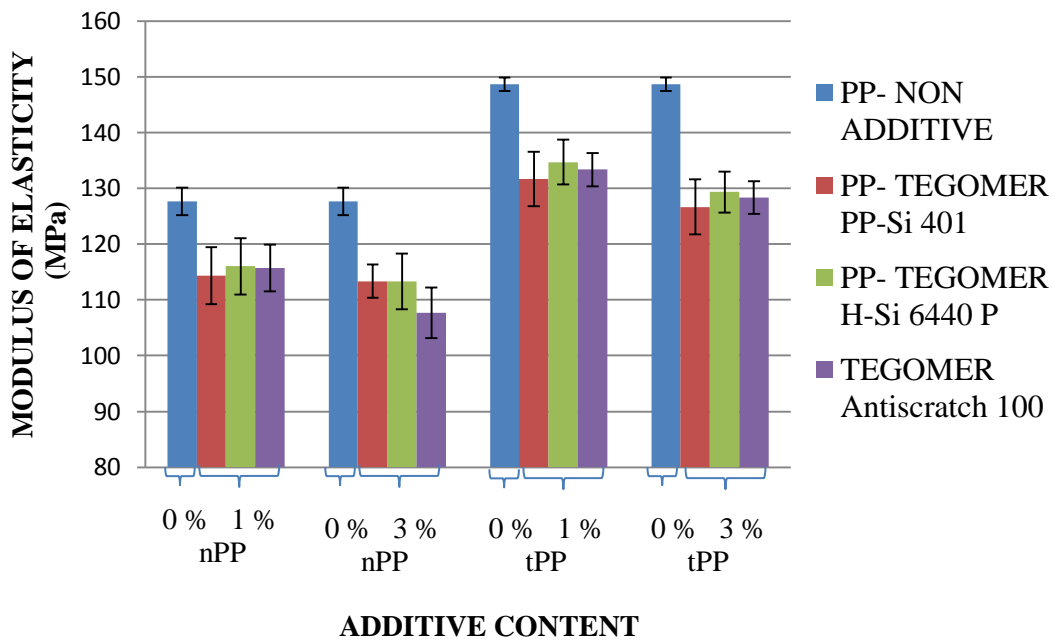
Figure 4.4 : Modulus of elasticity for all samples.

Elongation at break was greatly reduced by the inclusion of reinforcement but it was increased by additives as it can be seen Figure 4.5. A low elongation figure denoted a brittle rupture, while a high elongation showed that a material responds in a ductile manner. Percentage of elongation at break value was found 33.0 for nPP and it was found 24.6 for tPP. Addition of talc decrease the elongation at break. Percentage of elongation at break value of nPP- 1 % TEGOMER H-Si 6440 P was found 51.5 and it was found 60 for nPP- 3 % TEGOMER H-Si 6440 P. Addition of additive increased the elongation at break value. Moreover, increasing the additive content made the elongation at break value higher. TEGOMER H-Si 6440 P increased the elongation at break more than other additives for nPP and tPP. For each type of additives, the percent of increasing was the same for nPP and tPP.
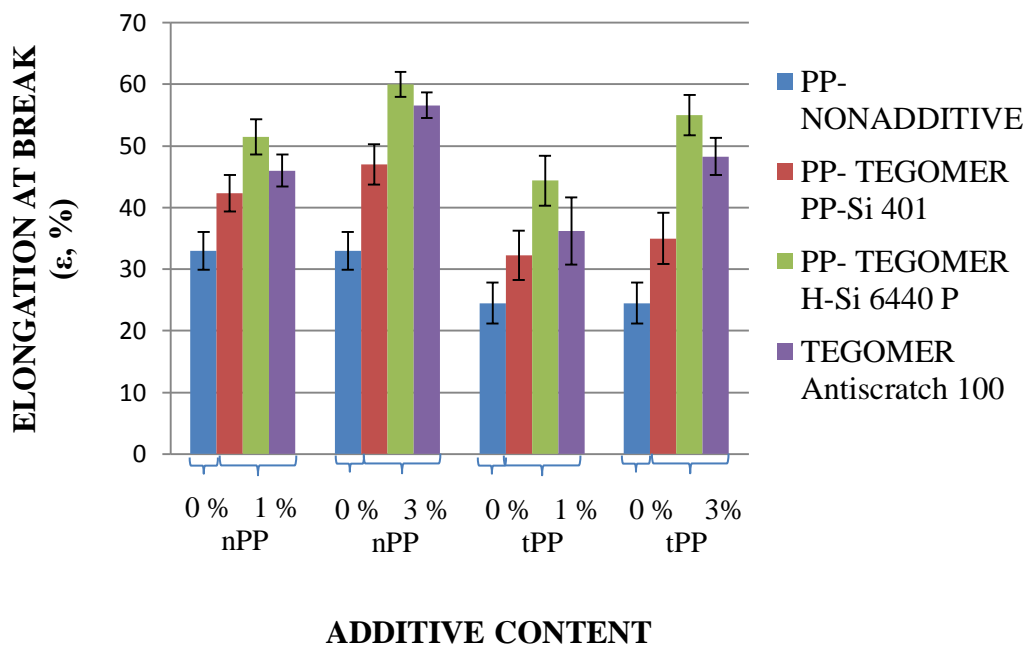
Figure 4.5 : Elongation at break for all samples.

4.3 Hardness Test Results

The hardness measurements were made with a Zwick Roell Shore-D measuring apparatus. A steel indentor was pushed against the material and the depth to which it penetrates was a measurement of hardness. All measurements of hardness in this report were made 15 s after the indentor had been pushed down into the material. Hardness Shore-D results were given in Table 4.1. It can be seen that addition of talc

increase the hardness but, inclusion of PDMS containing additives decrease the hardnesss of sample.

Table 4.1 : Shore-D hardness results.

Sample	Hardness Shore-D
nPP	26.5
nPP-%1 A	26.0
nPP-%3 A	26.0
nPP-%1 B	25.5
nPP-%3 B	25.5
nPP-%1 C	25.0
nPP-%3 C	25.0
tPP	27.0
tPP-%1 A	26.5
tPP-%3 A	26.5
tPP-%1 B	26.0
tPP-%3 B	26.0
tPP-%1 C	25.5
tPP-%3 C	25.5

4.4 Thermal tests results of the samples

Thermal properties of samples were analyzed by differential scanning calorimetry. Samples were heated from room temperature to 200°C. The enthalpy of melting, melting temperature and crystallinity of samples were given in Table 4.1.

The measurements indicated that the melting temperature of nPP is 165.13°C, whereas the melting temperature of tPP was found to be 164.02°C. This can be related to the effect of talc that prevents the molecular mobility of the segments. There are not many changes in Tm depending the amount of additives. Percent crystallinity (% X_c) of each material was calculated by using Eqution (4.1):

$$\% \ X_c = 100* \Delta H_m / (\Delta H_f \ x \ \theta_{PP}) \tag{4.1}$$

where ΔH_m is the melting enthalpy obtained from DSC thermograms, ΔH_f is the heat of fusion for fully crystalline PP (207 J/g), and θ_{PP} is the PP fraction in composition. The DSC results of samples were given in Table 4.2. Percent crystallinity of nPP was obtained 40.7. It was found 46.5 for tPP which was higher than that of nPP. As a

general trend, tPP based samples had higher $\%X_c$ in comparison to nPP based mixtures. This can be attributed to the nucleating effect of talc, which gives more time for PP during cooling to crystallize. Percentage of crystallinity and entalpy of melting increased by increasing additive content for nPP. Crystallinity of nPP-1% A and nPP- 1% B was the same with nPP. nPP-%1 C and nPP-%3 C had lower % crystallinity than other nPP samples. nPP-3% A had the highest crystallinity value in nPP based samples. On the other hand, the additive content did not affect entalpy of melting and % crystallinity of tPP as much as nPP. Each additive increased crystallinity of tPP. tPP- 3% C had the highest % crystallinity value in tPP based samples.

Table 4.2 : The DSC results of samples.

Sample	Tm [°C]	ΔHm [J/g]	%Crystallinity [%X_c]
nPP	165.1	84.2	40.7
nPP-%1 A	165.9	84.3	41.1
nPP-%3 A	166.0	87.8	43.7
nPP-%1 B	165.8	81.8	39.9
nPP-%3 B	165.7	90.3	45.0
nPP-%1 C	164.7	49.4	24.1
nPP-%3 C	166.0	74.3	37.0
tPP	164.0	57.8	46.5
tPP-%1 A	166.7	62.0	50.8
tPP-%3 A	164.8	65.4	55.4
tPP-%1 B	164.0	59.7	48.9
tPP-%3 B	165.6	56.9	48.2
tPP-%1 C	164.9	58.5	47.9
tPP-%3 C	163.8	66.1	56.0

4.5 Evaluation of scratch resistance

After applying scratch tests, the photos were taken with optical microscopy from 10 different points of scratches for the same sample. Scratch widths (μm) of both neat and talc reinforced PP samples were optically calculated in optical microscopy. Optical imaging of nPP, tPP, and tPP-%3 C were shown in Figure 4.6, Figure 4.7 and Figure 4.8 respectively. The scratch widths of nPP and tPP were found 458.0 μm and 636.2 μm by optical imaging, respectively. tPP based samples always showed higher scratch widths and lower scratch resistance. The results were similar with the literature, [4, 26 ,27].
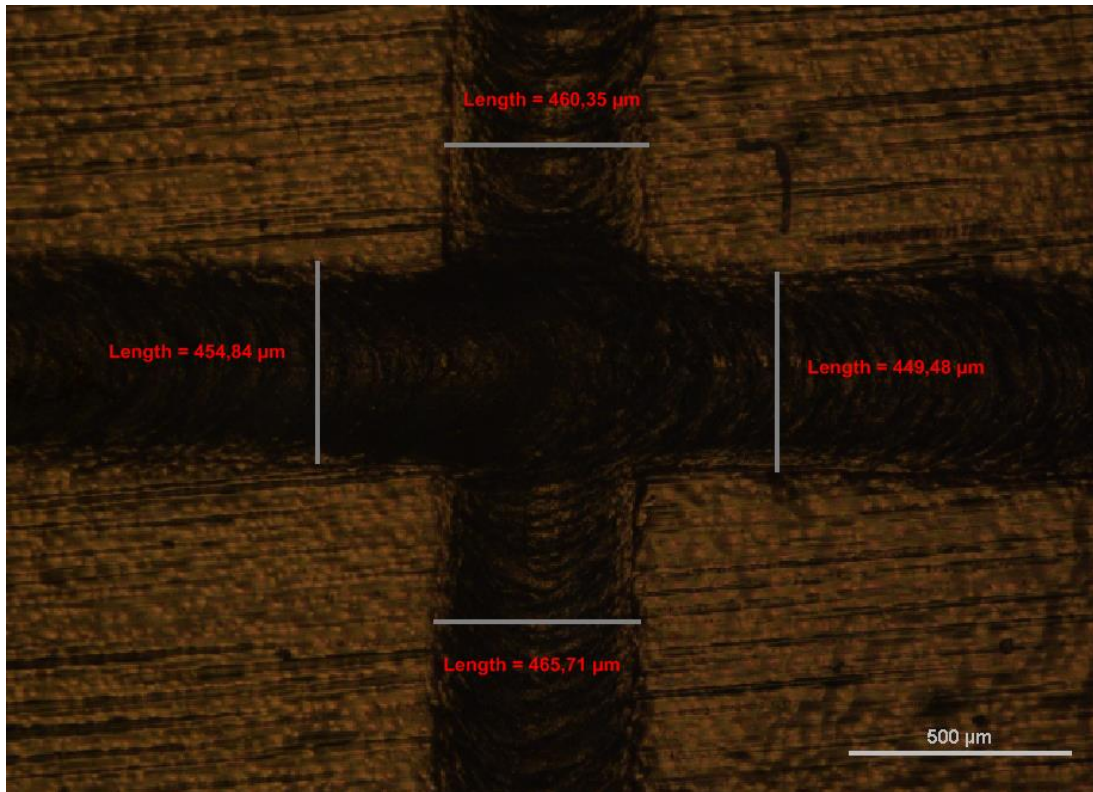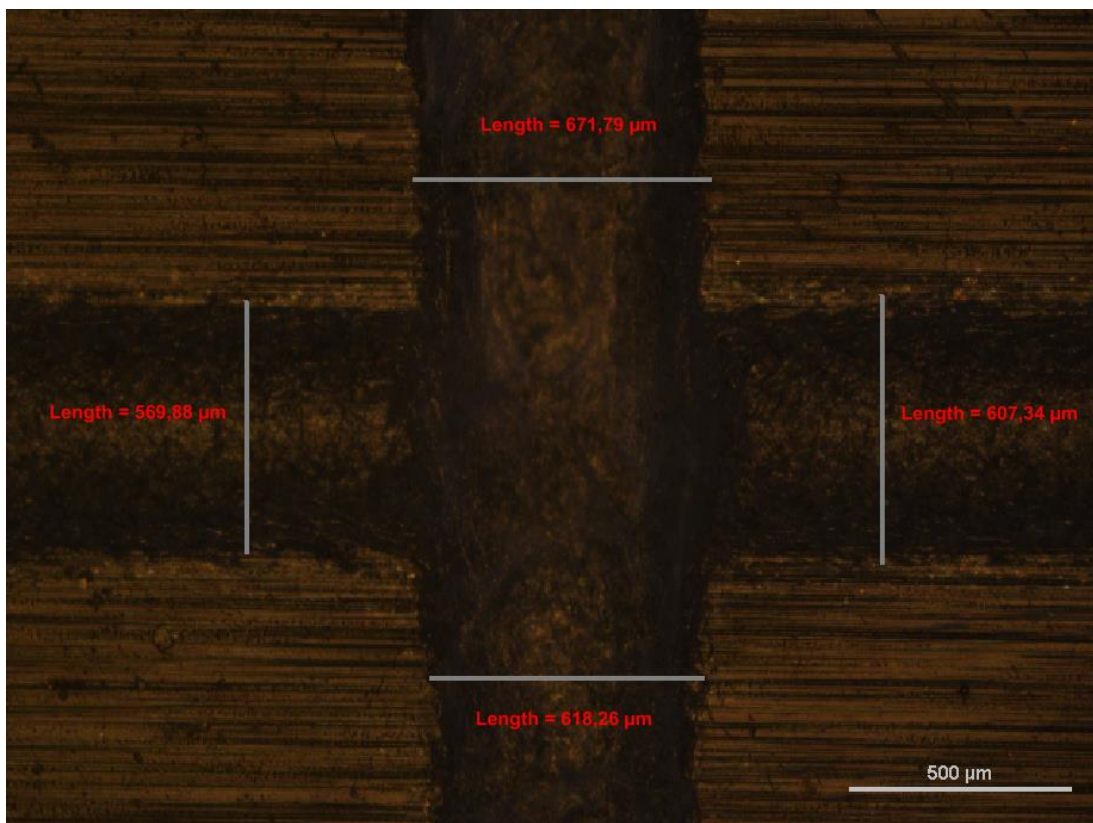
Figure 4.6 : Optical image of nPP.

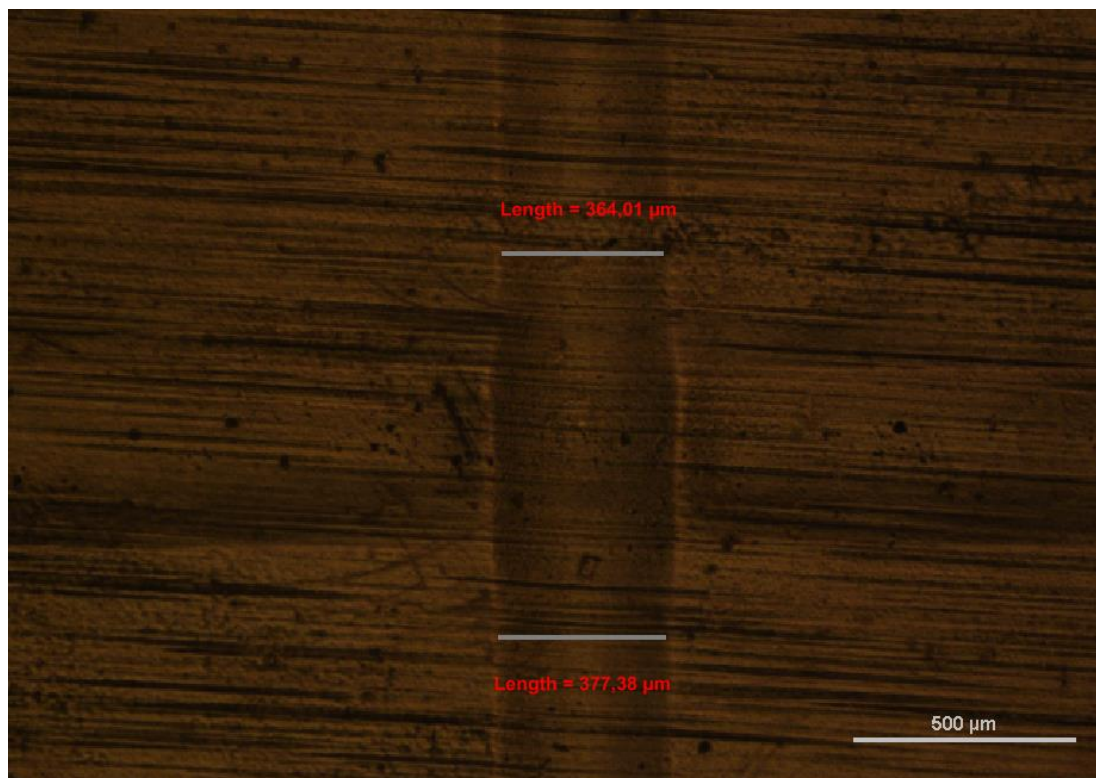**Figure 4.7 :** Optical image of tPP.

Figure 4.8 : Optical image of tPP-%3 C.

Talc can be added to increase scratch resistance, but in some studies these undesired results were found. Anti-scratch additives decreased scratch visibility and widths of scratches, and they enhanced the scratch resistance of PPs. Moreover, the increasing amount of the additives made the scratch visible only in one direction for nPP based samples as it can be seen in Figure 4.8. This occurred because of higher silicone content in the compositions.

The graph of scratch widths (μm) of the samples was shown in Figure 4.9 for all samples. When the scratch width of nPP- 1% B was found 400.7 μm, it was 395.0 μm for nPP-3% B. The scratch width of nPP- 1% C was obtained 385.0 μm whereas the scratch width of nPP- 3% C was obtained 373 μm. As the amounts of additives were increased, the scratch resistance of samples became higher. The most effective one for improving scratch resistance was found as 3 % TEGOMER Antiscratch 100 especially when containing % 3 in PPs. For each type of additives, the percent of decreasing was the same for nPP and tPP.
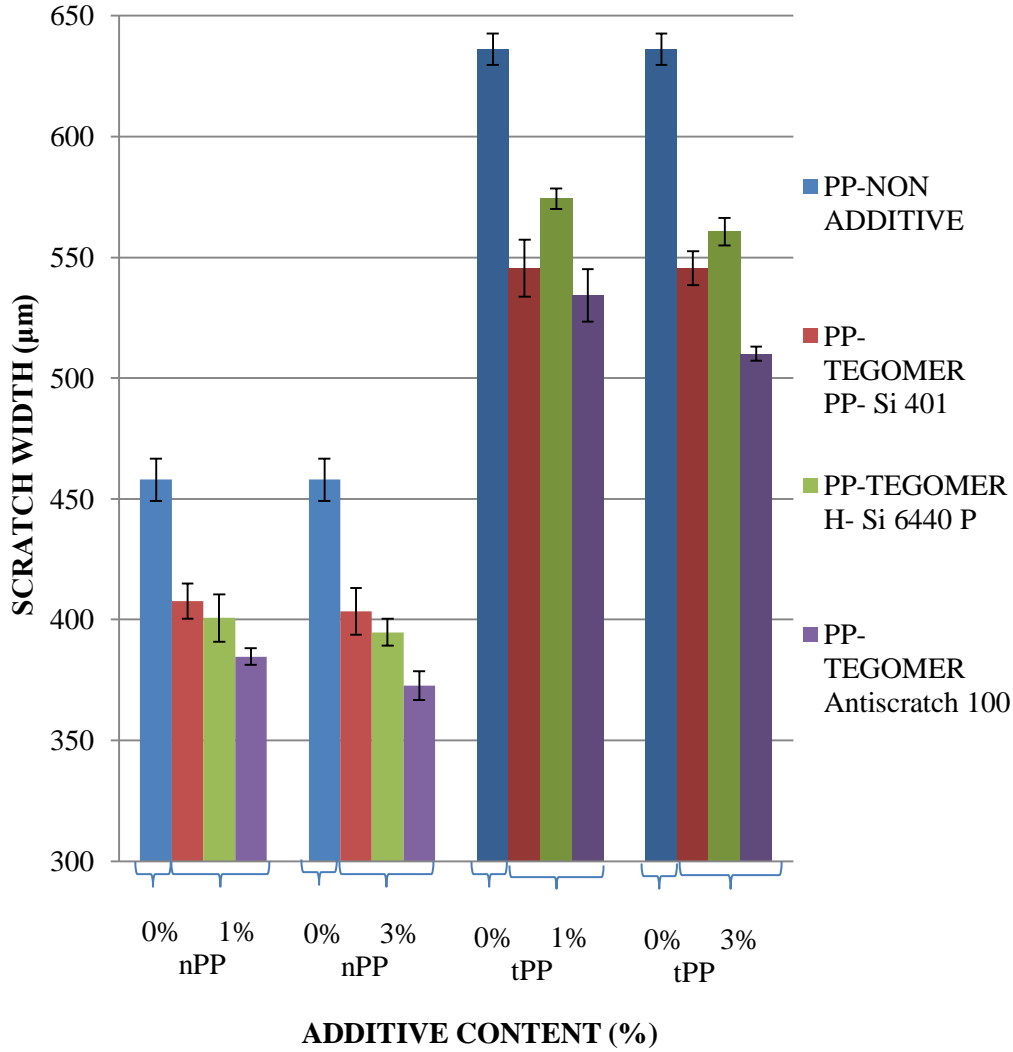
Figure 4.9: Scratch widths of nPP, tPP and the samples prepared.

Scratch hardness is one of the main characteristics of the material which indicates its scratch deformation resistance. In the manner indentation hardness, scratch hardness is a measure of force applied to the sample per unit area and it can be calculated as follows (4.2) :

$$H_{scratch} = L_{scratch}/ A_p \tag{4.2}$$

where $H_{scratch}$ is the scratch hardness in kg/mm^2, $L_{scratch}$ is the scratch load in *N*, and A_p is the projected load supporting area mm^2, which is $\pi w^2/4$ for a conical indenter, where w is the scratch width. Consequently, Equation 2. can be rewritten as follows (4.3) :

$$H_{scratch} = 4L_{scratch}/ \pi w^2 \tag{4.3}$$

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Good correlation was found between scratch visibility and scratch hardness based on scratch width measurements. Materials with higher scratch hardness were more resistant to scratch. As it was seen in Figure 4.10, the hardness of samples with anti-scratch additives became higher than non-additive nPP and tPP. It was also observed that the effect of additive content on the scratch hardness varied according to the additive type. tPP samples showed less scratch hardness than nPP samples according to the scratch width of samples. On the other hand, there were not many changes in the scratch hardness of tPP and nPP samples depended on additive content. While scratch hardness of nPP-1% C was obtained 17.5 kg/mm^2, it was found 18.6 kg/mm^2 for nPP-3% C. The scratch hardness of nPP-1% B was found 16.2 kg/mm^2, it was 16.7 kg/mm^2 for nPP-3% B.

Unfortunately, samples with talc reinforced PP always showed poor scratch resistance. Talc reinforced-polypropylenes exhibited voids and debonding of filler particles because of the layered structure of talc that encourages delamination. Additives act as lubricating agent on the surface to provide antiscratch effect and improved scratch resistance of PPs.
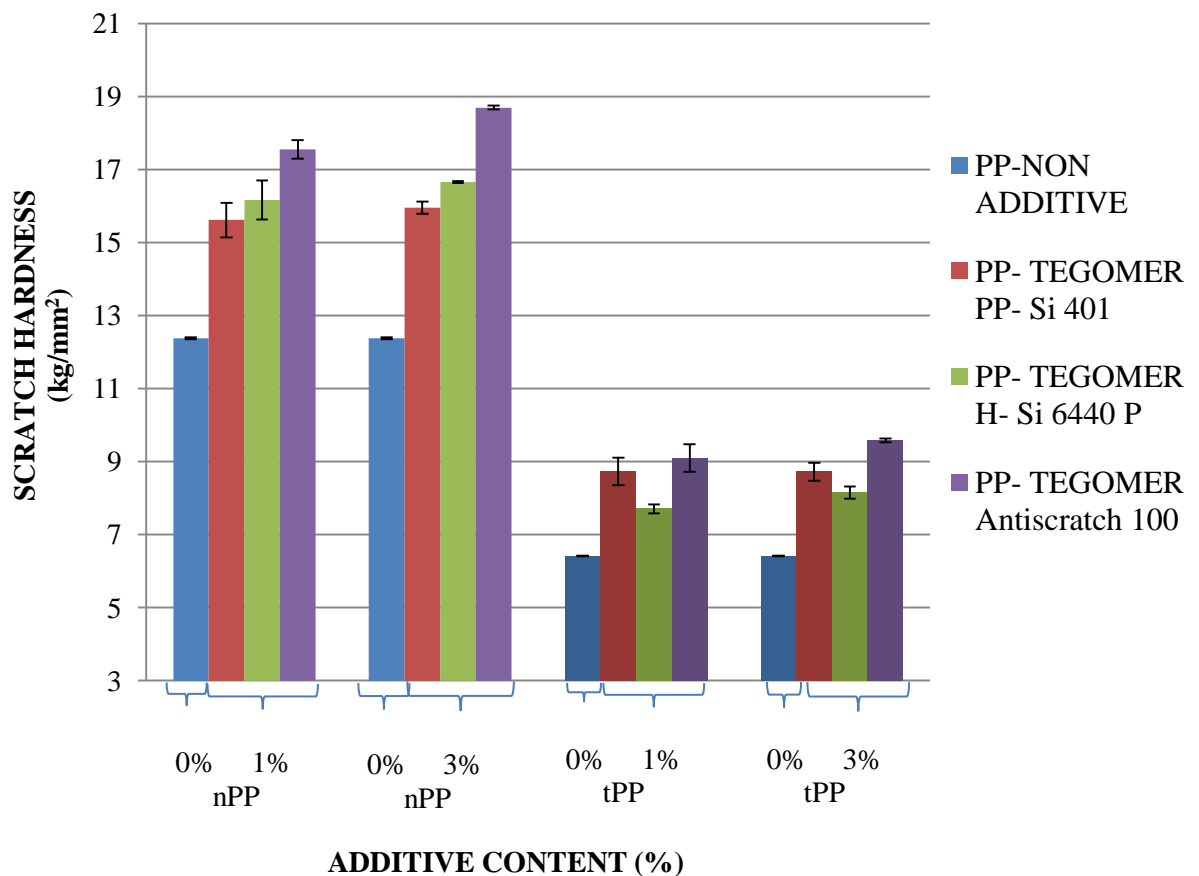
Figure 4.10 : Scratch hardness of samples.

4.6 Contact Angle Test Results

The contact angles values of samples were shown in Table 4.3 for deionized water, diiodomethane and ethylene glycol.

The water contact angle value of nPP and tPP was obtained as 90.1^o and 96.2^o respectively. Water contact angle values that were higher than $90°$ indicate surface hydrophobicity. The hydrophobicity of talc surfaces arises from the fact that the atoms exposed on the surface are linked together by siloxane (Si-0-Si) bonds and, hence, do not form strong hydrogen bonds with water. Water contact angle of nPP-3% C was found 104.0^o. PDMS has hydrophobic characteristic as mentioned in Section 3.2. So that samples with silicone based additives had higher water contact angle degree than nPP and tPP. Moreover, increasing additives content made contact angle degree higher as a result of that more hydrophobic surface occurred.

Water contact angles on all polymer surfaces studied are higher than those of diiodomethane (DIM). Water possesses both polar and dispersion surface energy components, while DIM has mostly the dispersion surface energy component.

Table 4.3 : Contact angle degree of samples.

Sample	water (^{o})	diiodomethane (^{o})	ethylene glycol (^{o})
nPP	90.1	56.2	67.5
nPP-%1 A	94.8	60.0	74.0
nPP-%3 A	96.2	61.0	76.6
nPP-%1 B	94.0	59.7	72.5
nPP-%3 B	96.8	63.0	72.7
nPP-%1 C	101.1	62.0	75.0
nPP-%3 C	104.0	66.8	78.0
tPP	96.2	57.0	60.0
tPP-%1 A	102.8	57.7	74.5
tPP-%3 A	104.1	58.0	75.2
tPP-%1 B	100.0	57.7	63.2
tPP-%3 B	104.0	59.7	64.8
tPP-%1 C	107.1	57.7	60.6
tPP-%3 C	112.6	59.8	62.7

The total surface free energy of samples were shown in Figure 4.11. PDMS containing samples had lower surface energy than nPP and tPP. nPP and tPP had the

highest surface energy which was 31.2 mJ/m^2 and 31.1 mJ/m^2 respectively. The surface free energy of tPP-1 % C was found 27.3 mJ/m^2 and it was found 24.3 mJ/m^2 for tPP-3 % C. tPP-3 % C had the lowest surface free energy. For each types of additives, as the amount of additive increased, the surface free energy decreased.
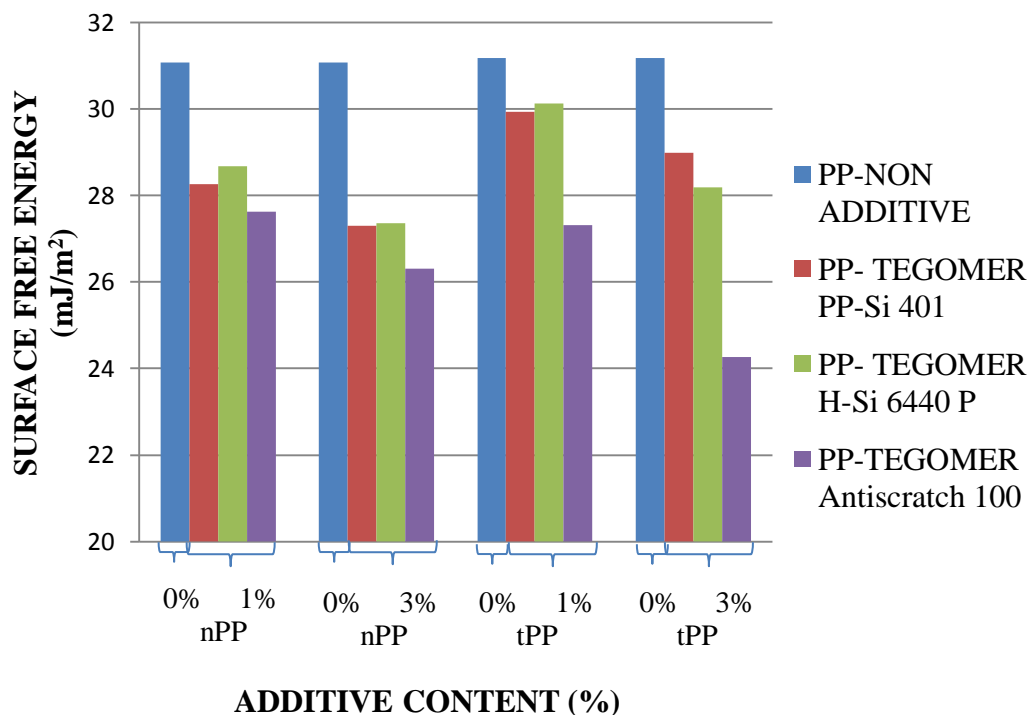

Figure 4.11: Surface free energy of sample.

4.7 MFR result of the samples

The melt flow rate (MFR) of nPP, tPP and samples with additives were measured according to ASTM D1238 standard. MFR values of nPP and tPP were obtained 5.4g/10 min, 5.2 g/10 min respectively. As it can be seen from Figure 4.12, the MFR values decreased slightly with the addition of the talc content. This result can be directly related to the lack of contribution of the talc to the flow. On the other hand, the MFR values of samples increased due to three kind of additives. TEGOMER H-Si 6440 P increased flowability of samples significantly when using 3 wt- % in both nPP and tPP. 3 wt- % of TEGOMER PP-Si 401 and TEGOMER Antiscratch 100 increased MFR values of nPP samples more than those of tPP samples. A higher MFR values allowed the polypropylene to fill the mold more easily.
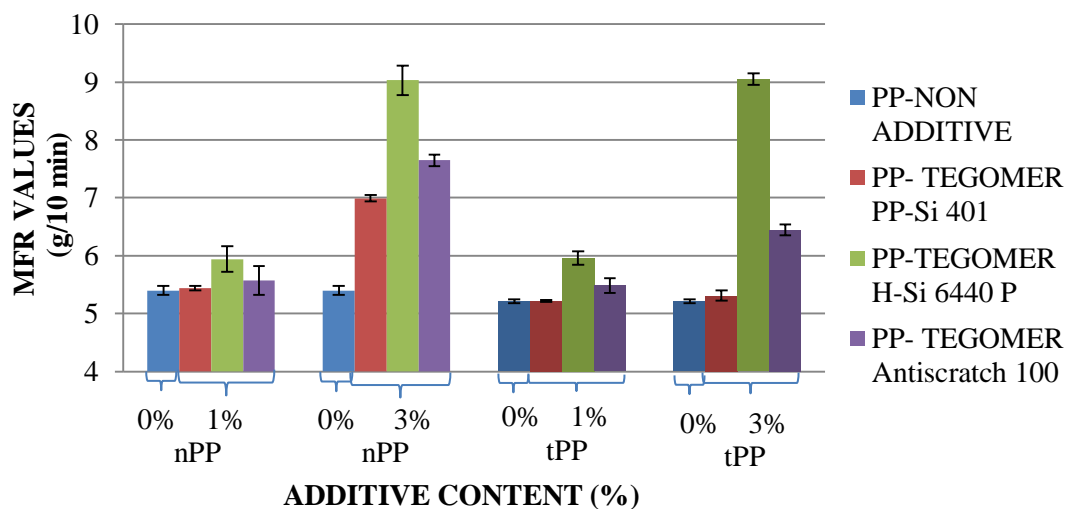
Figure 4.12 : MFR values of nPP, tPP and all samples.

4.8 Density Result

The density values of additives and all samples was calculated by Mettler Toledo's Density Kits. The results were shown in Table 4.4.

Table 4.4 : Density of additives and samples.

Sample	Density (g/cm^3)
TEGOMER PP-Si 401	0.847
TEGOMER H-Si 6440 P	0.997
TEGOMER Antiscratch100	0.493
nPP	0.910
nPP-%1 A	0.894
nPP-%3 A	0.894
nPP-%1 B	0.896
nPP-%3 B	0.895
nPP-%1 C	0.889
nPP-%3 C	0.886
tPP	0.998
tPP-%1 A	0.969
tPP-%3 A	0.968
tPP-%1 B	0.975
tPP-%3 B	0.974
tPP-%1 C	0.965
tPP-%3 C	0.963

The density of TEGOMER PP-Si 401, TEGOMER H-Si 6440 P, TEGOMER Antiscratch 100 were found 0.847, 0.997, 0.493 g/cm^3 respectively. TEGOMER The density value of nPP was found 0.909 g/cm^3, while it was found 0.999 g/cm^3 for tPP. Talc increased density of PP. TEGOMER Antiscratch 100 which was organically modified siloxane had the lowest density value so that the samples of nPP and tPP containing TEGOMER Antiscratch 100 had less density value than other samples as well. TEGOMER H-Si 6440 P showed higher density value due to containing of polycaprolactone groups which had higher density. The nPP and tPP samples which containing TEGOMER H-Si 6440 P had higher density value than other samples.

5. CONCLUSION

In this study, three different commercially available anti-scratch additives were used to improve scratch resistance of neat PP (nPP) and talc reinforced PP (tPP) samples. These additives are (1) a mixture of modified polyolefin-silicone block copolymer, (2) siloxane copolyester and (3) organically modified siloxane used as 1 and 3 wt-% both in nPP and in tPP. The effects of filler, additives and additive contents on the mechanical, thermal, and tribological properties were investigated.

FTIR-ATR analysis showed that additives had characteristic peaks of PDMS in their structure. Moreover, FTIR-ATR analysis of tPP- %3 C showed that, the surface of samples had characteristic peak of additives due to migration of additives as a slipping agent on the surface. FTIR-ATR spectra of inside of tPP- % 3 C was quite similar with PP but it also had characteristic peak of additive.

Mechanical property analysis of the samples showed that PDMS containing additives decreased modulus of elasticity but increased elongation at break value. On the other hand, talc as a rigid filler increased modulus of elasticity but decreased elongation at break value of samples. Tensile strength depended on additive content. When the additives were added 1%, an increase in tensile strength was observed due to the effect of other groups than PDMS. When 3% of additives were used in composition, decreasing of tensile strength was observed. Addition of talc decreased tensile strength this can be depended on particle size of talc or distribution of talc.

The Shore-D hardness measurements showed that talc as a rigid filler increased hardness of the samples, in contrast PDMS containing additives decreased hardness of the samples.

According to DSC analysis, it was concluded that the experimental melting temperatures of the polypropylene based materials were consistent with the theoretical values. tPP based samples had higher % crystallinity in comparison to nPP based samples. This can be attributed to the nucleating effect of talc. Percentage of crystallinity and entalpy of melting increased by increasing additive content for

nPP. On the other hand, the additive content did not affect entalpy of melting and % crystallinity of tPP as much as nPP. Each of additives increased crystallinity of tPP. tPP based samples always showed higher % crystallinity than nPP based samples.

The measurements performed with the optical microscope demonstrated that scratch width of polypropylene films decreased and therefore scratch hardness of the films increased considerably with the insertion of the silicone based additives. As the amounts of additives were increased, the scratch resistance of samples became higher for nPP and tPP. In general, talc used as a filler at automotive applications. Unfortunately, samples with talc reinforced PP always showed poor scratch resistance. PDMS containing additives were chosen as additives in PP systems to modify the surface characteristics of the samples and to improve scratch resistance of samples. PDMS containing additives were effective to decrease the width of scratches and improve scratch resistance. The most effective one for improving scratch resistance was found as 3 % TEGOMER Antiscratch 100.

Contact angle results showed that additives increased the contact angle degree of samples due to containing PDMS in their structure. As a result of that more hydrophobic surface occurred. Talc also increased the hydrophobicity of sample. Sample with PDMS containing additives had lower surface free energy than those of nPP and tPP. tPP- 3% C had the lowest surface free energy value.

Melt flow rate (MFR) analysis were carried out for all samples. The talc reduce the mobility of macromolecules in the interphases and decrease MFR value of PP. On the other hand, the MFR values of samples increased due to three kind of additives because of their silicone content. 3 wt- % of TEGOMER H-Si 6440 P was more effective to increase viscosity comparing to other additives. A higher MFR allowed the polypropylene to fill the mold more easily.

Density measurement showed that talc as a rigid filler increased the density of PP. TEGOMER Antiscratch 100 had the lowest density value and the samples of nPP and tPP containing TEGOMER Antiscratch 100 had lower density value than other samples as well. The samples which containing TEGOMER H-Si 6440 P had higher density value than other samples. This can be due to containing caprolactone groups which had high density in the structure of additive.

As a conclusion, for the additives containing nPP, while there is some decrease in modulus of elasticity and some increase in elongation at break, there is no significant change in tensile strength values. Although the most effective additive is found to be TEGOMER Antiscratch 100, the others can be used as well. Eventhough the additives had increased anti-scratch effect of tPP, due to the fact that tPP has poor scratch resistance, samples with nPP are preferred.

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APPENDICES

APPENDIX A: Optical images of samples.
APPENDIX B: DSC graphes of samples.
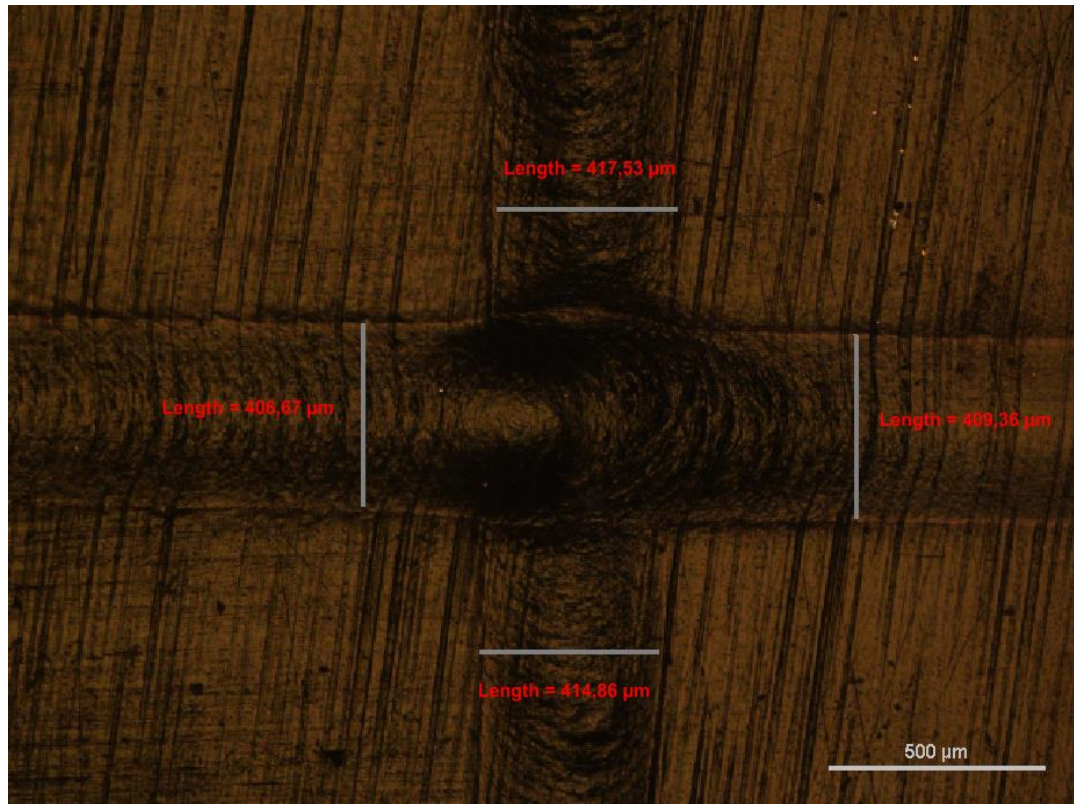
Figure A.1 : Optical image of nPP -%1 A.
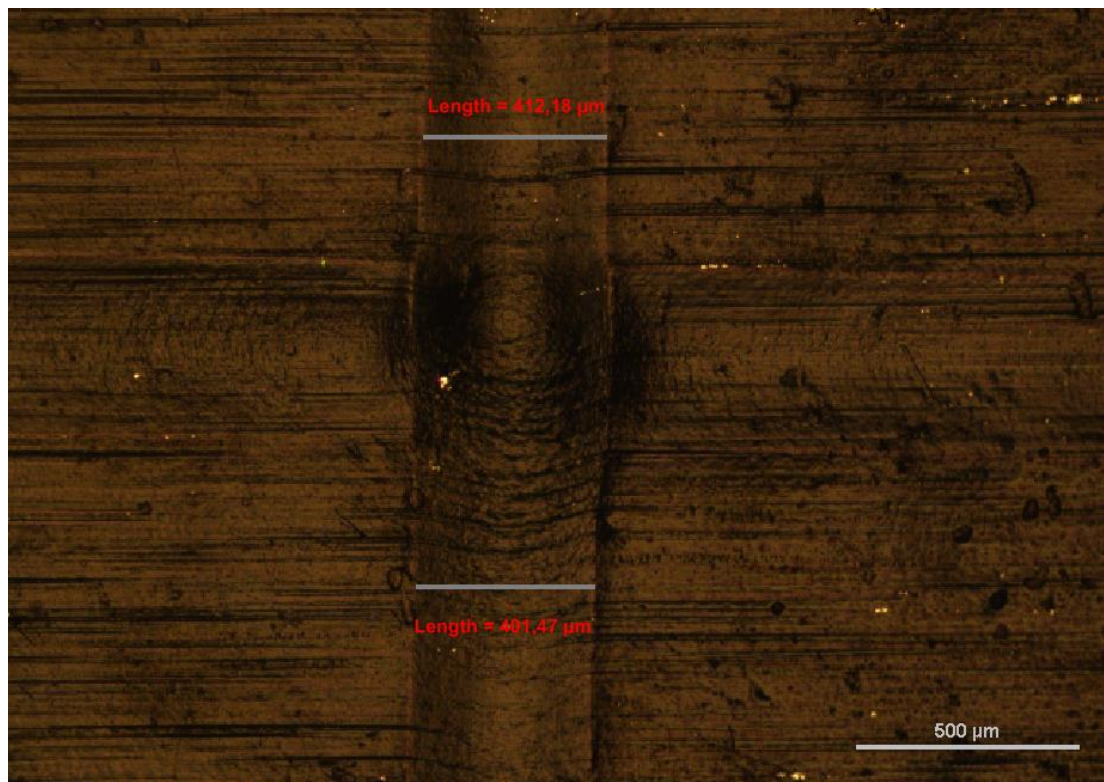
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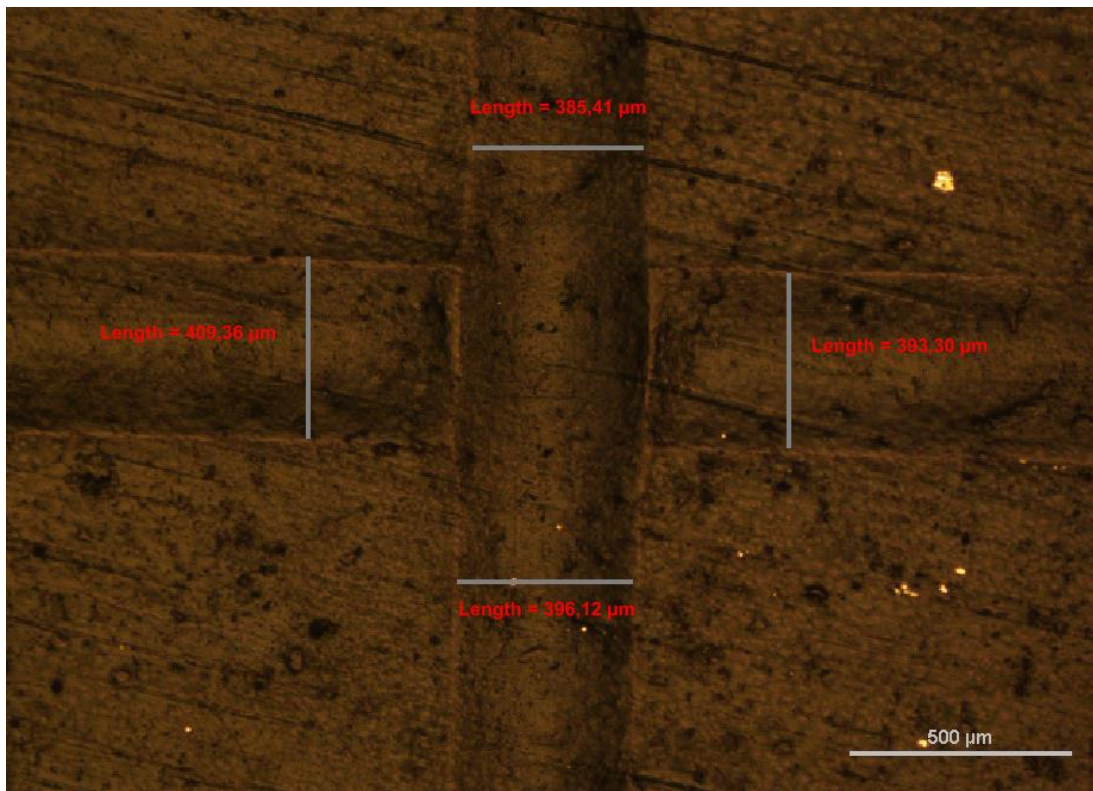
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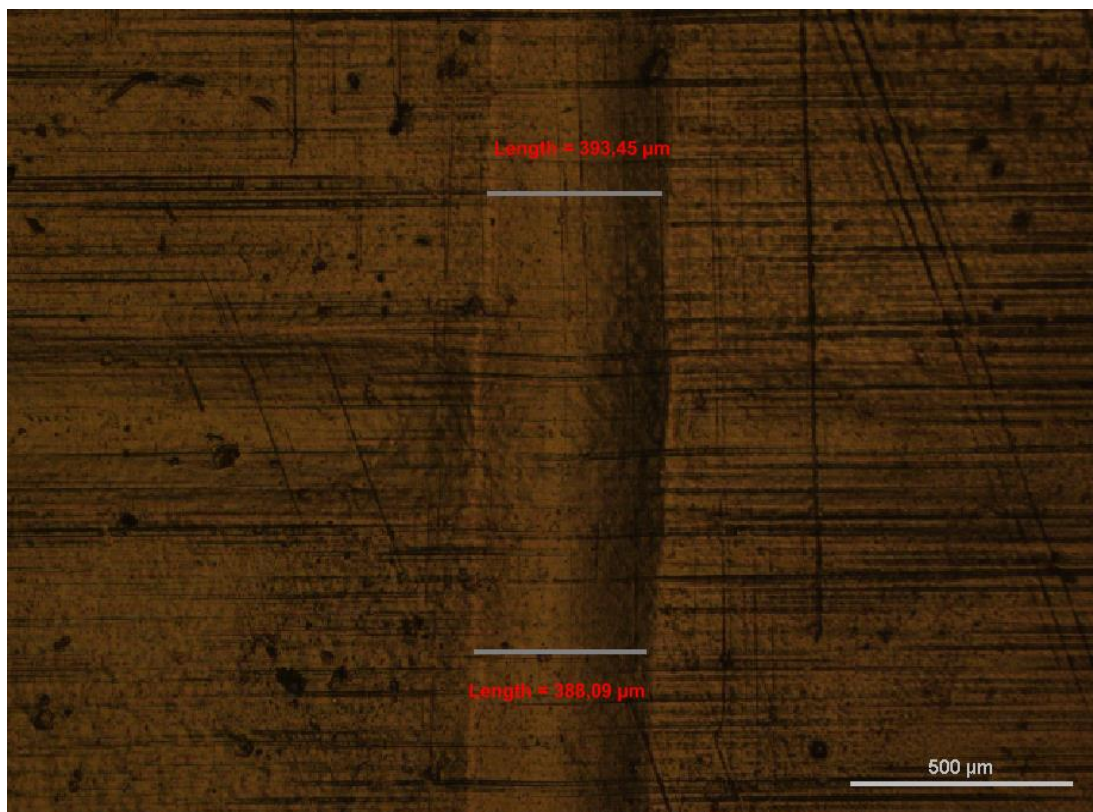
Figure A.4 : Optical image of nPP -%3 B.
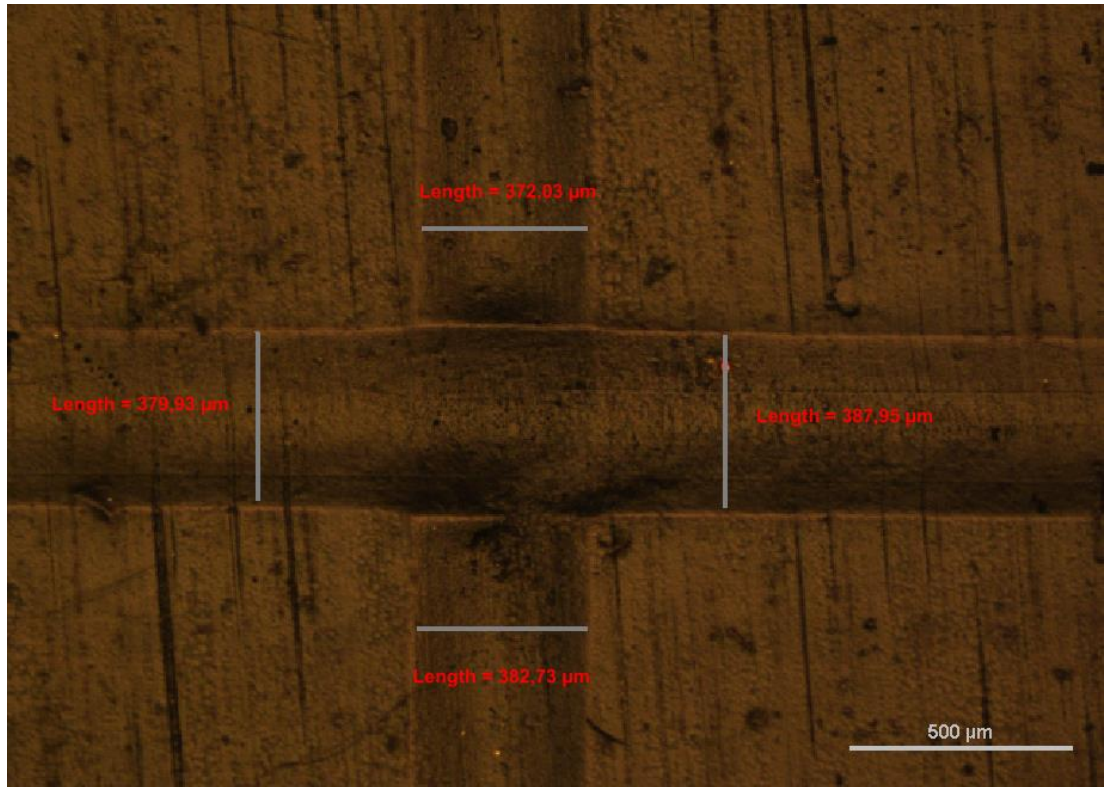
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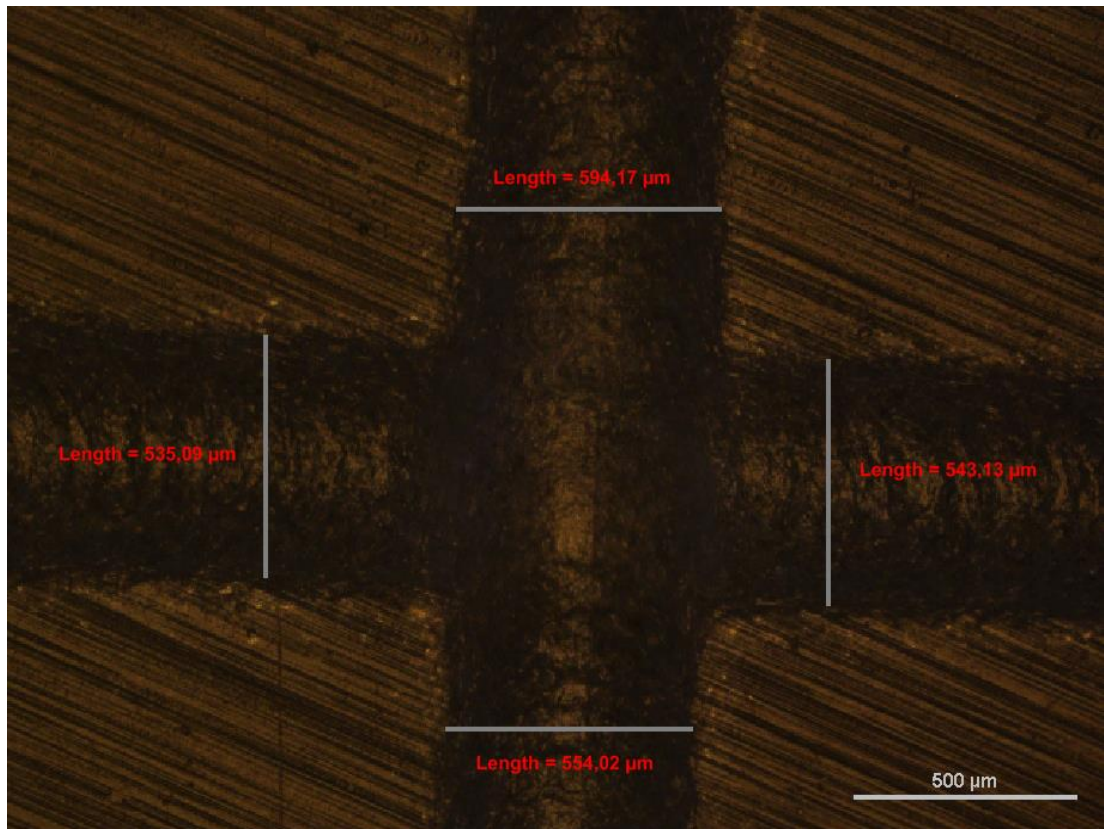
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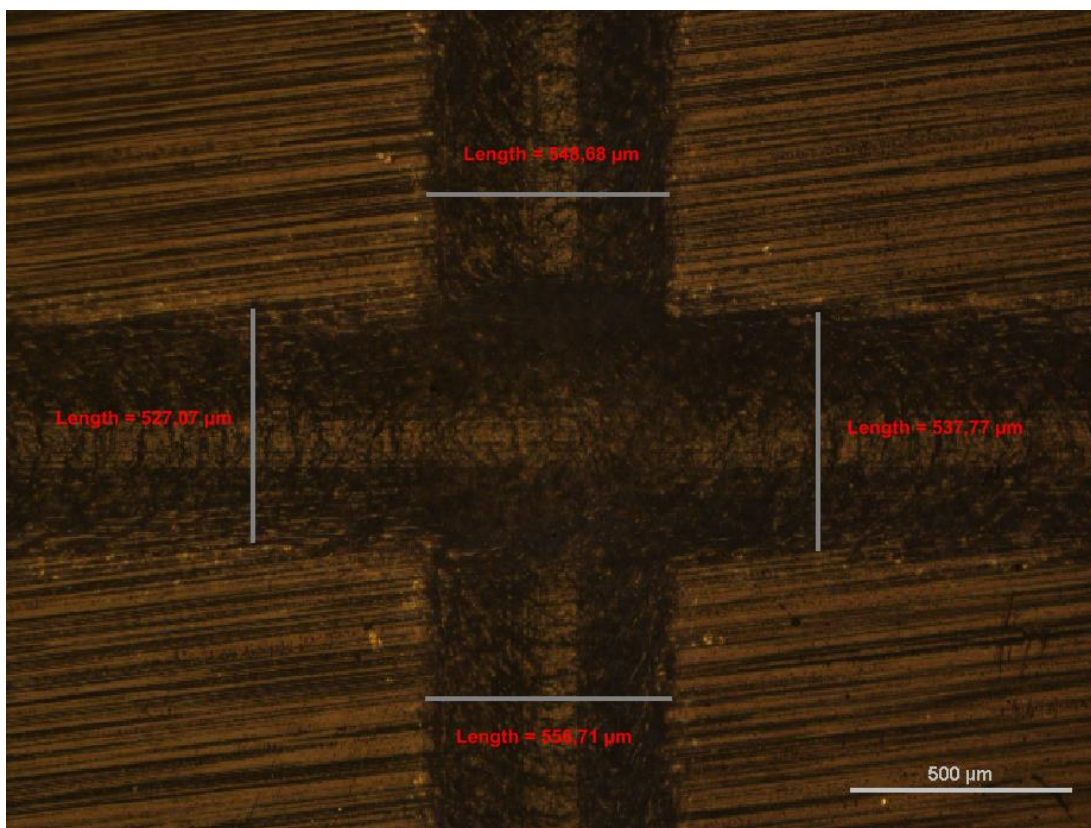
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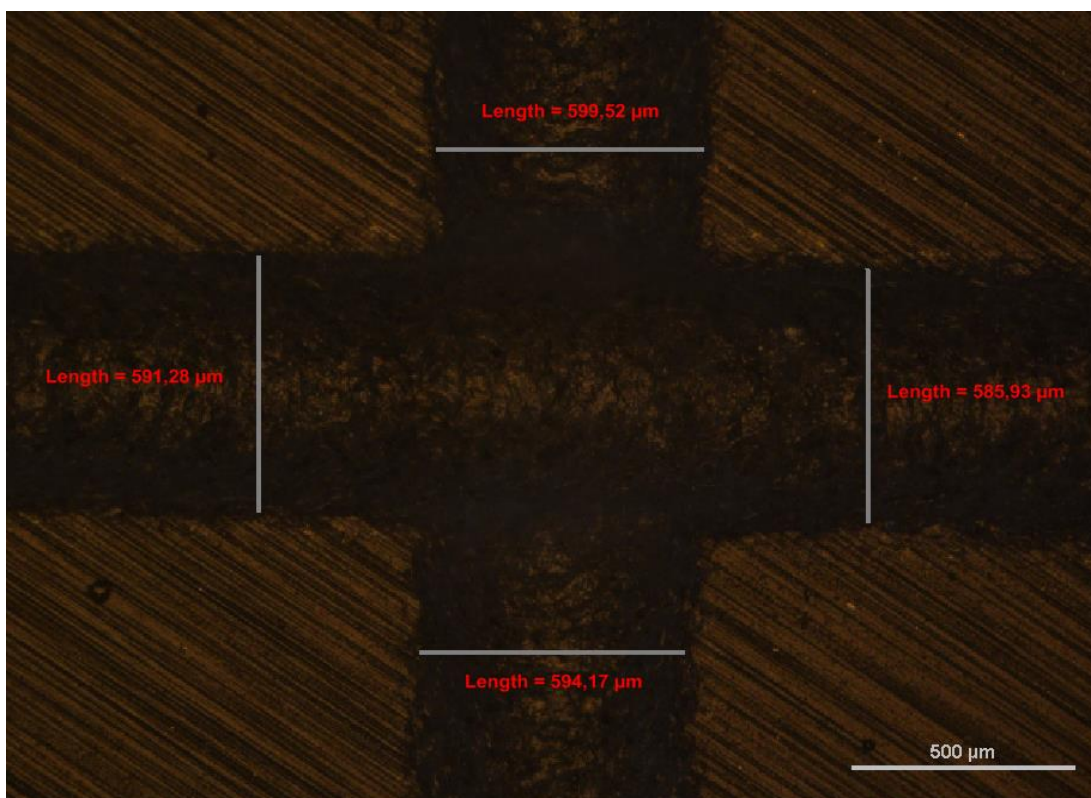
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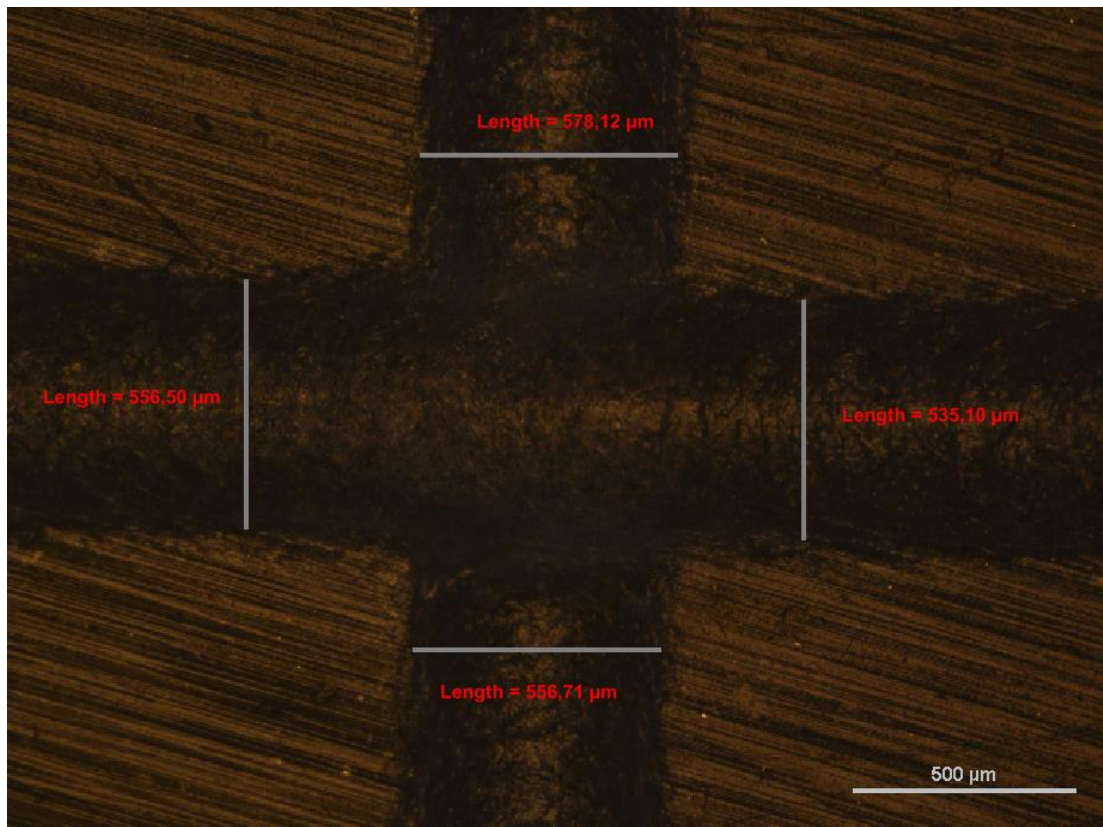
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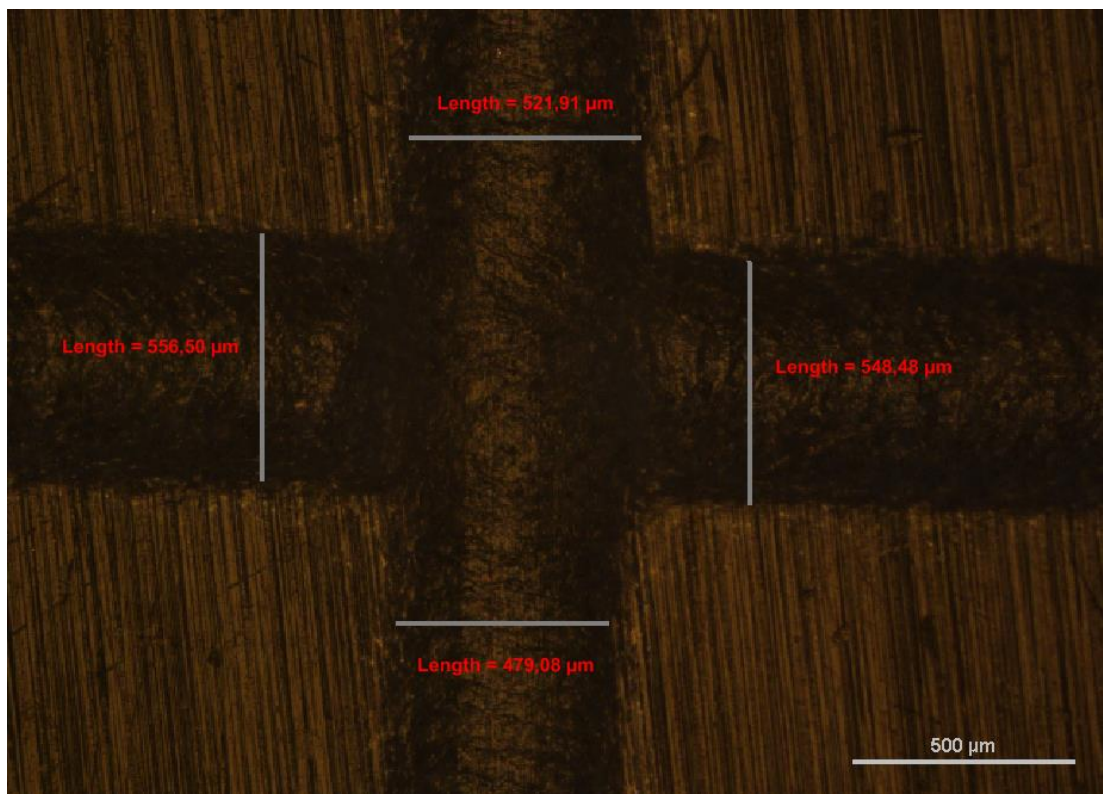
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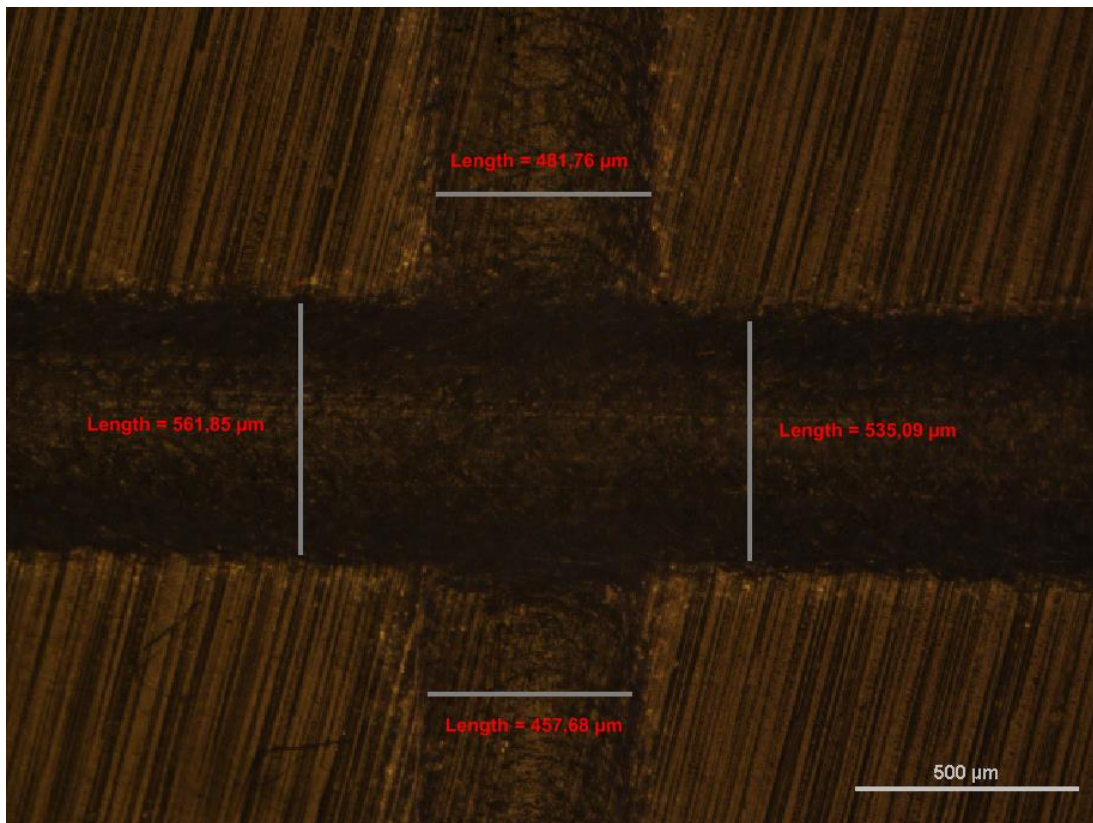
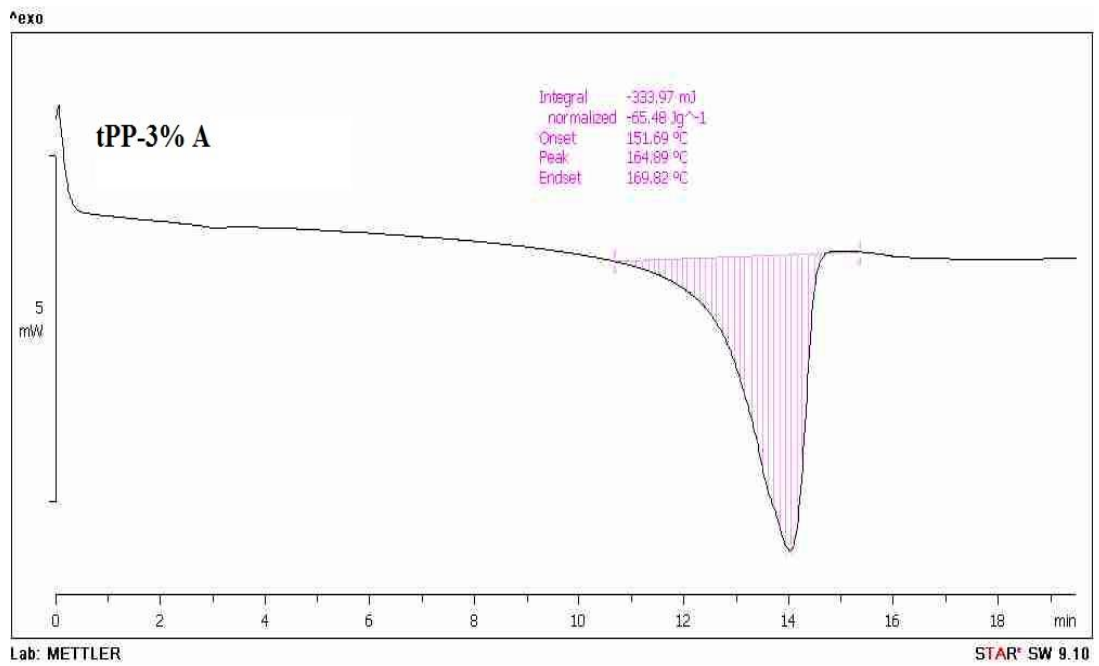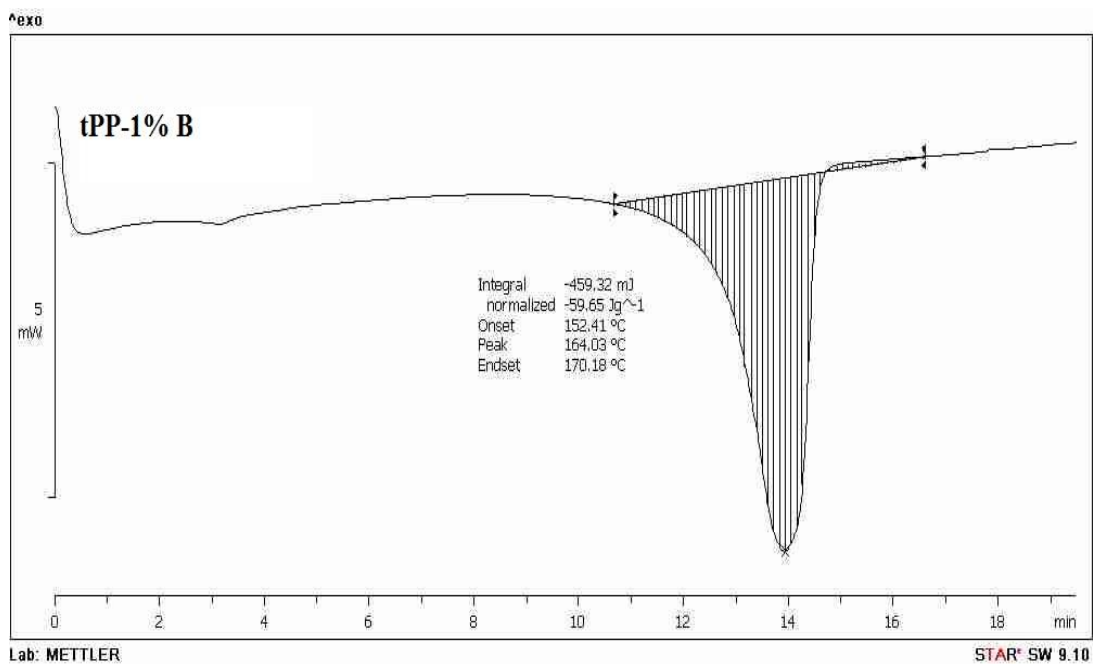**Figure A.11:** Optical image of tPP -%3 C.

APPENDIX B
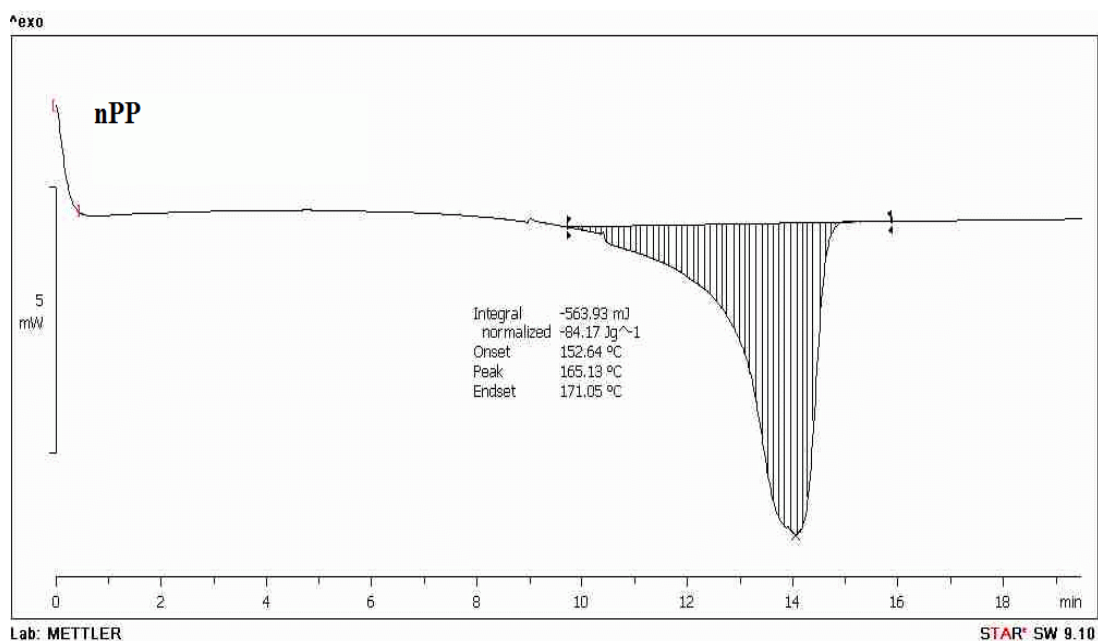
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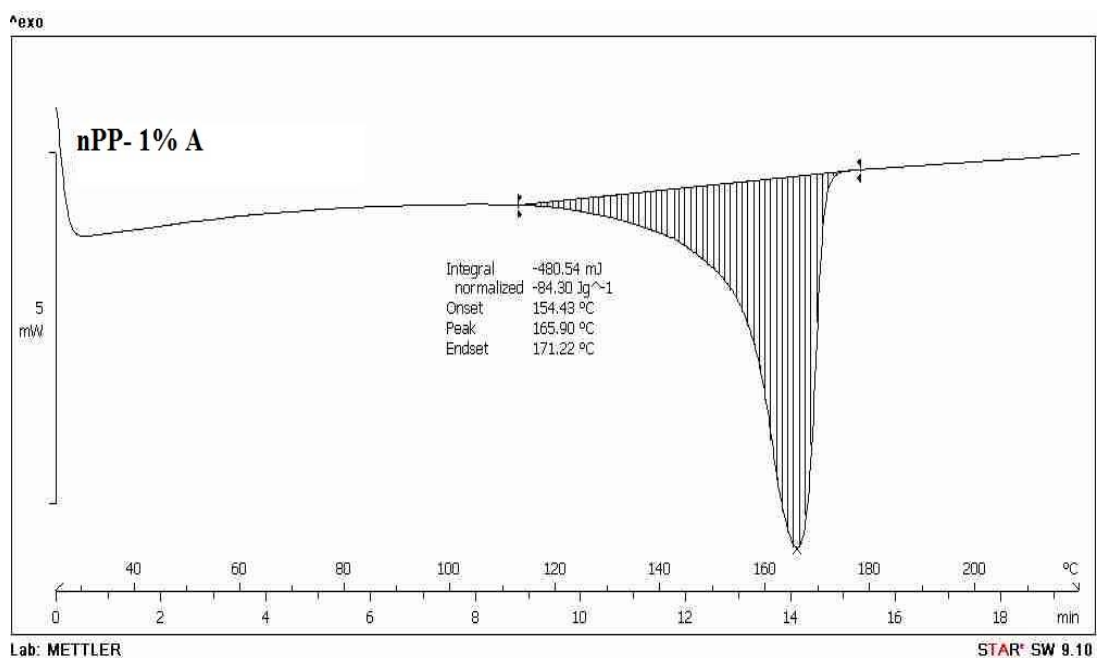
Figure B.2: DSC diagram of nPP-1% A.
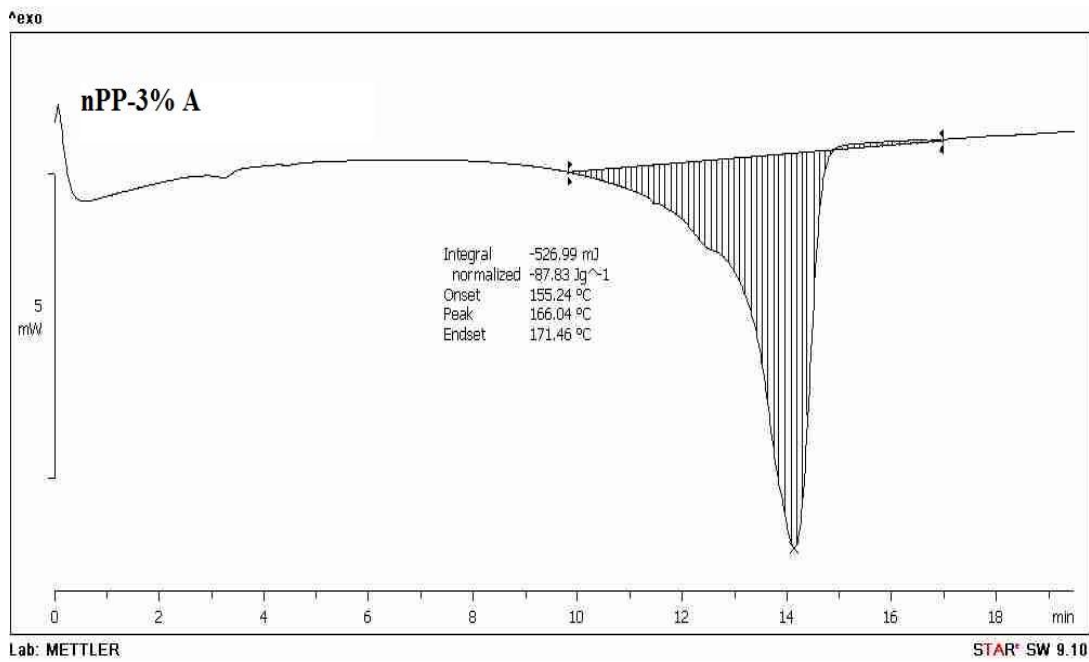
Figure B.3: DSC diagram of nPP-3% A.
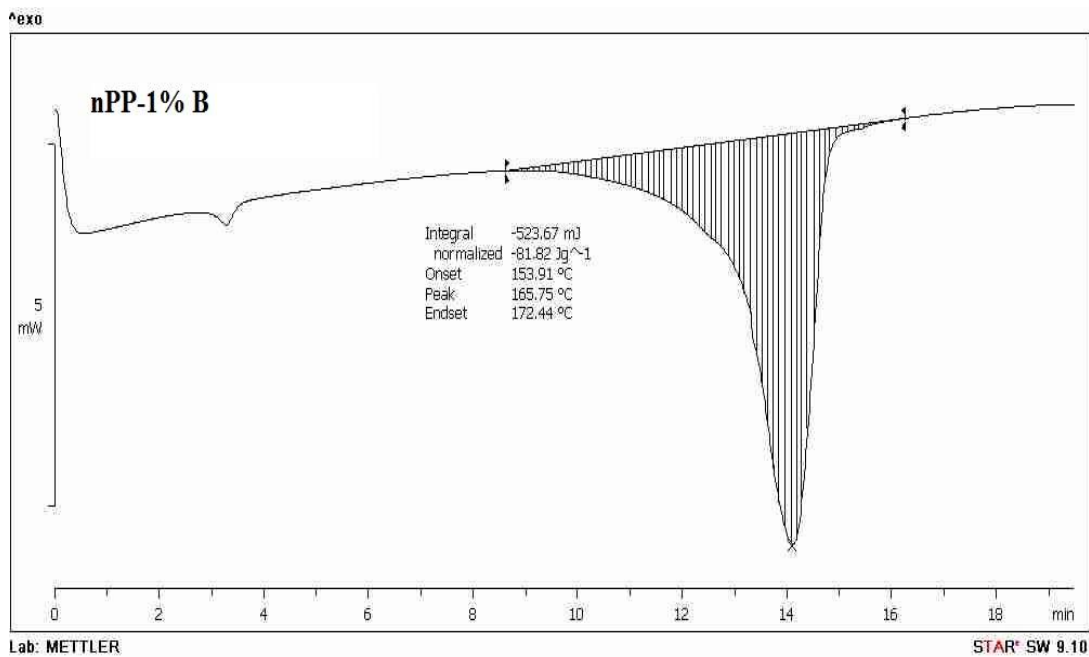
Figure B.4: DSC diagram of nPP-1% B.
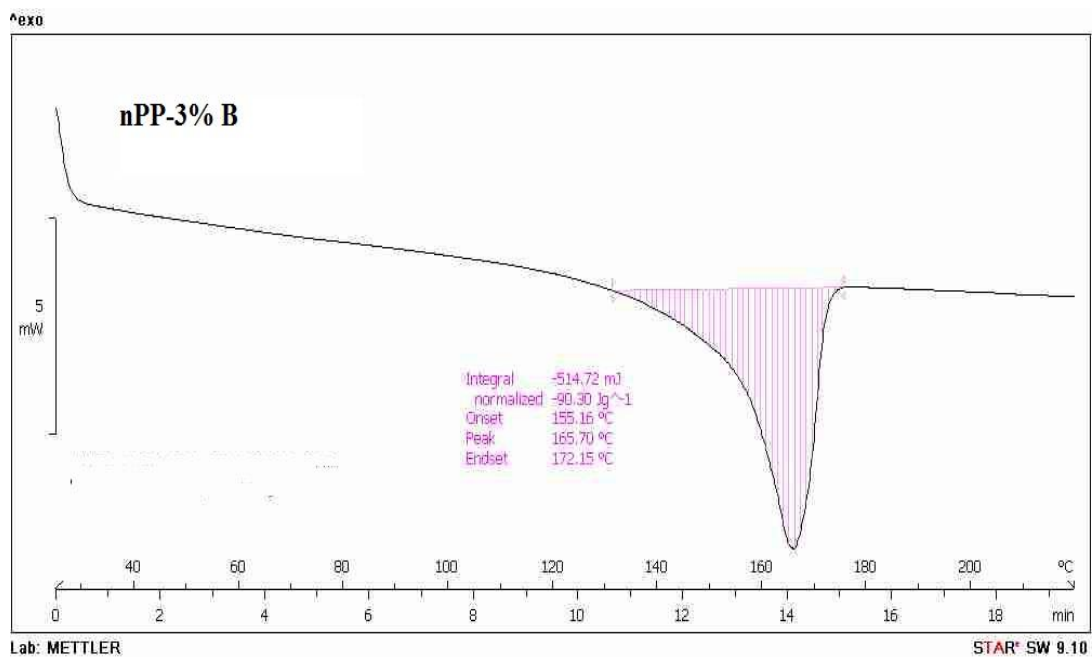
Figure B.5: DSC diagram of nPP-3% B.
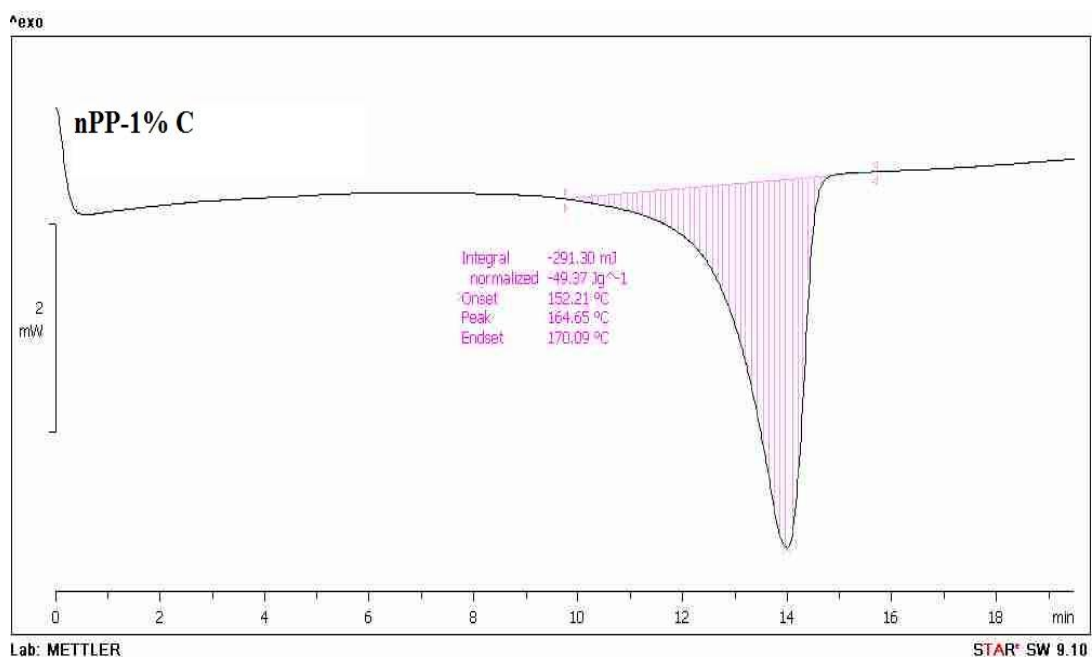
Figure B.6: DSC diagram of nPP-1% C.
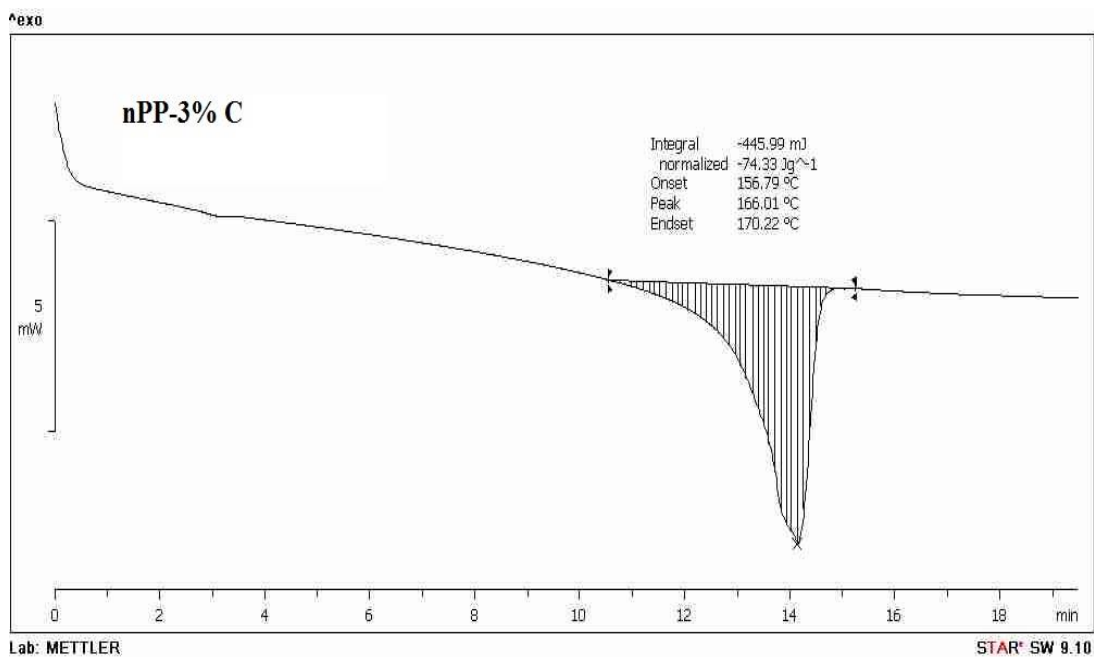
Figure B.7: DSC diagram of nPP-3% C.
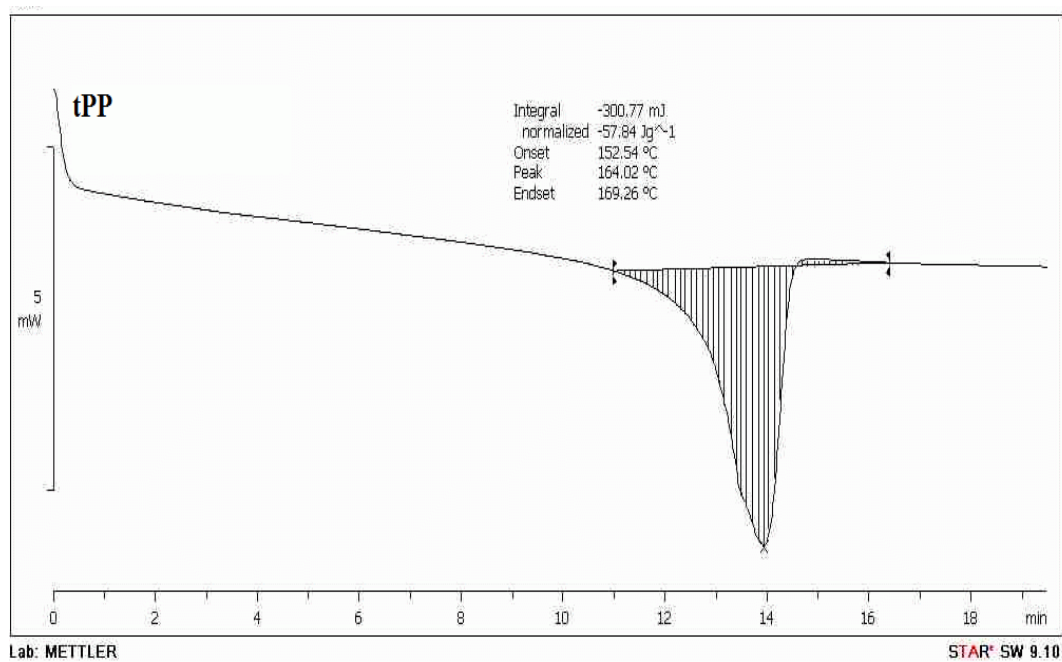
Figure B.8: DSC diagram of tPP
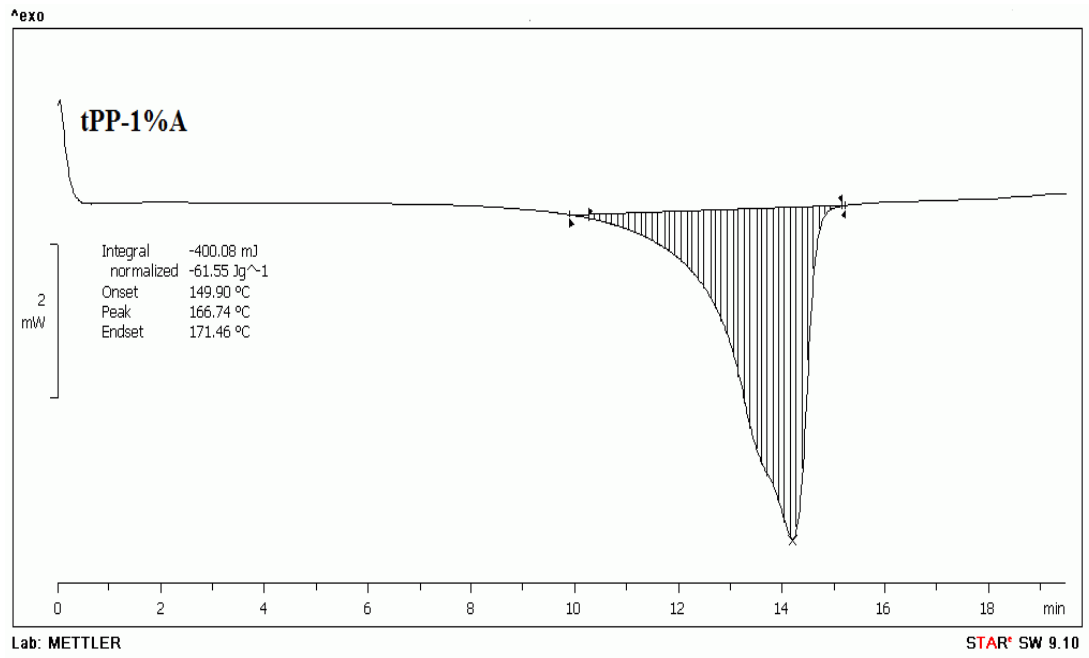
Figure B.9: DSC diagram of tPP-1% A.

Figure B.10: DSC diagram of tPP-3% A.

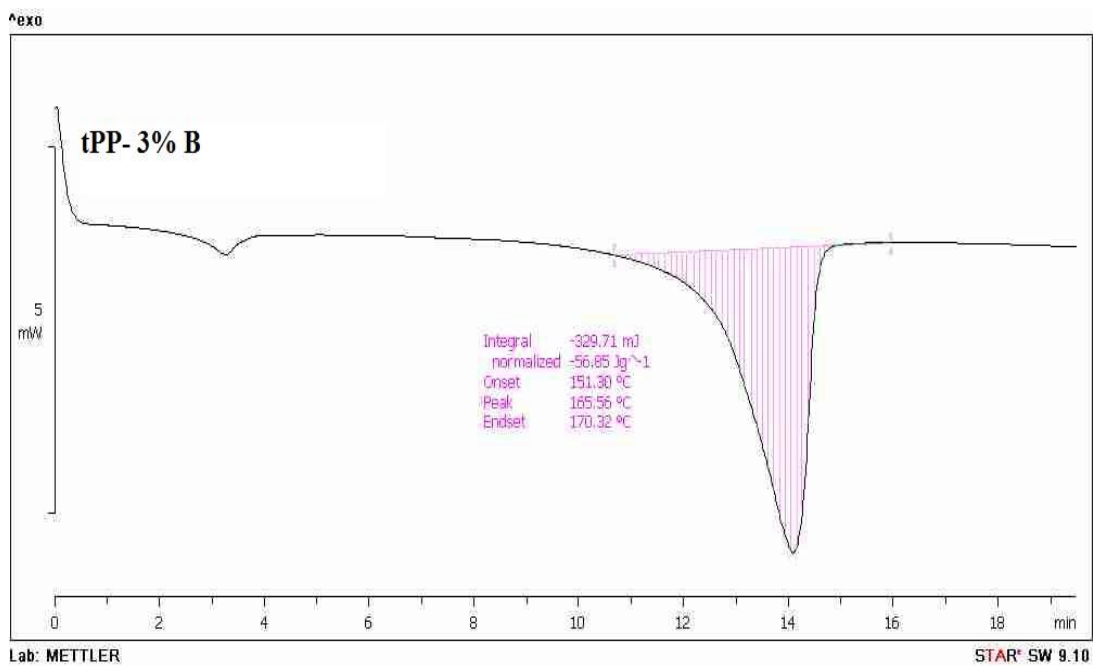**Figure B.11:** DSC diagram of tPP-1% B.

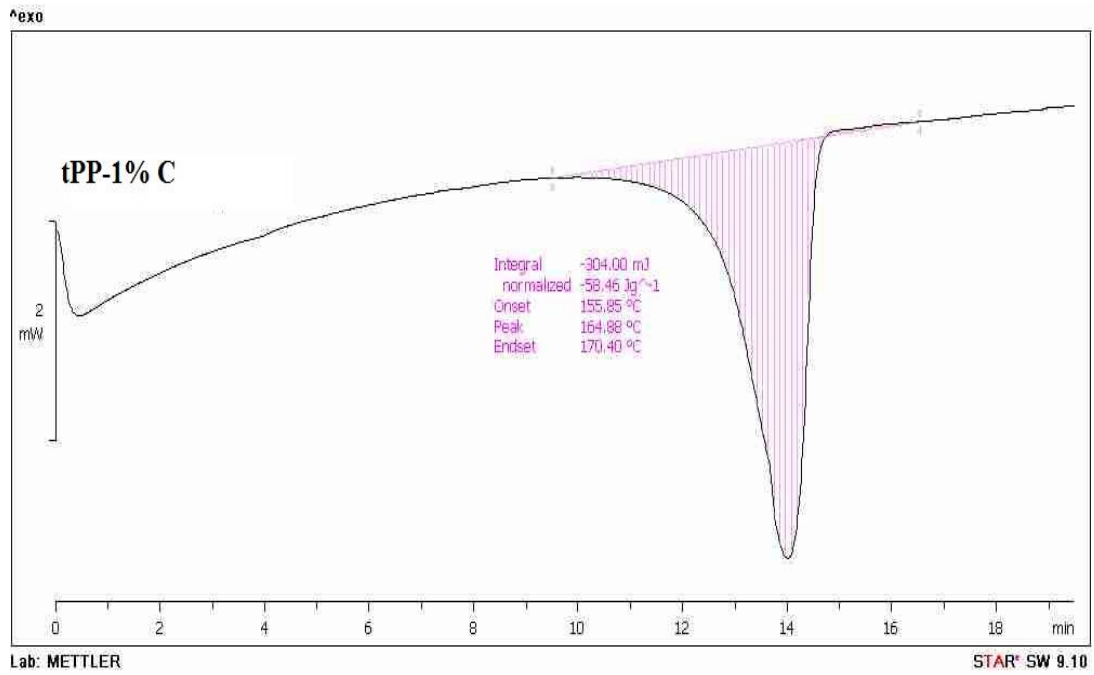**Figure B.12:** DSC diagram of tPP-3% B.

Figure B.13: DSC diagram of tPP-1% C.

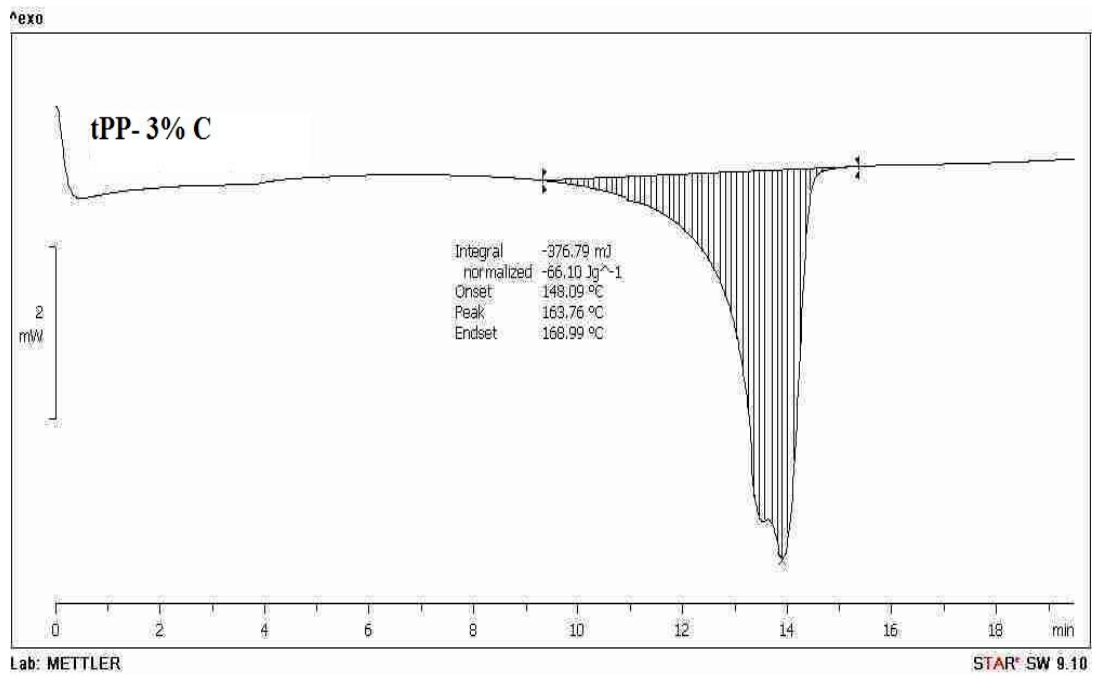**Figure B.14:** DSC diagram of tPP-3% C.

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PUBLICATIONS/PRESENTATIONS

- Herzer, N., **Guneysu, H**., Davies, D. J., Yildirim, D., Vaccaro, A. R., Broer, D. J., Schenning, A. P. (2012). Printable Optical Sensors Based on H-Bonded Supramolecular Cholesteric Liquid Crystal Networks. *Journal of the American Chemical Society*, *134*(18), 7608-7611.

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