INTERIOR MARKING INTO OXO-BIODEGRADABLE POLYETHYLENE SHOPPING BAGS TO ASSESS THE PRESENCE OF PRO-OXIDANT ADDITIVE BY USING ATR-FTIR TECHNIQUE

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

YASEMİN DURMUŞ

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
POLYMER SCIENCE AND TECHNOLOGY

JANUARY 2016

Approval of the thesis:

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Submitted by **YASEMİN DURMUŞ** in partial fulfillment of the requirements for the degree of **Master of Science in Polymer Science and Technology Department, Middle East Technical University** by,

Prof. Dr. Gülbin Dural Ünver
Dean, Graduate School of **Natural and Applied Sciences** ________________

Prof. Dr. Necati Özkan
Head of Department, **Polymer Science and Technology** ________________

Prof. Dr. İsmail Teoman Tinçer
Supervisor, **Chemistry Dept., METU** ________________

Assist. Prof. Dr. Salih Özçubukçu
Co-Supervisor, **Chemistry Dept., METU** ________________

Examining Committee Members:

Prof. Dr. Murat Şen
Chemistry Dept., Hacettepe University ________________

Prof. Dr. İsmail Teoman Tinçer
Chemistry Dept., METU ________________

Assoc. Prof. Dr. Yunus Karataş
Chemistry Dept., Ahi Evran University ________________

Assoc. Prof. Dr. Ali Çırpan
Chemistry Dept., METU ________________

Assoc. Prof. Dr. İrem Erel Göktepe
Chemistry Dept., METU ________________

Date: 08.01.16

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last Name: Yasemin Durmuş

Signature :

ABSTRACT

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Durmuş, Yasemin
M.S., Department of Polymer Science and Technology
Supervisor : Prof. Dr. İsmail Teoman Tinçer
Co-Supervisor: Assist. Prof. Dr. Salih Özçubukçu

January 2016, 128 pages

The production and consumption of synthetic polymeric materials and relevant plastic items have been increasing dramatically in last 50 years. Polyethylene (PE) with high versatility (HDPE, LDPE, LLDPE etc) has easy processability, and good thermal stability, resulting in the greatest applicability. Green house covers, mulch films, shopping bags, garbage bags, bottles etc. are all produced from PE. PE based materials are used for a short period time -and often only once- and then discarded. Polyethylene biodegrades slowly, especially when it is deprived of sunlight. This causes environmental pollution. Because of its low mass and highly contaminated state after use, recycling of PE is economically unfeasible. The use of pro-oxidant chemicals in its matrix is the solution to the environmental problems PE causes. Since the degraded products are more easily metabolized by microorganisms. Pro-oxidants containing transition metals, particularly Fe^{3+} stearate, are widely used as additives.

In this study, the purpose was to introduce a marking material into oxo-biodegradable polyethylene shopping bags to assess the presence of pro-oxidant additives, by using the ATR-FTIR and FTIR. Three different polymer markers; nitrile rubber, polyamide 12 and thermoplastic polyurethane, were used for this purpose. Selected polymer markers were preferred for being compatible, nontoxic, nonvolatile, cheap and available. It is shown that if these markers are added properly into the PE, even at very low concentrations like 0.09% by mass, could be detected by ATR-FTIR and FTIR. The best of the markers is assumed be nitrile rubber because of its unit absorption at 2238 cm^{-1} of CN group. Also, for selected samples, mechanical testing and thermal analysis were carried out to observe the properties of the polymer matrix and is found to be not altered the mentioned properties.

Keywords: Polyethylene, Nitrile Rubber, Polyamide 12, Thermoplastic Polyurethane, Interior Marker, Polyethylene Shopping Bags

ÖZ

İÇ MARKALAMA YAPARAK OKSO-BİYOBOZUNUR POLİETİLEN ALIŞVERİŞ POŞETLERİNDE PRO-OKSİDANT KATKI MADDESİ VARLIĞINI ATR-FTIR TEKNİĞİ İLE TAYİN EDİLMESİ

Durmuş, Yasemin
Yüksek Lisans, Polimer Bilimi ve Teknolojisi Bölümü
Tez Yöneticisi : Prof. Dr. İsmail Teoman Tinçer
Ortak Tez Yöneticisi: Yrd. Doç. Dr. Salih Özçubukçu

Ocak 2016, 128 sayfa

Son 50 yılda, sentetik polimerlerin ve ilgili plastik malzemelerin üretimi ve tüketimi artmıştır. Polietilen (PE), çeşitliliği (düşük, orta, yüksek yoğunluk ve benzeri), kolay işlenebilirliği, ısıl kararlılığı nedeniyle geniş bir kullanım alanına sahiptir. Polietilenden sera örtüsü, mulç film, alışveriş poşeti, çöp poşeti, şişe ve benzeri ürünler üretilir. Polietilenden üretilen malzemeler genelde tek kullanımlıktır. Polietilenin, özellikle az güneş ışığı alan bölgelerde, zor bozunur olması, doğada birikmesi, önemli bir sorundur. Düşük kütleli atık ürün olması nedeniyle geri dönüşüm de ekonomik olarak pek avantajlı değildir. PE'de okso-biyobozunur polimerik malzemelerin kullanımı çevresel kirliliğe çözüm olabilir. Böylece parçalanan PE, mikroorganizmalar tarafından daha kolay metabolize edilirler.

Bu çalışmanın amacı, polietilenin içine iç markalama yaparak, okso-biobozunur polietilen alışveriş poşetlerinin içindeki pro-oksidant katkı madderinin varlığını ATR-FTIR ve FTIR tekniğini kullanarak tayin etmektir. Bu amaç adına üç farklı polimer marker, nitril kauçuğu, poliamid 12 ve termoplastik poliüretan, kullanılmıştır. Bu işaretleyiciler (marker) polimere uyumlu, toksik olmayan, polimer içinde sabit, ucuz ve ulaşılabilirdir. Sonuçta, bu üç işaretleyicinin varlığı içinde çok düşük miktarlarda (0.09% ağırlıkça) ATR-FTIR ve FTIR ile gözlenmiştir. CN grubunun 2238 cm^{-1} verdiği birim soğurum dolayı, nitrile kauçuğu en iyi işaretleyici olduğu kabul edilmiştir. Bu karışımlarda ayrıca polimer matris özellikleri için mekanik test ve termal analiz yapılmıştır ve bahsedilen özelliklerde herhangi bir değişiklik olmadığı bulunmuştur.

Anahtar Kelimeler: Polietilen, Nitril Kauçuk, Poliamid 12, Termoplastik Poliüretan, İç Markalama, Polietilen Alışveriş Poşeti

To my dear mother

ACKNOWLEDGEMENTS

I would like to thank and express my appreciation to Prof. Dr. Teoman Tinçer for his guidance, continuous support, understanding and valuable discussion through this study. It was a great pleasure for me to work with him.

I would like to thank my co-supervisor Assist. Prof. Dr. Salih Özçubukçu for the supports through my studies.

I am very grateful to Prof. Dr. Murat Şen from Hacettepe University for giving me opportunity to use his laboratory. Also, I would like to thank Eyüp Karaca for his help and cooperation in Hacettepe Polymer Laboratory.

I would like to express thanks to Osman Yaslıtaş, Sevim Ulupınar and Salih Sarıkaya for their technical supports.

And, speaking of the lab environment, I would like to thank Ümit Tayfun, Tuba Kaya Deniz and Barış Koltuksuz for their advice, cooperation and friendship.

I would like to give special thanks to my dear colleague and hause mate İpek Önk for her endless motivation and help. I wish to thank my friends; Ahmet Kayalı, Selin Korkmaz, Çiğdem Atasoy, Mert Atasoy, Zorbay Çetin, Gurbet Çelik, Özge Azeri, Doğuşcan Ahiboz and Umut Cacan for their precious friendship, encouragement and fun.

Finally, I would like to thank to present my sincere appreciation to my mother Nazlı Metin, my aunt Sabahat Bayrakdar and my uncle Remzi Bayrakdar for their encouragement, support and belief in me all my life.

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ABBREVIATIONS

A : Absorbance
AI : Absorbance Index
DSC : Differential Scanning Calorimetry
g : grams
HDPE : High Density Polyethylene
J : Joules
LDPE : Low Density Polyethylene
LLDPE : Linear Low Density Polyethylene
min : Minutes
MPa : MegaPascals
NBR : Nitrile Butadiene Rubber
PA12 : Polyamide 12
PE : Polyethylene
psi : Pounds per square inch
rpm : Revolutions per minute
TPU : Thermoplastic Polyurethane

CHAPTER 1

INTRODUCTION

Accumulation of synthetic polymers in the landfills is 25 million metric tons in yearly basis [1]. Synthetic polymers have high versatility, desirable mechanical properties, chemical stability and biological inertness. Since synthetic polymers can be easily and inexpensively produced, it is inevitable that they are utilized for many applications, especially for single-use products and as a packaging material. The stability of these products is desirable for industrial purposes. On the other hand, the production of single-use products such as shopping and garbage bags from inert polyolefins, has its drawbacks. These products are widely used in daily life and, considering their low biodegradable characteristics, consequent environmental pollution is unavoidable [2,3].

Polyethylene (PE) is a polyolefin which is widely used due to its preferable mechanical characteristics, high diversity (HDPE, LDPE, LLDPE etc), good thermal properties, and easy processability with low cost [4]. Derivatives of PE are used to produce agricultural greenhouse and mulch films, food packaging, personal care products and disposable waste bags and carrier bags, such as shopping bags. Generally, products of PE are thrown away directly to the nature after a brief use. Therefore, PE accumulates in the environment due to its remarkable resistance to microbial attack; thus, generating pollution. Specifically, PE derivatives represent 64% of plastic material accumulation in the landfills. Recycling is economically unfeasible because PE films are very thin and have small masses [1].

Pollution caused by PE products can be reduced by providing them with biodegradable abilities.

1.1 Low Density Polyethylene

Low density polyethylene (LDPE) is a semi-crystalline polymer which has repeating -CH_2-CH_2- units. Tubular or a stirred autoclave reactor is used for LDPE production. Pressure and temperature parameters for this process are 82-276 MPa and 405-605 K, respectively. LDPE is obtained as the result of free radical polymerization. Peroxides and oxygen are used as initiators. It constitutes both long chain branches and short chain branches. Molecular weight distribution of LDPE affects its processability, melt strength, and film optical property, while its molecular weight distribution depends on the ratio of long chain and short chain branches. Since short chains disrupts chain packing of polymer, short chain branches decrease melting temperature and crystal density of LDPE. Thus, the ratio of long and short chain branches and the resulting molecular weight distribution significantly affect the mechanical and thermal characteristics of LDPE. High versatility is obtained by controlling the variation of these parameters. LDPE is used in many different application areas [5].

1.2 Resistance of Polyethylene

Microbial inertness of PE strongly depends on the molecular size of the polymer and its hydrophobicity. It possesses a high molecular weight and long chains, which cause serious problems in terms of biodegradation [6,7]. However, it is necessary to mention that, during the PE production process, tertiary carbons and oxygenated parts on the backbone could be formed, but the frequency of this type of defect is low, resulting in limited proper centers for radicalic reactions [8].

Additionally, PE’s repeating saturated -(CH_2-CH_2)- units lack any polar functional groups, such as nucleophilic or electrophilic centers, for starting radicalic reactions. Diffusion of water and oxygen is difficult on the surface of the polymer, especially in its crystalline zone [8]. Microorganisms are not produced metabolized molecules due to inappropriate environmental condition [6,7]. Consequently, they cannot cut long chains to form small fragments, in order to consume them using their enzymes [1,8,9].

In addition to all of these, the reason for biological inertness of PE is manufacturing processes that cause the increment stability of PE in the environment. In order to increase the life span of commercial PE, some stabilizers and antioxidants are added to prevent oxidation with atmospheric oxygen. Consequently, these additives make industrial PE more stable in the environment [1,7].

Based on this consideration, it could be concluded that PE is non-biodegradable polymeric material. As mentioned before, recycling process for PE products is economically unfeasible. On the other hand, environmental pollution due to PE can be prevented by converting stable PE to biodegradable PE. Biodegradable PE can be produced by adding functional group hydrocarbon backbone. Saturated carbon backbone could be disturbed by using pro-oxidant additive.

1.3 Biodegradation of Polymers

Biodegradable polymers can be examined in two groups:

- Some polymers are naturally biodegradable. Due to their chemical structure, these polymeric materials are subject to hydrolysis, photolysis, or pyrolysis, by direct action of enzymes, such as amylase and cellulase. Polysaccharides, proteins, lipids, and some polyesters could be produced from microorganisms, or bio-derived monomers can be used to produce such polymers. Nature of these polymers subsequently allows direct attack of microorganisms [10,11].

- The hydro biodegradable polymers need to go through chemical hydrolysis before the biodegradation process. This process occurs abiotically. Aliphatic polyesters and poly(lactic acid) could be given as examples of hydro

> biodegradable polymers. Additionally, this group includes oxo-biodegradable polymers. Synthetic inert polymers gain biodegradability by adding pro-oxidant (or pro-degrading) substances. These additives introduce abiotic degradation, with the help of external factors (e.g., UV radiation, heat, mechanical stress), that breaks long polymer chains. As a result, molecular weight of the polymer decreases and oxygen containing polar groups are formed, making the polymer more vulnerable to microorganisms [11].

According to TC249/WG9 of CEN (the European Committee for Standardization) oxo-degradation is "the degradation identified as resulting from oxidative cleavage of macromolecules", and oxo-biodegradation is "the degradation identified as resulting from the oxidative and cell-mediated phenomena, either simultaneously or successively" [10].

Oxo-biodegradable polymers provide significant economic advantages over biodegradable polymers. Manufacturing of biopolymers is 2.5 to 10 times more expensive than synthetic polymeric materials [11]. Also, recycling does not provide desirable consequences with respect to economic reasons. Since plastic packing materials carry contaminants such as residual food and biological substances, recycling of these polymeric materials are impractical. After the recycling process, plastics possess mostly insufficient mechanical properties. Additionally, collection and transporting of recycled polymer lead to high final production costs, when compared to production of oxo-biodegradable polymers [10,12]. Furthermore, bio polymers are produced by using renewable sources like plants, and they exhibit some physical and chemical properties which restrict their areas of application [11].

On the other hand, final production cost of oxo-biodegradable polymers is only about 10–20% higher than conventional polymers. It is vital to say that pro-oxidant additives can be used for commodity polymers such as polyethylene, polypropylene, and polystyrene. Additionally, commercial polymers containing oxo-biodegradable pro-oxidants do not lose any of their mechanical properties, when compared to the polymers that do not. Furthermore, residual products of the degradation process do not show any toxic effects on microorganisms. Consequently, using pro-oxidant additives to induce biodegradable characteristics for a widely used polymer like PE is an efficient practice in terms of both environmental and economical reasons [11].

1.4 Pro-oxidants

As previously mentioned, a convenient way to prevent inert polymeric material pollution in the environment is the usage of pro-oxidant additives. Burying in landfills is not a solution because of low biodegradable property of polyolefins. For instance, a bottle produced from PE shows minimal degradation on its surface, even after being buried in soil for more than 30 years [13].

To induce the degradability of PE, it is necessary to disturb the hydrophobic saturated long carbon backbone. With the help of pro-oxidant additives, functional groups are placed into PE chains. In other words, abiotic oxidation of polyethylene, which indicates the beginning of degradation, can be introduced by using pro-oxidants. When PE with prodegradant is exposed to UV radiation, heat, mechanical stress, or humidity, polymer matrix initially undergoes abiotic degradation. Then, residual product of abiotic degradation is consumed by microorganisms. This process is called biotic degradation [7,11]. Alternatively, polar group in the hydrophobic PE backbone can be achieved by using natural polymers such as cellulose and starch. Blending of PE and natural polymers enables degradation in polymer matrix, because natural polymers are vulnerable to microbial attack by nature. Also, blending increases the surface area of the synthetic bulk material; thus, making it more susceptible to abiotic oxidation. However, this scenario results in a complex interaction of abiotic and biotic degradation processes [2,9].

1.4.1 Pro-oxidants Containing Transition Metals

Transition metal ions are commonly used as pro-degradant additives. They have the ability to decompose hydroperoxide into free radicals, as seen schematically below:

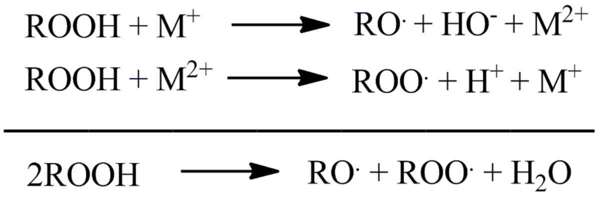


Figure 1.1 Metal ion catalysis of hydroperoxide decomposition into alchoxy and peroxy radicals [13]

Pro-oxidants containing transition metals such as Fe, Co, and Mn are widely used in the industry. These transition metals possess similar ion stability and oxidation numbers, differing by only one unit, e.g. Mn^{+2}/Mn^{+3}. These ions cause redox reaction with the help of external factors (UV light, heat, stress). In the presence of atmospheric oxygen, active and unstable hydroperoxides are formed as primary products in the carbon backbone by the help of ions. After that, free radicals are formed [3,7,14,15].

Nickel, silver, palladium, molybdenum, chromium, tungsten, and cerium can also be used for similar purposes. Pro-oxidants are formed by attaching metal ions to organic complexing agents. These complexes are activated by light or heat to start the degradation, which continues even without a source. Additionally, these complexes act as photoactivators in polymers even if in those that contain antioxidants and stabilizers. Also, it was shown that sulfur ligand (dibutylthiocarbamate) was used as a complexing anion. [16].

Acetyl acetonates, alkyl acetoacetates and alkyl benzoylacetates of manganese, cobalt, chromium, copper, and vanadium were cited as prodegradant systems. The alkyl acetoacetates and alkyl benzoylacetates of iron, nickel and zinc are also used to provide degradation characteristic to agricultural PE films. Examples of preferred prodegradants also include manganese stearate, manganese oleate, manganese acetate, cobalt acetate, cobalt stearate, cupric oleate, and ferric acetate [17].

Metal carboxylates such as cobalt, cerium and iron stearate and aliphatic poly hydroxyl–carboxyl acid were used together to form pro-oxidant. Citric acid is given as an example for acid structures in the report [18].

It was proven that fatty acid amide like oleamide could enhance prodegradant system containing transition metal salts such as cobalt nitrate or cobalt chloride [19].

1.4.2 Pro-oxidants Without Transition Metals

Although majority of pro-oxidants used in the industry contain metal ions there are some examples of pro-oxidants that do not contain transition metals.

Copolymerization is a way to improve photo-oxidation of inert PE. Polar carbonyl group can be incorporated into the polymer backbone, by copolymerization of ethylene with carbon monoxide. Side chain copolymerization of ethylene with methyl vinyl ketone gives ketone copolymer. Ketone copolymer in the backbone provides sunlight sensitivity, which promotes degradation. This process is called Ecolyte process [20].

The additives which constitute benzophenone provide degradability by UV light and air. Benzophenone based additives can also be used with other additives such as iron stearate and colored pigments, giving better results [21].

ɣ-pyrone ring compounds such as chromone, flavone, or xanthone are used to generate degradation ability in polymers. High presence of the additive in the polymer matrix causes migration to polymer surface. A low concentration is used to induce photodegradation [22].

Polyisobutylene is another pro-oxidant which does not contain transition metals. It improves the rate of the photodegradation of polyolefins [23].

Peroxide in the form of di-t-butyl peroxide, dicumyl peroxide, or diacetyl peroxide can be added to plastic to cut long chains to form small fragments. The master batch of peroxide contains 15-85% peroxide [24]. Also, peroxide can be utilized together with transition metal salts, antioxidants, and inorganic oxidants such as peroxides of alkali, alkaline earth, or transition metals [25].

Lastly, transition metal ions are widely used in polyolefins as pro-oxidants to provide biodegradability. PE degradation is commonly achieved by using stearates or organic ligand with transition metals as pro-oxidants. Transition metal complexes generally constitute Fe^{3+}, Mn^{2+}, and Co^{2+} metal ions. It is essential to point out that Fe^{3+} introduces photo-oxidation, but Mn^{2+} and Co^{2+} introduce thermo oxidation. As previously mentioned, after the oxidation process, chain scissions occur and PE chain fragments could be metabolized. Mechanical and optical properties of polymer resins stay nearly unchanged during their life spans [7].

1.5 Iron (III) Stearate Synthesis:

Essentially iron and stearate salts are used as pro-oxidant chemicals. Iron (III) stearate is synthesized as a result of metathesis reaction. Two alternatives of synthesis techniques could be followed as given below:

- Iron (III) chloride is dissolved in the calcium stearate aqueous solution. The mixture is agitated at 65°C for 30 to 40 minutes. After this process, precipitation is obtained. The precipitate is taken and dried at 60°C. The equation shows how reaction proceeds [26]:

$$3(C_{17}H_{35}COO)_2Ca + 2FeCl_3 \longrightarrow 2(C_{17}H_{35}COO)_3Fe + 3CaCl_2$$

- Solution of iron (III) chloride was entrained to sodium stearate aqueous solution. Agitation was carried out for 30 to 40 minutes; between 80°C and 90°C. The precipitate was separated and dried at 60°C. The equation shows how reaction proceeds [26]:

$$3(C_{17}H_{35}COO)Na + FeCl_3 \longrightarrow (C_{17}H_{35}COO)_3Fe + 3NaCl$$

1.6 Oxo-Biodegradation of PE

Oxo-biodegradation process consists of two steps: abiotic degradation and biotic degradation. Firstly, abiotic degradation occurs and it initiates the biotic degradation, which is the second stage of the degradation process.

1.6.1 Abiotic Degradation

Light, heat and mechanical stress leads to some irreversible changes on the polymer structure. These transformations are the initial step of what is called abiotic biodegradation. During the abiotic process, structure of polymer losses its mechanical properties significantly. Then, abiotic degradation induces biotic degradation [27].

Rate of biodegradation reaction is obtained in the abiotic process. During this period, hydrophobic nature of the polymer evolves into a hydrophilic nature. Thus, polymer gains wettability and becomes more vulnerable to enzymatic reactions. After consumption of long and short term stabilizers and antioxidants, abiotic degradation begins. The first step is the reaction of the polymer with the atmospheric oxygen. This process produces oxygenated groups that have hydrophilic structures, thanks to the pro-oxidant additive. During abiotic process, oxygen incorporates with carbon backbone and forms radicalic fragments that possess polar functional group such as carboxylic or hydro-carboxylic acids, esters, aldehydes, and alcohols [7,8,13].

Degradation starts in the amorphous region at the surface of the polymer. Compared to the crystalline part, water diffusion is easier in the amorphous region. Also, surface of the polymer is subject to high intensity of oxygen and high temperature. Brittle layer is formed on the polymer surface, and erosion degradation (surface degradation) takes place. Finally, degradation proceeds towards the center of the polymer and bulk degradation occurs.

During the degradation process, molecular weight of polymer decreases due to chain scission and crosslinking. Two types of chain cleavage occurring are depolymerization and random. Depolymerization chain scission occurs in the terminal of the chain. On the other hand, random chain cleavage occurs in the backbone of the polymer. Molecular weight decline due to random chain scission is higher than depolymerization. Consequently, mechanical characteristic of polymers decreases due to dramatic losses in molecular weight [6,10].

Increasing number of polar groups in the polymer backbone and structural changes in PE during the degradation process can easily be observed by using FTIR technique. It is proven that, pro-oxidant additive containing LDPE shows degradability properties under environmental weathering or heat. After weathering, polar groups are formed in the polymer backbone -in the carbonyl region between 1800 cm^{-1} and 1650 cm^{-1}- and increased absorption is observed. The reason for this is the formation of oxidized products such as carboxylic acids (1708-1698 cm^{-1}), aldehydes (1740-1733 cm^{-1}), and lactones (1786-1780 cm^{-1}). During abiotic process, formation of hydroperoxides and alcohols are also observed. The peaks belonging to these groups are seen at 3800-3050 cm^{-1} [28]. It is clearly demonstrated that apolar, saturated, hydrophobic backbone turns into hydrophilic form. Polar groups in the backbone causes further oxidation of polyethylene. Consequently, molecular weight of PE decreases dramatically in this stage. That means that PE chains become vulnerable to biological action.

Abiotic degradation is accelerated by UV radiation (photodegradation), thermal degradation, or mechanical stress, as mentioned before [7,8,13,29].

1.6.1.1 Photodegradation

One of the reasons for abiotic degradation is sun light and UV light (high energy radiation). Degradation due to light is called photodegradation. It could be said that UV radiation is the most powerful factor in polymer degradation. This external effect causes fragmentation in the polymer chain with the help of oxygen. As a result of UV radiation absorption, hydroperoxide group is generated. This group is unstable both photolytically and thermally. Hydroperoxide group forms radical groups, which cause the fragmentation of the backbone. Eventually, due to chain scission, PE backbone becomes sensitive to microorganismal action [4].

1.6.1.2 Thermal Degradation

Thermal degradation is another type of abiotic degradation that gives similar results with oxidation by light. However, ketone products, as primary oxidized groups, are stable under heat, but sensitive to light. Ketone groups on the polymer backbone undergo Norrish I and/or Norrish II reactions (Fig.1.2). After this photo-oxidation, they are consumed. Intensity of temperature determines the rate of thermal degradation. As temperature increases, degradation also increases [13].

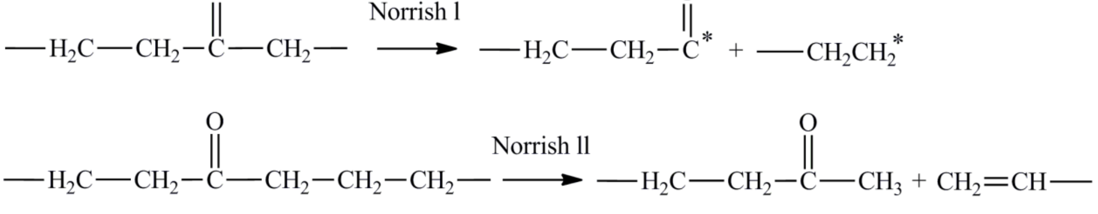


Figure 1. 2 Photolysis reactions of ketones [13]

1.6.1.3 Degradation from Mechanical Stress

Although mechanical influences are not the main reason for biodegradation process, mechanical force applications on polymers increase the rate of degradation. Morphology of the polymer affects the degradation process. It is obvious that mechanical actions, such as compression, tension, and/or shear forces, cause some transformation in the morphology of polymer. After the mechanical processes, polymer becomes more vulnerable to oxidation reaction. Mechanical stress influences photodegradation in a positive way [13, 27, 30].

Figure 1.3 displays abiotic degradation process of pro-oxidant containing PE. Pro-oxidant includes iron transition metals. First, pro-oxidant experiences redox reaction under radiation, and generates radicals. These radicals initiate the degradation process. They abstract the hydrogen in the polymer backbone. Then, atmospheric oxygen is captured to form peroxide. Peroxide structure causes polar groups such as alcohol ketones and double-bond containing structures to appear. Finally, aldehyde is obtained and ester and lactones are formed, which are vulnerable to microbial attack.

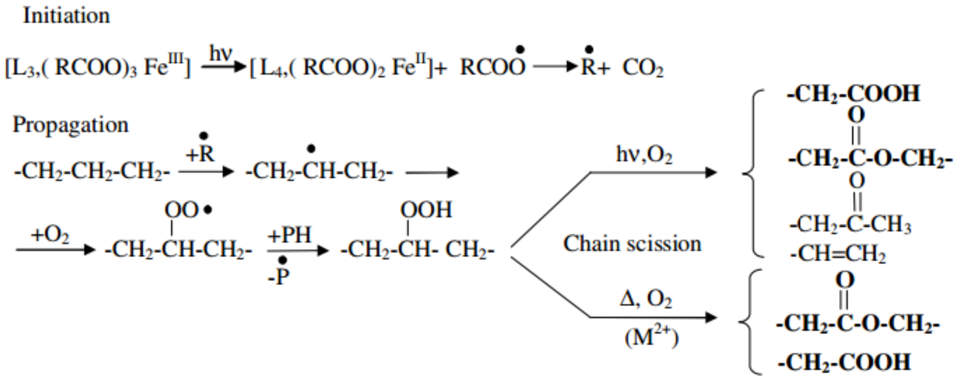


Figure 1. 3 Abiotic degradation of PE with pro-oxidant content PH polymer chain, L suitable ligand [8]

1.6.2 Biotic Degradation

The second stage involves depleting low molecular weight compounds, and polar and oxidative carbon backbone fragments being produced in abiotic process by microorganisms (bacteria, fungi and algae). The significant point during this step is that the microorganism growth is sustained due to depletion of low molecular weight compounds. The consumption of abiotic degradation products, such as ketones, esters and lactones, indicates microorganism growth.

At the final step, microorganisms consume fragments of PE to form carbon dioxide, water, and biomass, as end products [13].

Biodegradation process contains chemical and biological complexities which make it difficult to understand its mechanisms [29,31].

Two approaches are carried out to test biodegradation of pre-oxidized PE, to provide better understating of biotic degradation. First approach deals with the biodegradation process for pre-oxidized PE film in the natural environment. After the abiotic process, PE film is examined under natural conditions such as soil, compost, or waste water sludge. Under these conditions, mineralization of pre-oxidized PE film was clearly observed with various microbial incolumn. In the second stage, mineralization of PE film is carried out under controlled experimental conditions. A defined microbial strain that is formulated from defined chemical compounds is used. This method enables to systematize the biodegradation process and to reproduce it [29,31].

1.7 Controlling the Degradation

As discussed before, due to the nature of synthetic hydrocarbon polymers, these polymers show high resistance to degradation. However, biodegradability is a requirement for inert polymers due to environmental concerns. Non-biodegradable polymers could gain oxo-biodegradable abilities with the aid of pro-degradant additives [32].

Although degradation of plastics is significant, polymers should protect chemical and physical stability during their service life because of commercial concerns [32]. Desired service life of oxo-biodegradable polymers differ according to application area. For instance, green house covers would require much longer life, but shopping bags are supposed to degrade in a short time. Therefore, adjustment of life cycle of oxo-biodegradable plastics is an important issue.

It is expected for oxo-biodegradable polymers to protect their properties during production process and expected service time. After this time period, biodegradable plastics should disintegrate to be metabolized as an end product. Life span of biodegradable polymers is affected by many factors.

Amount of pro-oxidant added into the polymer matrix affects the degradation time. Pro-oxidants can be added in the polymer resin between 1 to 5% concentrations. As the amount of pro-oxidant in the polymer matrix increases, service life of the plastic decreases [11]. However, it should be underlined that, high content in the polymer matrix causes some problems. It can migrate to the surface of the polymer. Adding pro-oxidant provides faster biodegradation, but at high concentrations it could be toxic for microbial strain. For instance, Co containing pro-oxidant could be fatal for microorganisms at high concentration. Therefore, pro-oxidant content in the polymer matrix is a critic issue [29].

Another important parameter for adjustment of life span of oxo-biodegradable polyolefins is controlling the beginning and the rate of peroxidation process. Amount and type of short and long term stabilizers influence peroxidation process.

During the process, thermal antioxidants provide protection from degradation. It prevents the formation of hydroperoxide groups, and controls the pro-oxidant action in the polymer matrix. Process stabilizers such as organic phosphites prevent degradation at the processing temperatures [33]. However, they do not affect the formation of peroxide during the service life.

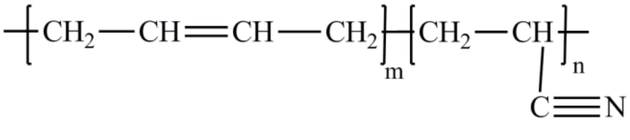
Long terms stabilizers also affect biodegradation property of polymers. Long term stabilizers like UV absorbers bring stability during use and storage.

Furthermore, addition of organic dyes and inorganic pigments can affect degradation rate since their structure possess some pro-oxidant-like unsaturated structures. Particle size, surface treatment, crystalline form, and metal ion dopants can influence photoactivity of these substances [34].

Consequently, life time of the polymer can be controlled by arranging the amount of pro-oxidant in the polymer matrix. Also, correct combination of pro-oxidant, and long and short term stabilizers is a crucial issue to adjust polymer service life. Based on this consideration, life span of polymer can be adjusted to be as low as 3 days or 5 years [35].

1.8 Nitrile Butadiene Rubber

Nitrile butadiene rubber, namely acrylonitrile butadiene rubber, is a synthetic rubber that is copolymer of acrylonitrile and butadiene monomers. The structure of the rubber is seen below.



$$-\left[CH_2-CH=CH-CH_2\right]_m\left[CH_2-\underset{\displaystyle C\equiv N}{\underset{|}{CH}}\right]_n-$$

Figure 1.4 Structure of Nitrile Butadiene Rubber [37]

In production process, two important parameters, polymerization design and temperature, affect the final product properties. NBR are produced by two ways: cold process and hot process. Obtaining linear polymer with less gel, cold polymerization technique is carried out from 5 °C to 30 °C. Gel is the branching of the polymer chain. On the other hand, hot process is used to produce firmer structures. During this process temperature is kept between 25 °C and 50 °C [36].

Additionally, nitrile content strongly affects chemical and physical properties of rubber. Nitrile content can vary between 15% and 50%. Increasing the nitrile concentration in NBR, Tg, hardness, tensile strength, heat resistance etc. increases, but resilience and permeability decreases. 31-35% nitrile content is widely used in the commercial area [37].

1.9 Polyamide 12

Among the polyamides present in market, one of them is polyamide 12, namely nylon 12. It is a type of aliphatic polyamide which is highly processable.

Monomer of nylon 12 is aminolauric acid. It contains amine group on one end and acid group at the other end as repeating units. It polymerizes itself and constitutes 12 carbon atoms in the backbone. The structure is seen in Figure 1.5.

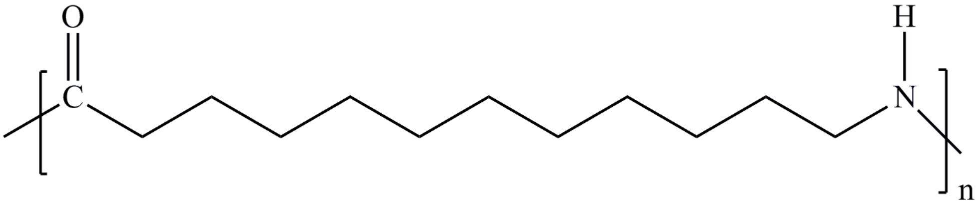


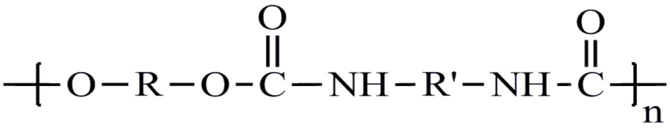
Figure 1.5 Structure of Polyamide 12 [38]

The polymerization form is hydrolytic polycondensation polymerization. During the process, temperature is kept between 260 °C and 300 °C. The concentration of amide group in the polymer backbone affects properties of polyamide. Lowest concentration polyamide gives semi-crystalline structure. Additionally, it shows the lowest absorption of humidity (~2%) among the polyamides [38].

1.10 Thermoplastic Bio Based Polyurethanes

Thermoplastic polyurethanes (TPUs) are a type of block copolymer that are composed of hard and soft segments. Generally, hard segments are alternating diisocyanates and short chain extender sequences. The soft segments consist of long chain diols like polyester, polyether, or polycaprolactone. The type of polyols determines the final features of polyurethane. Presence of diols in the TPU structure leads linear thermoplastic polyurethane. On the other hand, polyols in the structure provides thermoset property to polyurethane [39].

Bio-based polyurethane from vegetable oils can be studied in three different types: polyester polyol, polyether polyol, and oleochemical polyols. Polyester based bio polyurethane is naturally vulnerable to hydrolysis and microorganism attack [40]. Figure 1.6 shows simple representation:



$$\left[O-R-O-\overset{\overset{O}{\|}}{C}-NH-R'-NH-\overset{\overset{O}{\|}}{C} \right]_n$$

Figure 1. 6 Structure of Polyurethane

1.11 Aim of the Study

The aim of this thesis is to prepare an interior marker to be put into oxo-biodegradable PE shopping bags, in order to assess the presence of any pro-oxidant additive used by the company, following the FTIR-ATR technique.

Thus, the confidence level for the usage of pro-oxidant additive in PE shopping bags is improved.

In order to achieve this purpose, three different master batches were prepared by using nitrile-butadiene rubber (NBR), polyamide 12 (PA12), and bio-based thermoplastic polyurethane (TPU) polymers. Shopping bag raw material containing interior marking with different concentrations, and pro-oxidant additive with fixed concentration was prepared by using extruder. The LDPE sets were prepared as thin films in order to detect interior marking observability, by using ATR-FTIR technique.

NBR, PA12, and bio-based TPU were chosen as the interior marking in PE matrix due to its compatibility with PE, non-toxicity, nonvolatile property, economy, and availability. Additionally, iron stearate was used as a pro-oxidant additive since this additive is commonly used in the commercial area. This type of stearate provides biodegradable property to inert polymer when it is exposed to light. It is not sensitive to thermal oxidation. It is a reasonable option for thermal processes.

ATR-FTIR method was used to detect interior marking, because this technique is widely used for polymeric analysis with low cost. Also, it gives fast and reliable results.

CHAPTER 2

EXPERIMENTAL

This chapter includes the materials and the used in the thesis project. Additionally, process of sample preparation and analysis methods are expressed.

2.1 Materials

In the study, low density polyethylene (LDPE) was used as a polymer matrix. Nitrile butadiene rubber (NBR), polyamide 12 (PA12), and thermoplastic polyurethane (TPU) was used as interior marker polymers. In addition, Fe stearate master batch was utilized as oxo-biodegaradable pro-oxidant additive.

2.1.1 Low Density Polyethylene (LDPE)

LDPE is the product of Petkim Petrokimya Holding A.Ş. (Turkey) which is marketed under the commercial name Petilen F2-12. The specifications of F2-12 LDPE are seen Table 2.1 [41]:

Table 2.1 Specification of LDPE

Property	Unit	Value	Test Method
Density, 23°C	(g/cm^3)	0.918- 0.922	ASTM D-1505
Melt Flow Rate (MFR) (190°C / 2.16 kg)	(g/10min)	2.1 – 3.0	ASTM D-1238
Melting Temperature	(°C)	100-115	ASTM D-3418

2.1.2 Nitrile-butadiene Rubber (NBR)

M300-1041 nitrile-butadiene rubber (Goodyear) was used in this thesis study. Its nitrile content is ~ 20%. Tg value is -60 °C for ~20% acrylonitrile content.

2.1.3 Polyamide 12 (PA12)

Polyamide was purchased from Rilsamid by Arkema (France). Trade name of the product is AESN Noir P201 TL. General information is shown in Table 2.2 [42].

Table 2.2 Specification of PA12

Property	Unit	Value	Test Method
Density	(g/cm^3)	1.01	ISO 1183
Melt Volume Index (235°C / 5 kg)	(cm^3/10 min)	5	ISO 1133
Melting Temperature	(°C)	176	ISO 11357

2.1.4 Thermoplastic Polyurethane (TPU)

Thermoplastic polyurethane was supplied from Merquinsa (Spain). According to ASTM-D6866, it is a polyester based bio-TPU, which contains 46% bio-based content. Its trade name is Pearlthane® ECO D12T85. Some of its characteristics are illustrated in the table below [43]:

Table 2.3 Specification of TPU

Property	Unit	Value	Test Method
Density	(g/cm^3)	1.15	ISO 2781
Melting Flow Index 10g/10 min	(°C)	190-200	ISO 1133

2.1.5 Oxo-biodegradable Pro-oxidant

In this study, Fe stearate master batch was used as a pro-oxidant additive which was supplied as pellets. The degradant was supplied from ÇEV-R Çevre Teknolojileri (formerly TRPOLİMER A.Ş.) (Turkey). The trade name of the product is 1NTR001.

2.2 Instrumentation

This section contains instrument types which were used to prepare samples. Brabender was used to obtain master batches of samples. Dilute LDPE sets containing pro-oxidant additive were prepared by using extruder machine. Hydrolic press was used to make thin films. Finally, the sets were analyzed by the ATR-FTIR instrument. Moreover, property of polymer matrix was checked out by applying mechanical tests and thermal processes.

2.2.1 Hydraulic Press

Hydraulic press of PHI Corporation was used to make thin films. Constant temperature and pressure adjustments were provided.

2.2.2 Extruder

In this thesis, twin screw extruder was used in order to add pro-oxidant additive. Type of extruder was Haake extruder, Haake Rheomax OS PTW16 twin-screw system, and Haake PolyLab OS RheoDrive 4 drive system, which is produced by Thermo Electron Corporation. The extrusion took place at 75 rpm with ten different temperature zone adjusted as seen below:

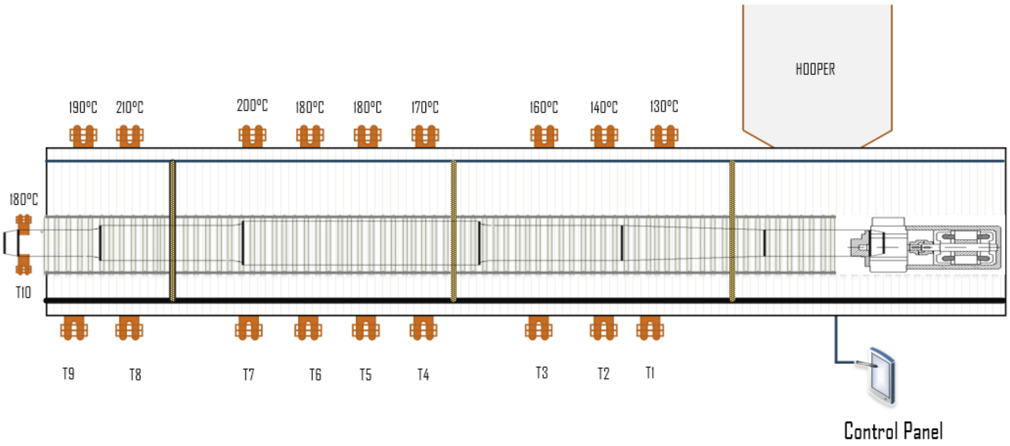


Figure 2.1 Illustration of Extruder Machine with Temperature Zone

2.2.3 ATR-FTIR Spectroscopic Instrument

Thermo Scientific Nicolet™ iS™10 FT-IR Smart Omni-Transmission Spectrometer were used for analyzing every thin film. The crystal type was anvil diamond. The resolution and number of scans were set as 8 cm^{-1} and 24 s^{-1}, respectively.

2.2.4 Universal Testing Machine

LLYOD LR5K Mechanical Tester was used for mechanical testing. Applied load value was 100N which has 015235 serial no, 0.5% grade. It is produced by LLOYD Instruments LTD Segenworth Fareham (England).

2.2.5 Thermal Analysis

Differential scanning calorimetry (DSC) analysis was carried out by using SCINCO DSC N-650 type.

2.3 Experimental Procedure

This part gives information about the experimental setups and procedures. The followed procedure includes preparing master batches, thin films and testing and analysis of the obtained thin film samples.

2.3.1 Preparing Blend Master Batches

The master batches were prepared in Brabender Plasticorder Torque Rheomether. Contents of master batches were acrylonitrile-polyethylene (AN-PE), polyamide12-polyethylene (PA12-PE) and thermoplastic polyurethane–polyethylene (TPU-PE). The sets of master batches were arranged in weight ratios of 30% (w/w), 40% (w/w), and 50% (w/w) concentration. For AN-PE master batch sets, the temperature was constant at 180 °C and mixed at 75 rpm for 10 minutes. For PA12-PE master batch was set 210 °C and mixed at 75 rpm for 5 minutes, then rpm was increased to 150. At this rpm, master batch was mixed for 5 minutes. These conditions were also applied for TPU-PE master batches. Before mixing, PA12 and TPU were dried to remove moisture at 60 °C for 12 hours in the oven.

2.3.2 Preparing Dilute Samples

These sets were prepared in weight ratio 1% (w/w), 0.8% (w/w), 0.5% (w/w), 0.25% (w/w), 0.15% (w/w) and 0.09% (w/w) marker concentration. The pro-oxidant additive concentration was kept constant for 1% (w/w) ratio for every sample set.

2.3.3 Preparing Dilute Film Samples

AN-PE, PA12-PE and TPU-PE sets which were consist of 1%, 0.8% 0.5% 0.25%, 0.15%, 0.09% weight to weight ratio samples were produced by Haake extrusion machine. After this step by using hydraulic press produced by PHI Corporation, thin films were made. Thickness of films varied between 65 µm to 35 µm. AN –PE sets pressed at 180°C. Firstly, pellets were melt at 5000 psi between steel plates for 5 minutes, and then pressure was increased steadily until 20000 psi and waited for 5 minutes. Finally, films were quenched into top water for 1 minute and cooled to room temperature. The same steps were applied for PA12-PE and TPU-PE sets, but applied at 210°C temperature.

2.4 Analysis and Testing of Obtained Films

The content of this section is analysis and testing type which were applied during the study. Presences of interior marker polymers were proved by using ATR-FTIR instrument. Then, stability of polymer matrix was investigated by applying mechanical tests and thermal analysis.

2.4.1 Spectroscopic Analysis

ATR-FTIR measurements were taken in order to follow the existence of marker polymer in dilute sample. According to master batches spectrum of AN-PE, PA12-

PE and TPU-PE reference peaks were firstly determined. Based on this consideration, differential peaks were observed.

2.4.2 Mechanical Testing

1%, 0.5% 0.09% concentrated samples of each polymer sets and pure PE films were performed mechanical testing. These results were evaluated under the consideration of ultimate tensile strength (MPa), stress at yield (MPa) and percentage strain at break. AN-PE, PA12-PE and pure PE films thickness varied between 0.55-0.350 μm. TPU-PE films were 270-150 μm. Dog bone shaped films had gauche length 50 mm, width 3 mm, and speed of drawing was 50 mm/min. Mean of results which were performed at least 4 different films were reported and sketched stress- percentage strain graph of each.

2.4.3 Thermal Analysis

For this stage, the samples which were also used for mechanical testing were analyzed. Firstly, to obtain thermal properties of sample, DSC analysis was carried out for temperature range 25°C to 200°C at heating rate of 20°C/min. Finally, isothermal process was carried out at 200°C.

CHAPTER 3

RESULTS AND DISCUSSION

In this thesis, FTIR-ATR instrumentation technique was chosen as a methodology. FTIR spectroscopy is commonly used in polymer industry since it provides both quantitative and qualitative analysis for polymers [44]. By using this method, composition of polymers, copolymers, polymer blends, composites could be obtained. This technique is used to determine not only chemical nature of the polymer but also its chemical order. Streoregularity, crystallinity, branching or crosslinking of polymers can be achieved [6,45,46]. It also gives reliable and fast results with easy sample preparation. That is why FTIR-ATR method was preferred for this study to detect interior marking in PE matrix.

All dilute raw materials with predetermined concentrations were prepared by using extruder and thin films were made by using hydraulic press. Preventing thermal degradation during these processes, optimum pressure and temperature were set.

Additionally, iron stearate was used as a pro-oxidant type since pro-oxidant additives which contain transition metals particularly iron is widely used in industry. Also, it was reasonable choice for this study due to thermal processes. This pro-oxidant prevented thermal degradation during processes because it was triggered by light not heat.

3.1 IR Spectra of Pure Polymers

LDPE was used as a polymer matrix. Additionally, three different polymers were chosen as marker polymers. The polymer markers were selected for being compatible with PE, nontoxic, nonvolatile, cheap and available.

It is seen in this study that vibrations of CH_2 groups could be seen only at 2926 cm^{-1} but there should be also another peak at 2851 cm^{-1}.That means CH_2 group vibrations are not seen in details in the spectrum. Since sample films are a bit thick; therefore, loss of incident radiation energy takes place [44].

3.1.1 IR Spectrum of Pure PE

PE constitutes -(CH_2-CH_2)- repeating units; therefore, the ATR-FTIR spectrum of PE contains C-H and C-C linkage vibrations. The spectrum is seen below (Fig.3.1). Two stretching vibrations and four deformation vibrations occurs due to vibrations of CH_2 groups. In-phase (symmetrical) or out-of-phase (asymmetrical) vibrations of CH_2 groups could be seen at 2926 cm^{-1} and 2851 cm^{-1}. Deformation vibrations of CH_2 could also place in-plane or out-of-plane. In-plane vibrations which is named scissoring vibrations of CH_2 groups are seen near 1460 cm^{-1} and 720 cm^{-1}. Additionally, the peak near 1300 cm^{-1} represents out-of-plane deformation modes [47]. It is necessary to add that peak which is near 1894 cm^{-1} related to the crystalline structure of PE but the band which is 1303 cm^{-1} gives information about amorphous character of the polymer [44]. Deformation and stretching vibrations of C-C linkages in PE are highly coupling and shows weak absorptions.

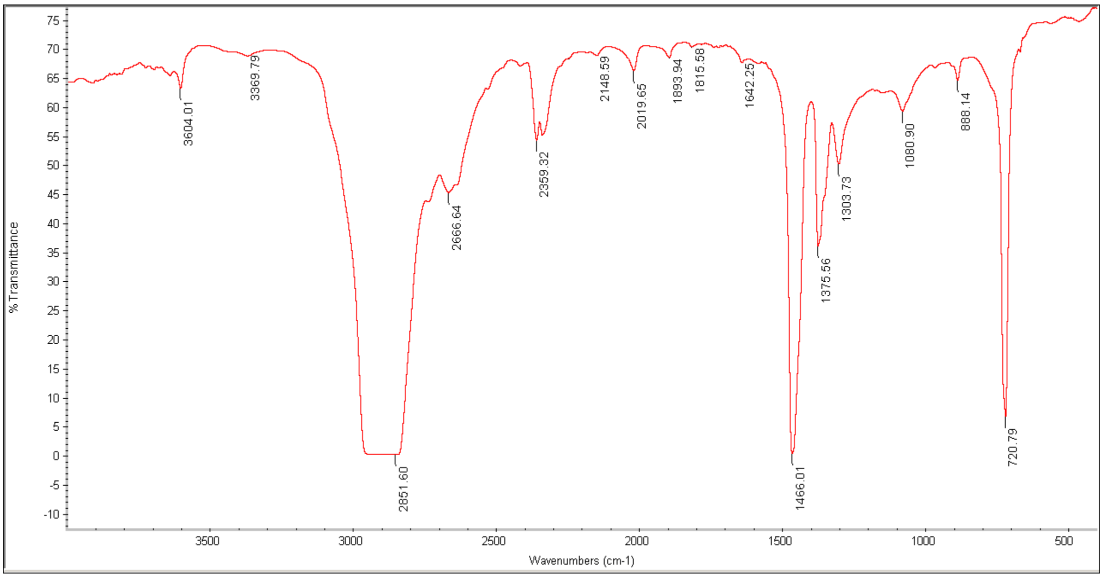


Figure 3.1 Pure PE Spectrum

3.1.2 IR Spectrum of Nitrile Butadiene Rubber (NBR)

NBR was chosen first interior marker polymer since polymer contains -CH_2- which makes it compatible with PE. NBR is result of copolymerization between acrylonitrile and butadiene. Polyacronitrile constitues -$(CH_2\text{-}CH(\text{-}C{\equiv}N))_n$- repeating unit as well as polybutadiene is formed -$(CH_2\text{-}CH{=}CH\text{-}CH_2)_n$-. Property of final NBR depends upon ratio of these units.

Polyacrylonitrile contains -C≡N group and butadiene includes part C=C double bond; therefore, peaks of these two part is seen in the spectrum.

Nitrile group, -C≡N, stretching vibration is seen the band near 2238 cm^{-1} [48]. This specific peak was followed as a marker peak. Double bond in the butadiene part absorbs near 1640 cm^{-1} and 969 cm^{-1}. Furthermore, presence of C-H bond in this part shows a band near 1440 cm^{-1} [49].

The spectrum containing 27% acrylonitrile content is given as an example spectrum (Fig. 3.2)

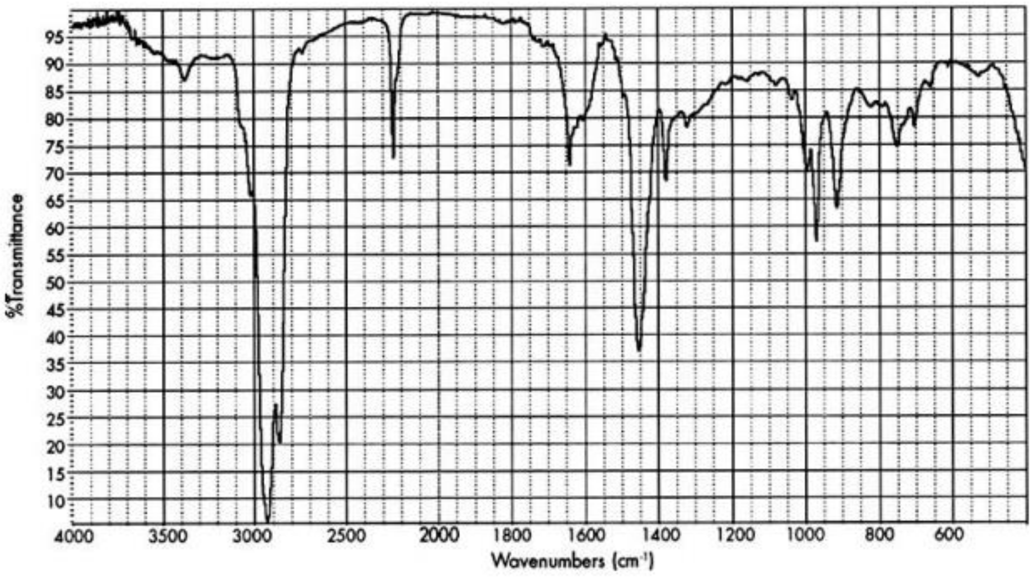


Figure 3.2 NBR (27% Nitrile Content) Spectrum [50]

3.1.3 IR Spectrum of Polyamide 12 (PA12)

PA12 was chosen as second interior marker polymer in this study. PA12 contains the longest -(CH_2)- part on the polymer backbone among the polyamides, it, therefore, sustains compatibility with polymer matrix at reasonable level. Additionally, absorption of humidity is lowest.

PA12 is a type of secondary polyamide which possesses polyamide characteristic peaks. The spectrum could be seen following (Fig. 3.3). Free N-H stretching vibrations due to free N-H bonds is seen in the region between 3280 cm^{-1} and 3330 cm^{-1} in the spectrum. Carbonyl peak is specific for this polymer due to hydrogen bonding with N-H and O=C group. Particularly, in solid state, carbonyl group in amide is seen 1640cm^{-1}. This specific peak was preferred as a marker peak. The reasons of 1290 cm^{-1} and 1300 cm^{-1} peaks are O-C-N and N-H bonds. These peaks have weak absorptions [47].

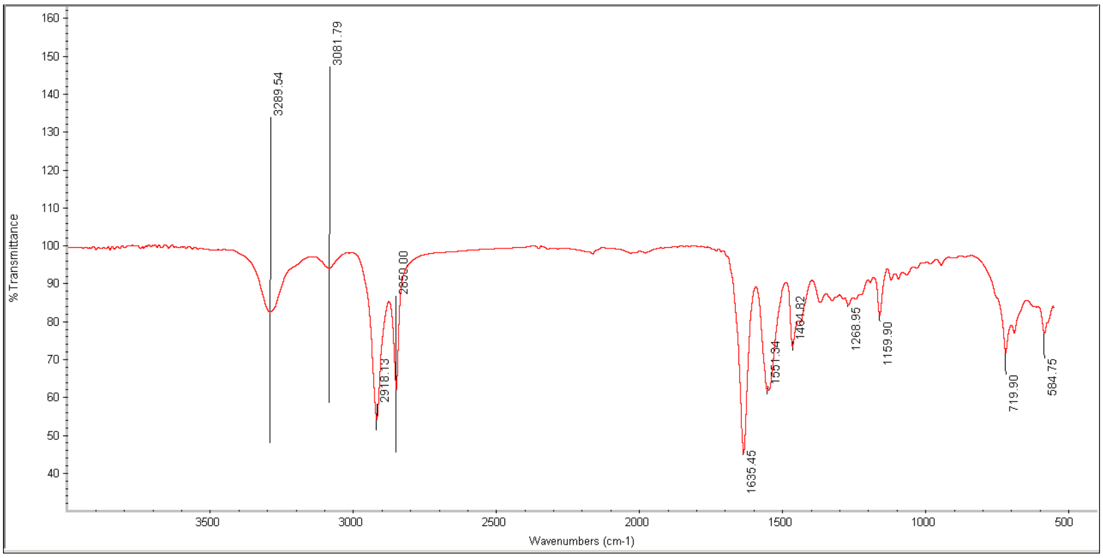


Figure 3.3 Pure PA12 Spectrum

3.1.4 IR Spectrum of Thermoplastic Polyurethane (TPU)

In this thesis, thermoplastic polyurethane was preferred as third interior marker polymers.

TPU is obtained by polymerization of a diisocyanate, a short chain diol (chain extender) and a long chain diol. The result of this reaction a block copolymer is formed. It could be said that soft segment of TPU provides compatibility with PE at acceptable level.

TPU contains both N-H and C=O groups in the hard segment. There is strong hydrogen bonding interaction between these two groups. As a result of this overlapping bands are observed in the spectrum (Fig. 3.4). In the spectrum, N-H stretching vibration is seen at near the 3325 cm^{-1}. Furthermore, a strong peak which belongs to hydrogen bonded carbonyl group in the structure is seen at approximately 1730 cm^{-1}. This peak was chosen as a reference peak for the TPU based interior marker. In addition to all of these, CH_2 group vibration is observed at near 2900 cm^{-1} and 2850 cm^{-1} [51].

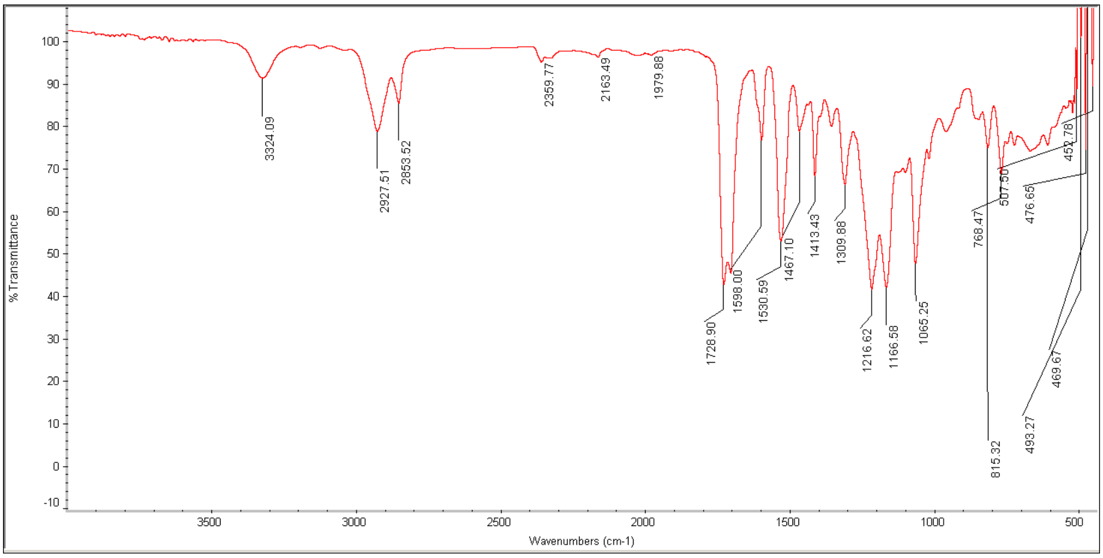


Figure 3.4 Pure TPU Spectra

3.2 IR Spectra of Nnitrile Butadiene Rubber (NBR) Master Batches

Under the light of peak assignment of pure nitrile butadiene rubber, -C≡N (cyano group) was chosen as an interior marker peak. The peak was seen between 2238 cm^{-1} and 2237 cm^{-1} in the spectrum. The master batches were prepared three different concentrations. Nitrile butyl rubber content in the master batches is 30% (w/w), 40% (w/w) and 50% (w/w). For this stage, high amount of polymers were mixed. If blend was not mixed desirable level, quality of raw material would affect in negative way. Therefore, compatibility of NBR and PE was critical matter for this step.

3.2.1 NBR 30% (w/w) Concentrated Master Batch Absorbance Index

This master batch set was arranged in weight ratios of 30% (w/w) nitrile butadiene rubber content by using Brabender. Four thin films were prepared and for each film two cross-sections were taken for FTIR analysis. In this thesis, both transmittance and absorbance spectra of samples were taken into consideration. Transmittance spectra were used to detectability of interior marker peak. After analyzing of spectra, the marker peak was decided which is nitrile peak at 2237 cm^{-1} (Fig.3.6). Furthermore, absorbance spectra of sample was used to obtain quantitative information about sets since absorbance is linear function and gives better information about attenuation of radiation.

Absorbance spectrum was determined by using ATR-FTIR Omnic program. This program provided to attain absorbance spectrum from transmittance spectrum of samples. Height of reference peak which was nitrile peak at 2237 cm^{-1} was measured as absorbance by using program. Moreover, absorbance of PE peak at 720 cm^{-1} was got by using same way. Additionally, absorbance of nitrile peak was divided to absorbance of PE peak which was used to determined absorbance index values of samples (AI 2237 cm^{-1}). This evaluation is given as a simple expression below:

$$Absorbance\ Index\ for\ Nitrile\ Rubber = \frac{absorbance\ of\ 2237\ cm^{-1}\ peak}{absorbance\ of\ 720\ cm^{-1}\ peak}$$

Absorbance index values of samples were used to minimize error due to thickness differences between films since thicker films compare to thin films give higher absorbance values. Moreover, mean and standard deviation of absorbance indices were calculated. The purpose of obtaining mean and standard deviation values of the set is to show interval of absorbance indices for this set. Most likely, the peak for this specific concentration would be observed within the interval. Otherwise, absences of the marker or an impurity absorbing are considered.

Absorbance indices of NBR 30% is given in the Table 3. 1. For each set, FTIR measurements were carried out at least six samples to ensure better confidence.

Table 3.1 Absorbance Index Values of NBR 30% (w/w)

at 2237cm^{-1}	1	2	3	4	5	6	7	8
AI x10^{-1}	3.975	4.657	4.322	4.691	4.136	4.515	4.197	4.063

Figure 3.5 shows absorbance index variation of each sample. Mean and standard deviation of the set was calculated to estimate precision of the measurement. The results of the set were close to each other and show repeatability. These two numbers which are 0.431 and 0.027 show the average of eight sample absorbance indices and corresponding standard deviation, respectively. This evaluation was applied for all interior marker master batches and dilutes sets absorbance index values to show interval. It could be expected that prospective absorbance values for this concentrated set would be within this interval.

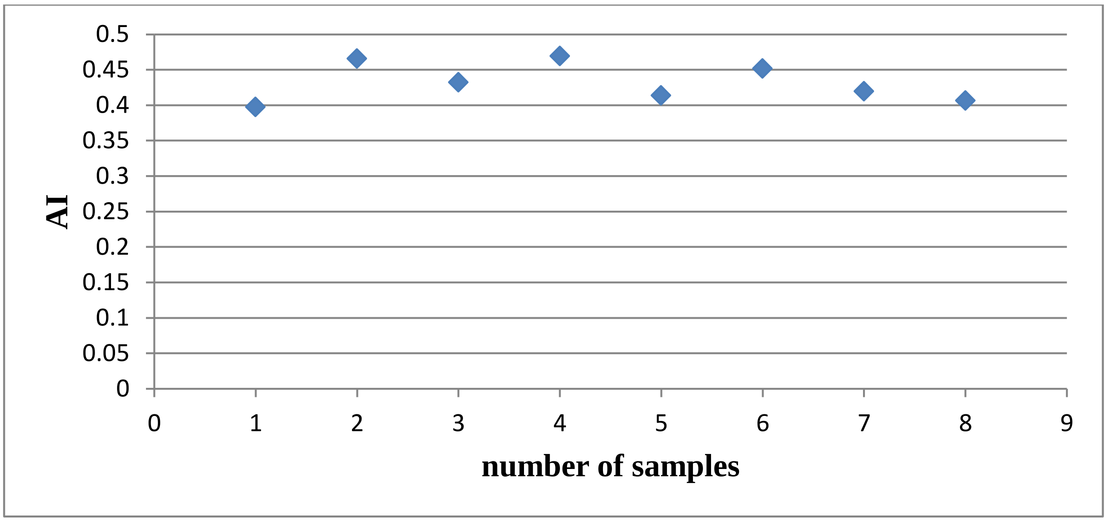


Figure 3.5 Absorbance Index Values of NBR 30 % (w/w) Set with Range [0.431±0.027]

The Figure 3.6 is the spectrum of 30% (w/w) concentrated acrylonitrile butadiene rubber master batch. The reference peak is certainly observed at 2237 cm^{-1}.

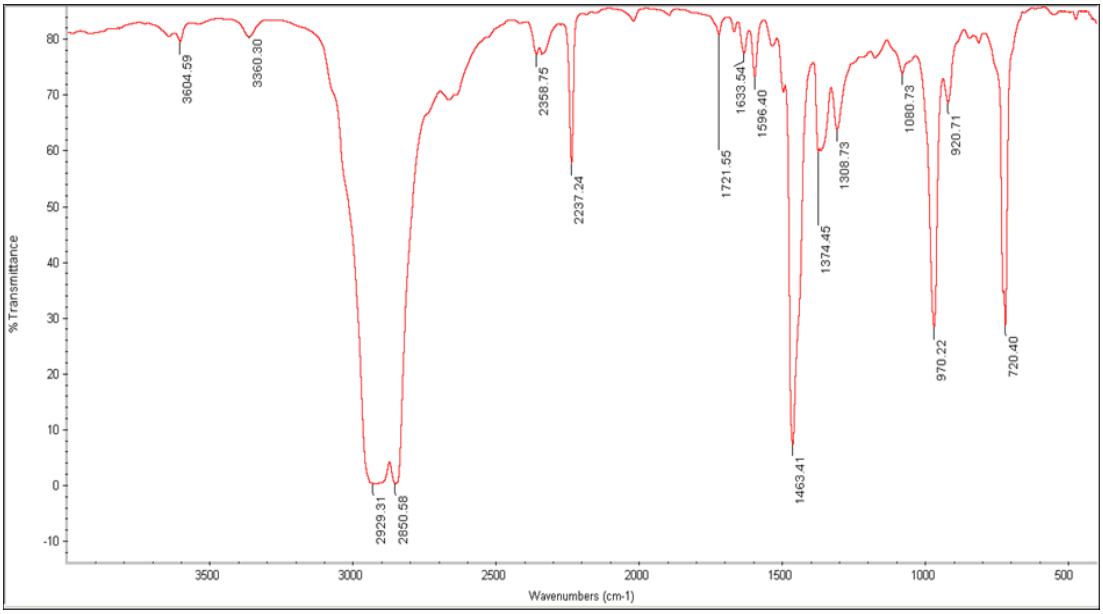


Figure 3.6 Spectrum of NBR 30% (w/w) Sample

3.2.2 NBR 40% (w/w) Master Batch Concentrated Master Batch Absorbance Index Values

This master batch set was prepared in weight ratios of 40% acrylonitrile concentration by using Brabender. The same steps were followed with NBR 30% master batch. Absorbance index results of this set are summarized in Table 3.2.

Table 3.2 Absorbance Index Values of NBR 40% (w/w) Set

at 2237cm^{-1}	1	2	3	4	5	6	7	8
AI x10^{-1}	4.357	4.816	6.159	5.425	5.699	6.084	5.781	5.911

Following sketch displays absorbance index of each samples. Mean of samples are 0.553 with a standard deviation value which is 0.064 (Fig.3.6).

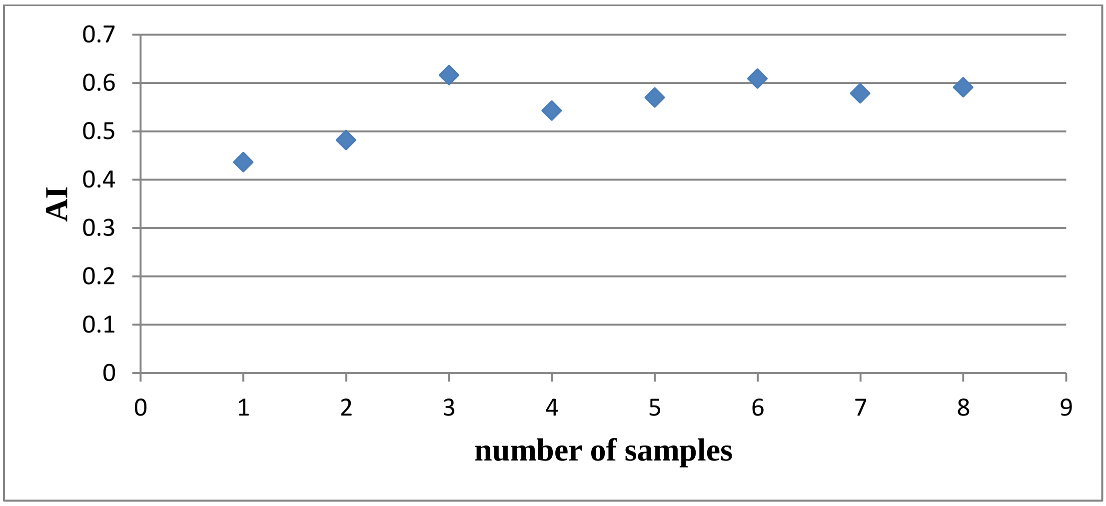


Figure 3.7 Absorbance Index Values of NBR 40 % (w/w) Set with Range [0.553±0.064]

3.2.3 NBR 50% (w/w) Master Batch Concentrated Master Batch Absorbance Index Values

Table 3.3 indicates absorbance indices of 50% (w/w) acrylonitrile concentrated master batch samples. The results were again very repeatable. The absorbance indices were in remarkable level to follow FTIR.

Table 3.3 Absorbance Index Values of NBR 50% (w/w) Set

at 2237cm^{-1}	1	2	3	4	5	6	7
AI	1.065	1.090	1.053	0.973	1.021	1.015	0.981

The mean of these absorbance indices is 1.028 with a standard deviation of 0.043. Absorbance index data is close to each other and repeatability was also very good.

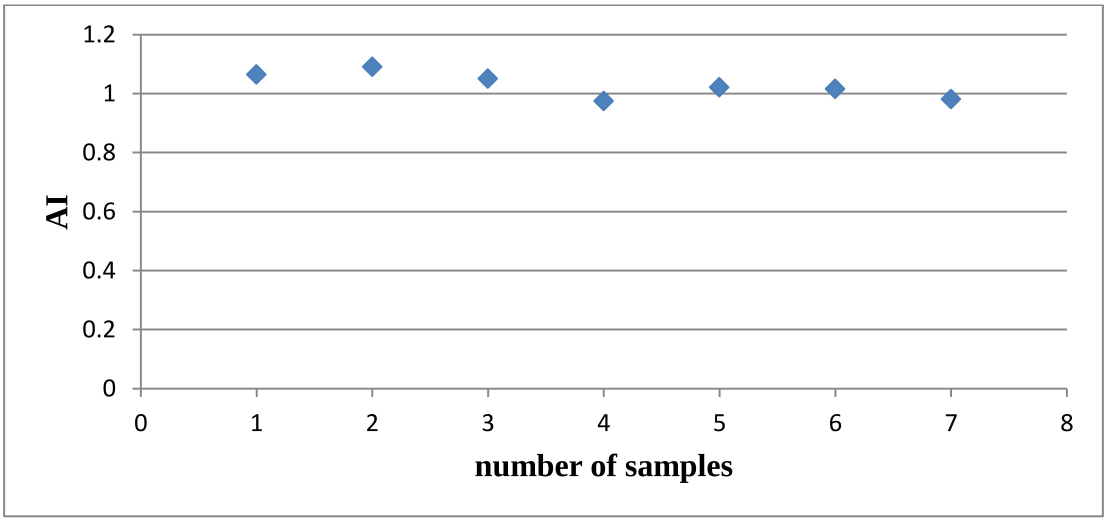


Figure 3.8 Absorbance Index Values of NBR 50% (w/w) Set with Range [1.027943±0.043017]

3.2.4 Evaluation of Master Batches Sets

The chart contains absorbance index values of NBR 30% (w/w), NBR 40% (w/w) and NBR 50% concentrated master batches (Fig. 3.9). NBR 50% concentrated master batch obviously gives the highest absorbance indices. Absorbance index value of the highest concentrated set was seen between 1.09 and 0.9. The results of NBR 40% (w/w) and NBR 30% (w/w) were observed within 0.6 and 0.3 interval. It is evidently perceived that as nitrile concentration of master batches increases, the absorbance index also increases. That refers increment of NBR content in the master batches brings high nitrile peak absorption.

It is evidently seen that there was an agreement between independent test results; thus, repeatability was obtained for each set. That states compatibility of PE and nitrile butadiene rubber was provided at required level. It could be assumed that compatibility was provided butadiene part of the rubber since it constitutes C-H_2 structure like PE. Under these considerations NBR master batches could be used interior marker in LDPE.

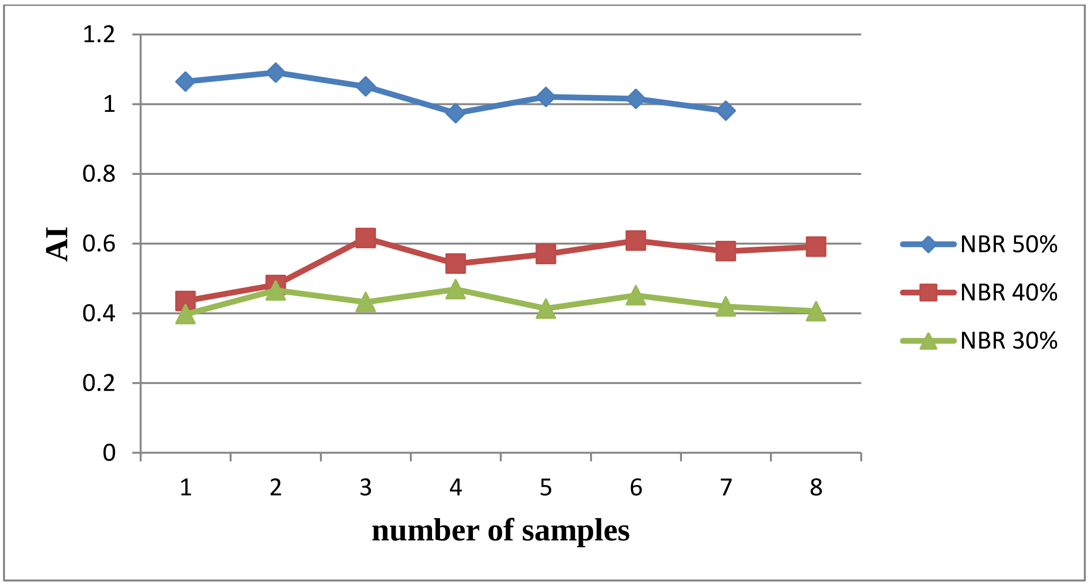


Figure 3.9 Comparison of NBR Master Batches Absorbance Index Values

3.3 NBR Master Batches as the Marker

LDPE shopping bag with different NBR concentrations which are 1% (w/w), 0.8% (w/w), 0.5% (w/w), 0.25% (w/w), 0.15% (w/w) and 0.09% (w/w) were prepared by using extruder. For all samples sets, Fe stearate master batch was added at a constant concentration, 1% (w/w). Maximum 1% (w/w), medium 0.5% (w/w) and minimum

0.09% (w/w) concentrated sets for the markers are discussed; however, absorbance indices of all dilute samples were considered for comparison of sets. The absorbance indices were attained by using absorbance spectra provided by Omnic program in ATR-FTIR instrument.

3.3.1 NBR 1% (w/w) Set

NBR 1% (w/w) set was prepared from 50% (w/w) ratio acrylonitrile master batch because of its straightforward calculations of the final concentrations. Dilution process was carried out by using extruder. Table 3.4 shows absorbance index value of each sample.

Table 3.4 Absorbance Index Values of NBR 1 % (w/w) Set

at 2237cm^{-1}	1	2	3	4	5	6	7	8
AI x10^{-3}	7.466	6.269	10.00	9.146	7.509	11.57	5.964	7.208

Evaluation of absorbance index values was assessed by considering following figure (Fig. 3.10). Absorbance of samples varied between 6.269 x10^{-3} and 11.57 x10^{-3} with a standard deviation of 1.934x 10^{-3}.

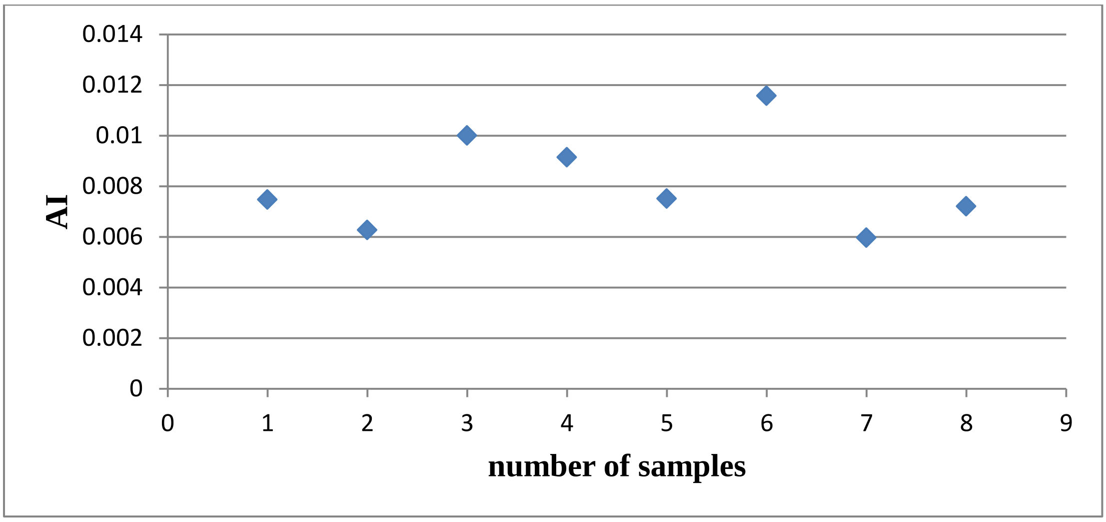


Figure 3.10 Absorbance Index Values of NBR 1% (w/w) Set with Range [0.00814±0.001934]

After taken a second standard deviation of the data, it was reduced six data point. Highly scattered data was removed in order to provide better estimation about interval of corresponding set. The purpose of taking second deviation is to provide better prediction about concentration of the interior marker polymer in FTIR controlling. Most probably, NBR 1% (w/w) concentrated interior marker polymer set gave absorbance index values with the range between 0.01 and 0.006. These six values were used to comprise interval of all sets. These absorbance index values provide repeatability even better with standard deviation 1.374×10^{-3} (Fig. 3.11).

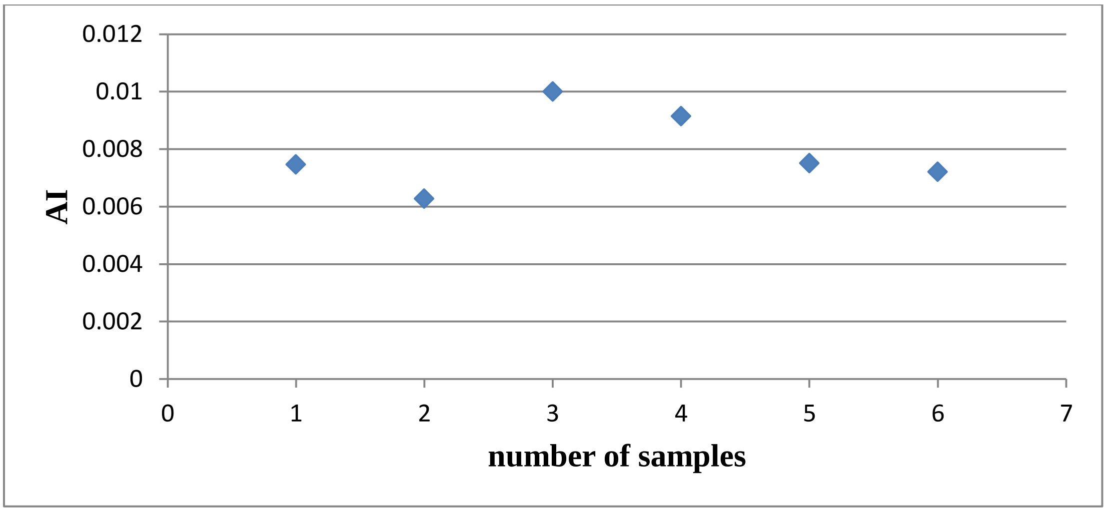


Figure 3.11 Absorbance Index Values of NBR 1% (w/w) Set with Range [0.00793±0.001374] (second deviation)

The spectrum belongs to nitrile butadiene rubber 1% (w/w) sample (Fig. 3.12). The spectrum is dominated by strong PE peaks; however, the peak of interior marker is slightly observed at 2236 cm^{-1}.

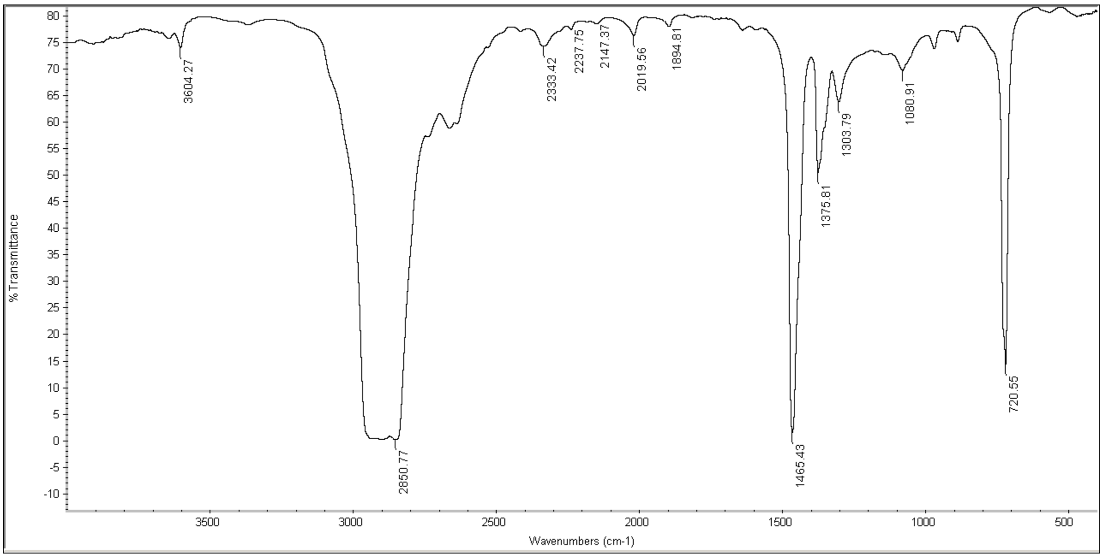


Figure 3.12 Spectrum of NBR 1% (w/w) Sample

The following figure reveals comparison of NBR 1% (w/w) spectrum and pure PE spectrum as an extended form along y axis. In that case interior marker peak is more observable compare to non-extended form of spectrum. The reference peak is observed clearly around 2236 cm^{-1}.

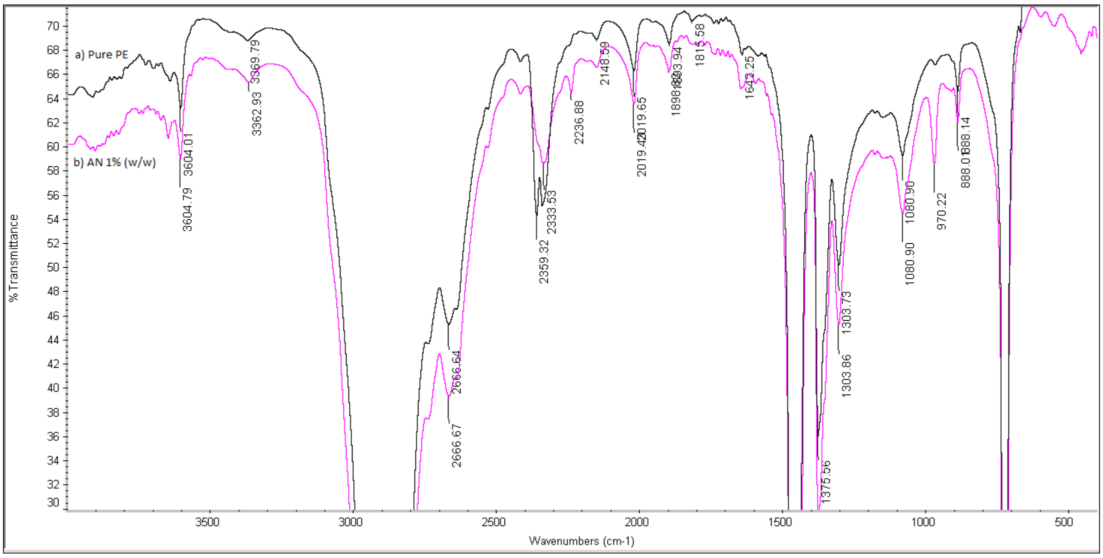


Figure 3.13 Comparison of Pure PE and NBR 1 % (w/w) Sample Spectrum

a) Pure PE b) NBR 1%(w/w) Sample

3.3.2 NBR 0.5 % (w/w) Set

NBR 0.5% (w/w) set was also prepared by using 50% (w/w) nitrile butadiene master batch. The absorbance index values could be seen in Table 3.5. Absorbance index values vary between 4.948×10^{-3} and 6.698×10^{-3}.

Table 3.5 Absorbance Index Values of NBR 0.5 % (w/w) Set

at 2237cm^{-1}	1	2	3	4	5	6	7	8
AI x10^{-3}	4.948	5.995	5.326	5.599	5.533	5.917	6.289	6.698

As it is seen in Figure 3.14, average of absorbance index values is 5.238×10^{-3} which is sufficiently high to detect in the spectrum. Standard deviation is 0.555×10^{-3}. Repeatability of the measurement was observed.

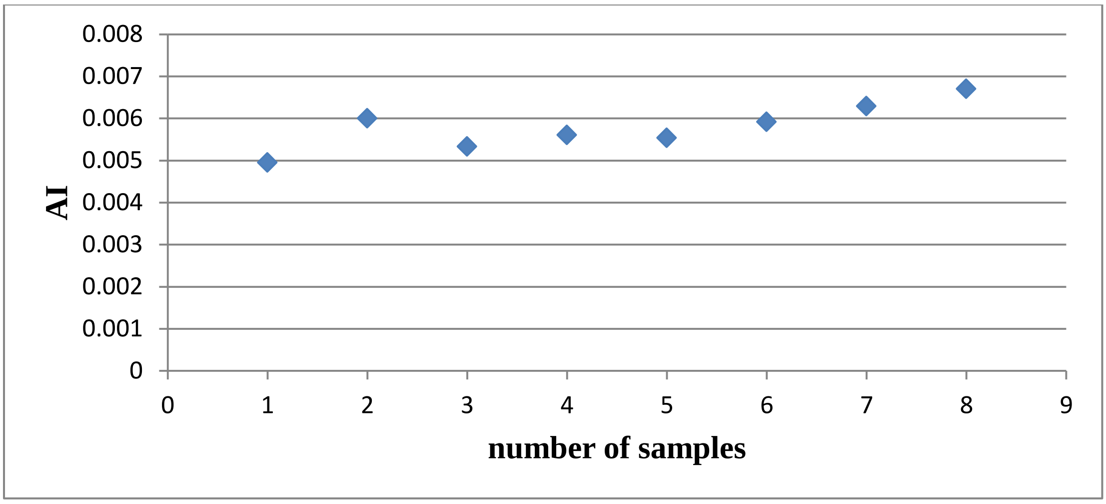


Figure 3.14 Absorbance Index Values of NBR 0.5% (w/w) Set with Range [0.005235±0.000555]

There is an example of spectrum this set (Fig. 3.15). The non-extended spectrum of the sample reveals substantiality similarity with pure PE spectrum.

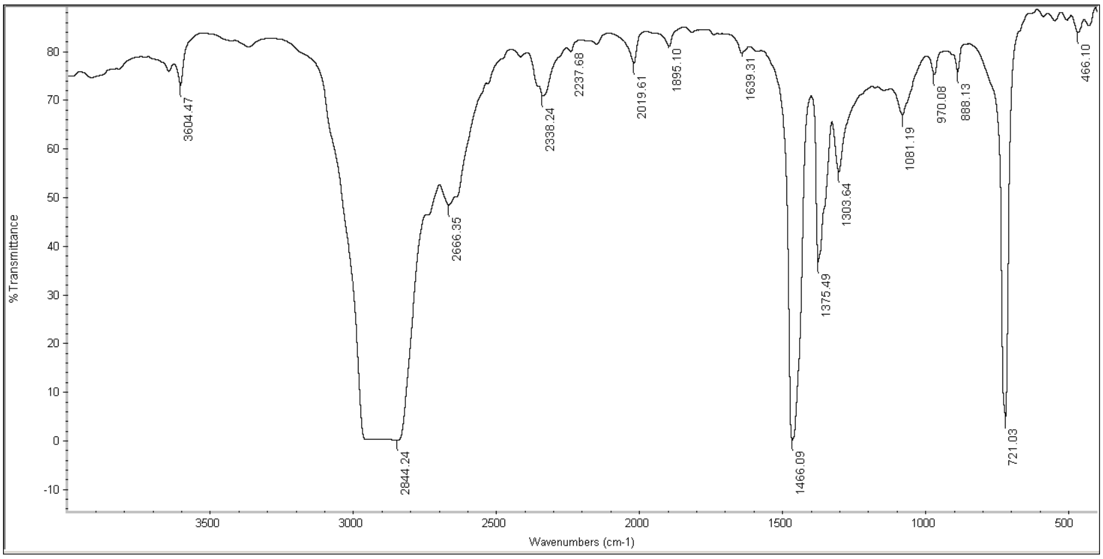


Figure 3.15 Spectrum of NBR 0.5 % (w/w) Sample

However; the marker peak is seen in expanded form of the spectrum. As it is mentioned before, when pure PE and NBR 0.5% spectra are compared, peak of interior marker polymer is seen around 2236 cm^{-1} clearly (Fig. 3.16).

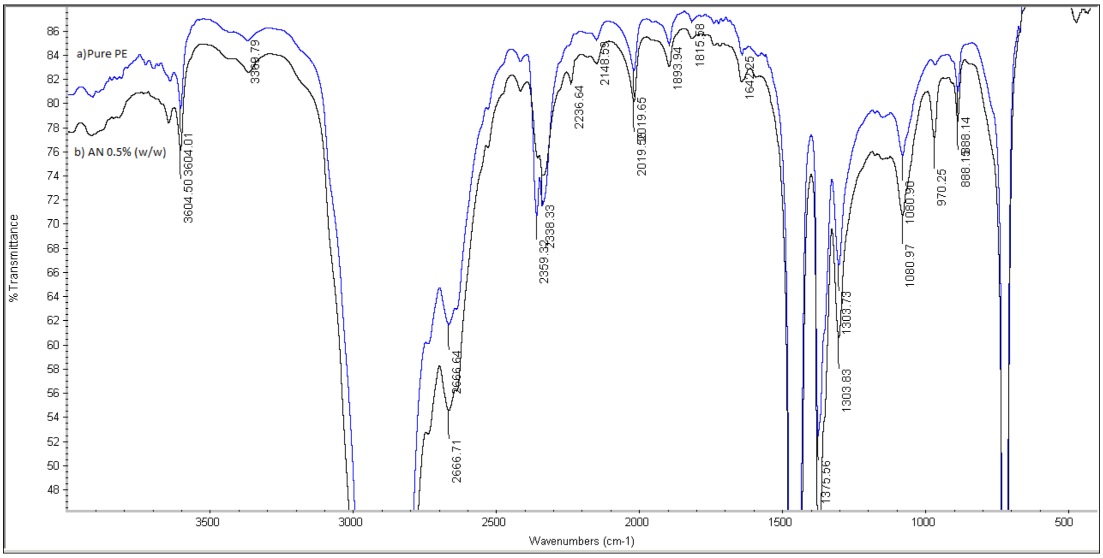


Figure 3.16 Comparison of Pure PE and NBR 0.5 % (w/w) Sample Spectrum

a) Pure PE b) NBR 0.5% (w/w) Sample

3.3.3 NBR 0.09% (w/w) Set

NBR 0.09% (w/w) was built up by utilizing weight ratios of 30% (w/w) master batch. Six samples were used to obtain absorbance index (Table 3.6). The set which contains minimum concentrated interior marker polymer gave absorbance index between 3.715x10^{-3} and 2.232x10^{-3}.

Table 3.6 Absorbance Index Values of NBR 0.09% (w/w) Set

at 2237cm^{-1}	1	2	3	4	5	6
AI x10^{-3}	3.715	2.232	3.094	2.789	2.378	2.860

Next graph indicates absorbance indices of the set together. As it is demonstrated standard deviation is reasonable when compare the mean value of the set. Repeatability is maintained even small concentration.

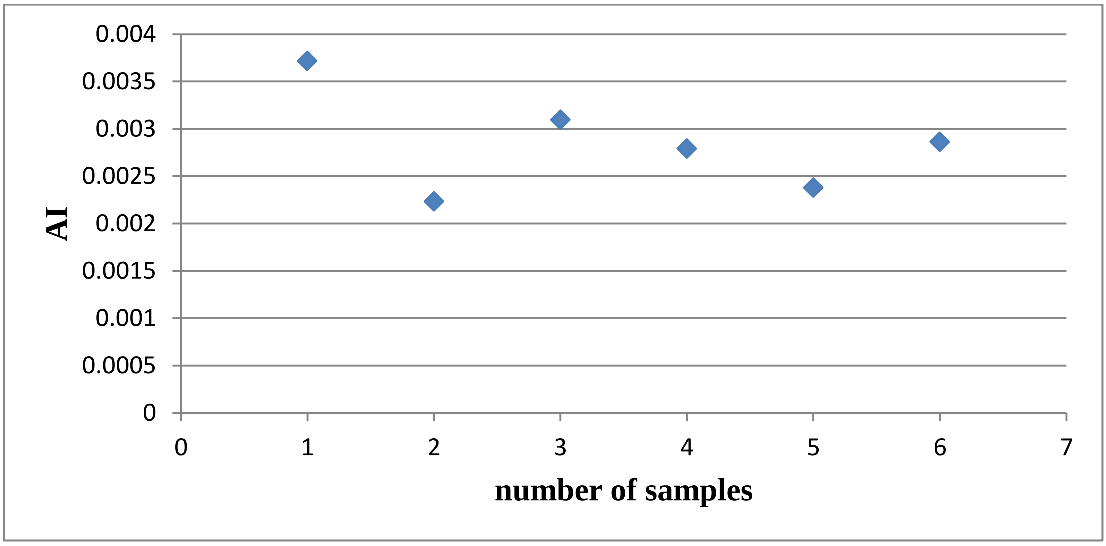


Figure 3.17 Absorbance Index Values of NBR 0.09% (w/w) Set with Range [0.00284±0.000582]

Following spectrum belongs to a sample from NBR 0.09% (w/w) set (Fig.3.18). In that case the marker peak is observed slightly .

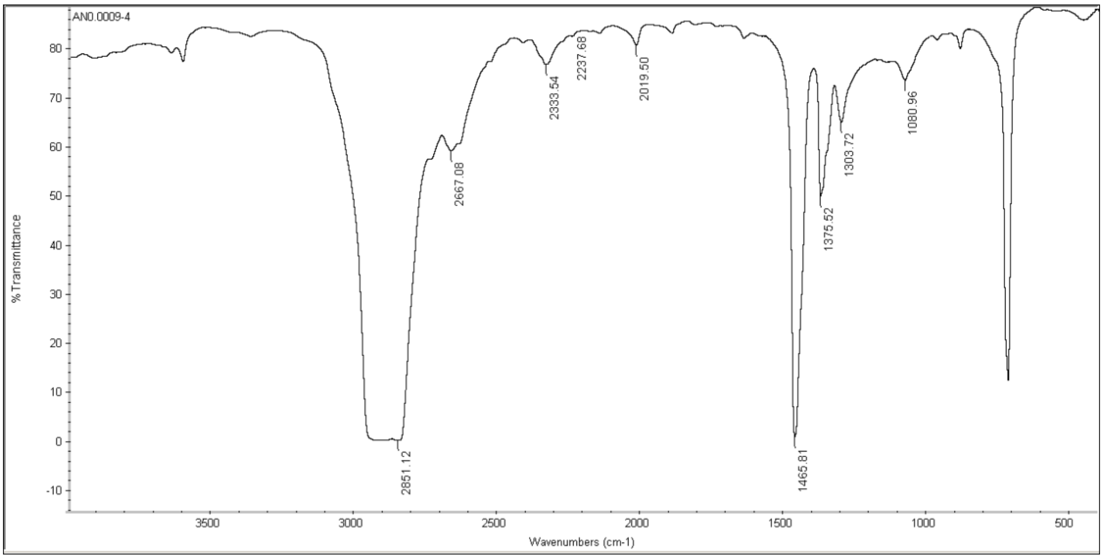


Figure 3.18 Spectrum of NBR 0.09% (w/w) Sample

In spite of the fact that the absorbance index values were smaller than previous that of discussed sets, the interior marker peak was seen in the expanded form of the spectra. The marker peak was seen around 2238 cm^{-1} in Fig. 3.19.

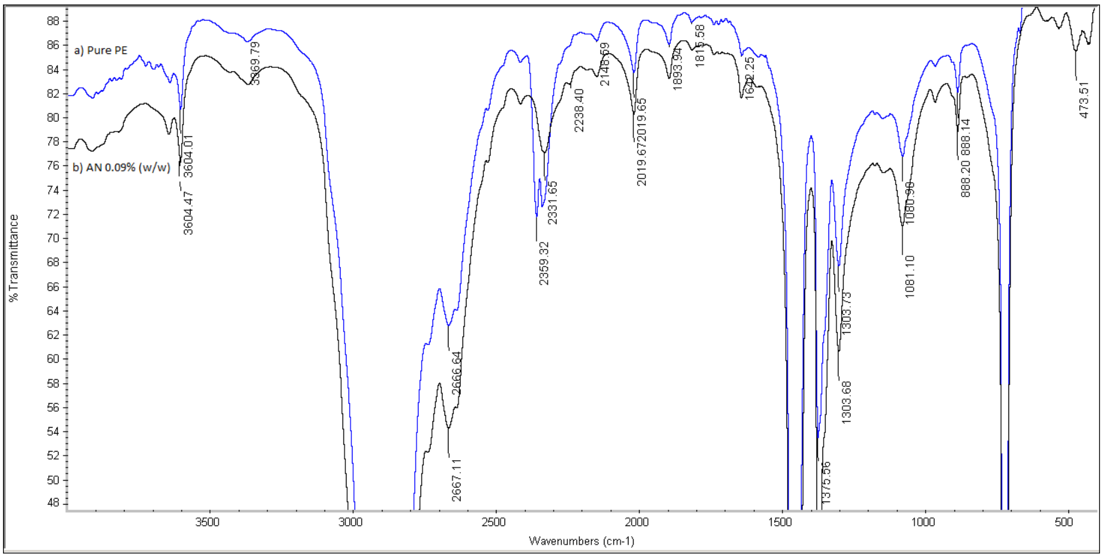


Figure 3.19 Comparison of Pure PE and NBR 0.0.09% (w/w) Sample Spectrum

a) Pure PE b) NBR 0.09% (w/w) Sample

3.3.4 Evaluation of the Sets

In Figure 3.20, comparison of absorbance index values for all LDPE sample sets is given. The spectra, absorbance index values with graphs, means and standard deviations could be seen for 0.8% (w/w), 0.25% (w/w) and 0.15% (w/w) sets in appendix part (see Appendix B). Furthermore, absorbance data for both 2237 cm^{-1} and 720 cm^{-1} peaks were given in detail for whole sets in Appendix A. As it is recognized that weight ratios of 1% and 0.8% sets gave approximately the same absorbance index rates since the concentrations of these sets were nearly the same. NBR 0.5% (w/w) set gave absorbance index values around 0.06. This result is almost average absorbance index value of maximum and minimum concentrated sets. Additionally, smaller concentrated sets which are 0.25% (w/w) and 0.15% (w/w) and 0.09% (w/w) seem to have virtually the similar absorbance index results. The absorbances indices of these sets are present the interval between 0.004 and 0.002. It is essential to point out that NBR 0.25% (w/w) set possesses higher mean absorbance index value than 0.15% (w/w) and 0.09% (w/w). However, NBR 0.15% (w/w) set has surprisingly lower mean value than minimum concentrated set.

It could be suggested that these absorbance index values could be obtained another reference peak. This reference peak is also strong peak in on the NBR spectrum arising from presence of double bond in the structure. It is known that PE contains unsaturated groups from the original process; however, concentration of this group is much smaller than that butadiene part in the NBR rubber. Therefore, presence of this part and effect on absorbance index could be ignored. Additionally, instead of using height of two selected references peak and dividing into them each other to eliminate thickness differences, area of reference peaks could be also used to obtain absorbance index values. This way could be alternative to detect presence of interior marker polymer in the PE matrix.

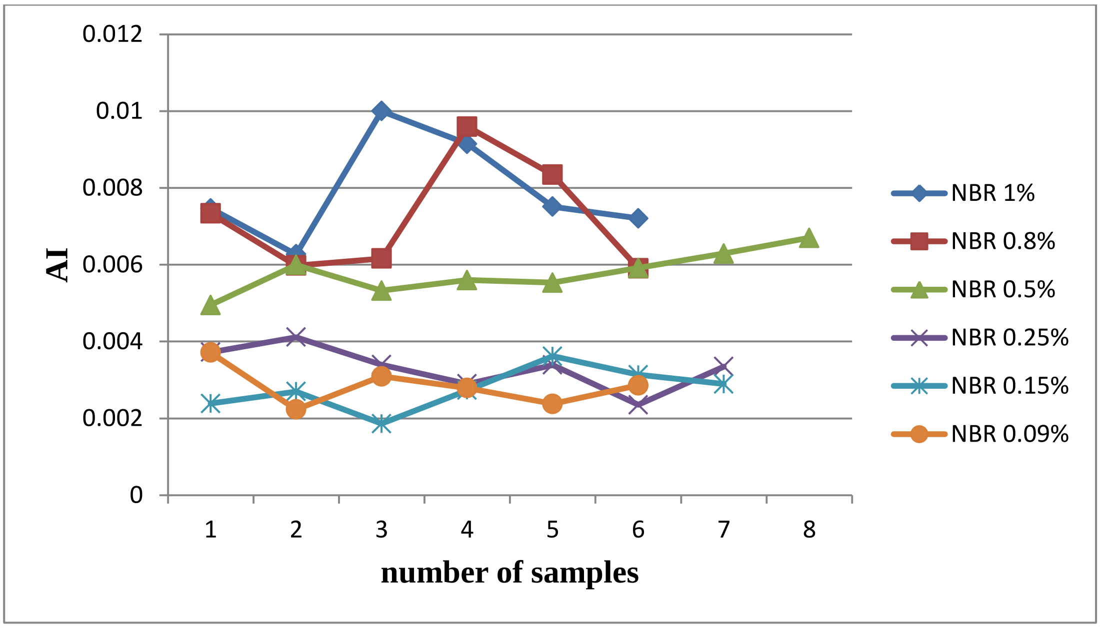


Figure 3.20 Comparison of NBR Dilute Sets Absorbance Index Values

NBR 0.5% (w/w) interior marker set gave much more consistent data than the rest of sets. Also, reference peak is clearly seen expanded form of spectrum which is desired. That refers for better visualization, a magnification is required for existence of marker by the company. Otherwise, it is unrecognized which is good. Therefore, it could be used as an interior marker in the LDPE matrix

3.4 IR Spectra of Polyamide 12 (PA12) Master Batches

When pure PA12 spectrum was analyzed, it was definitely recognized that PA12 possessed unique peaks compare to PE peaks. The carbonyl group in the polyamide 12 structure was chosen as a second interior marking peak. The reference peak is seen at 1640 cm^{-1}. This carbonyl peak is different from any ordinary carbonyl peak because of the fact that there is hydrogen bonding between N-H and O=C group. Therefore, this peak shifts toward smaller wavelength which makes it unique. The second reason why PA12 was chosen as an interior marker at the first place is that PA12 has -CH_2- group which makes it compatible with PE.

3.4.1 PA12 30% (w/w) Master Batch Concentrated Master Batch Absorbance Index Values

For PA12, the same procedure was followed with NBR master batches. Firstly, the master batch set was arranged in weight ratios of 30% (w/w) PA12 content by using Brabender. Four different thin films were used for FTIR analysis. Two sections were taken for each film to form set. The transmittance spectrum was determined by ATR-FTIR instrument as well as absorbance values were obtained by using absorbance spectrum of each sample. Calculating absorbance indices of the sets, absorbance of 1640 cm^{-1} belonging PA12 and absorbance of 720 cm^{-1} peaks were taken. Here, it was assumed that the peak 720 cm^{-1} just belongs to PE matrix not -(CH_2)- group of PA12. Also, absorbance index values were used to eliminate thickness differences among four distinct films. Corresponding table about absorbance indices of this set could be seen below (Table 3.7).

Table 3.7 Absorbance Index Values of PA12 30 % (w/w) Set

at 1640cm^{-1}	1	2	3	4	5	6	7	8
AI	4.496	4.518	3.764	2.539	2.208	2.287	2.109	2.150

Figure 3.21 shows variation of absorbance index values. The absorbance index values were found rather large. That refers the marker peak could be easily recognized in the spectrum. However, it is necessary to mention that two samples gave higher absorbance index values than any other sample. Consequently, these two could be removed to obtain better average and estimation about interval of the corresponding set. Therefore, second deviation was calculated. These values were used to compare for all master batches absorbance indices.

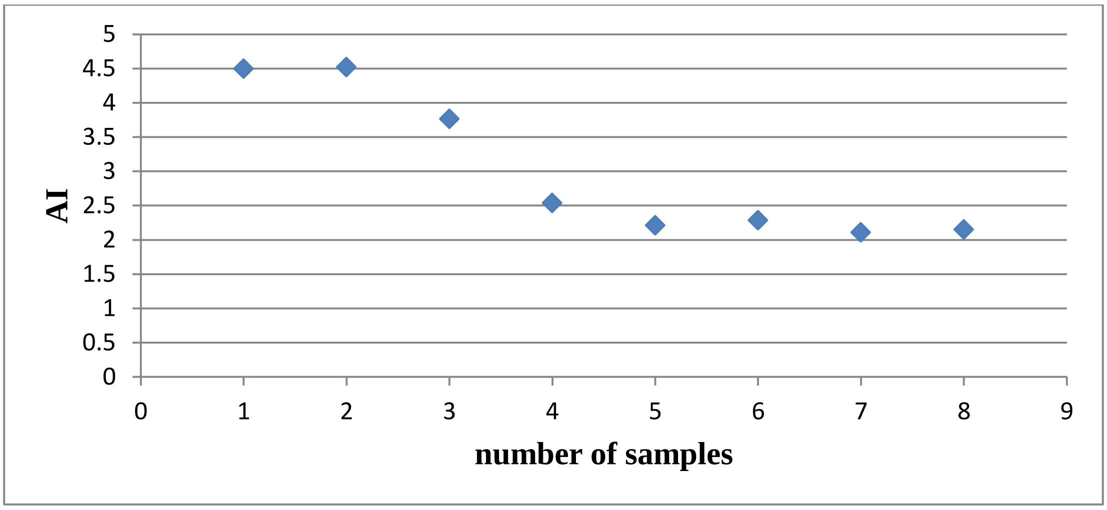


Figure 3.21 Absorbance Index Values of PA12 30% (w/w) Set with Range [3.0089±1.068]

Figure 3.22 shows, mean and standard deviation of absorbance index data after calculating second deviation. In that case variations of the values are slight. Mean and standard deviation are 2.5095 and 0.633197, respectively. The gap between maximum and minimum value was narrowed to better estimation about precision of measurements.

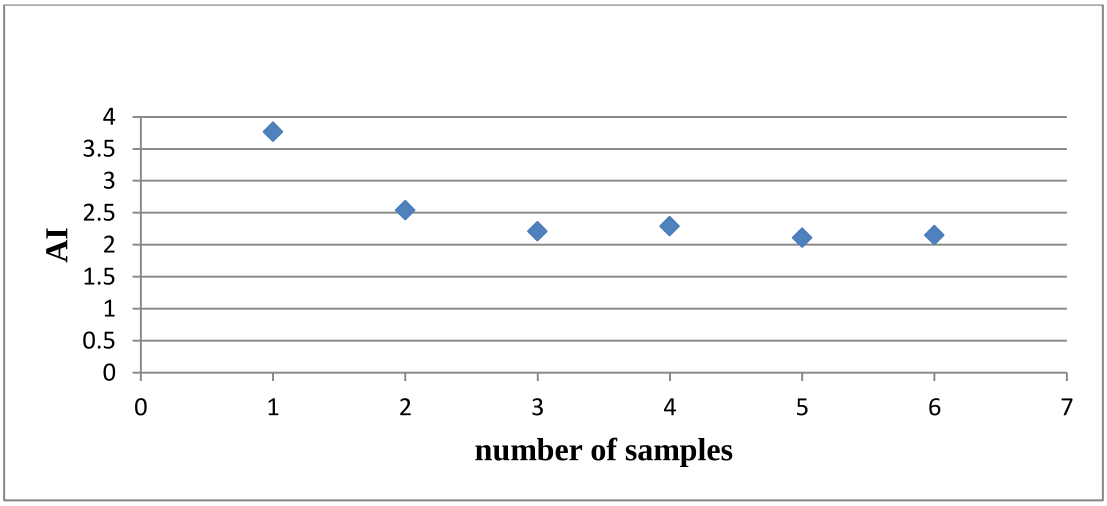


Figure 3.22 Absorbance Index Values of PA12 30% (w/w) Set with Range [2.5095±0.633197] (second deviation)

Figure 3.23 displays spectrum of a sample belonging to PA12 30% (w/w) master batch set. Polyamide peaks are observed clearly.

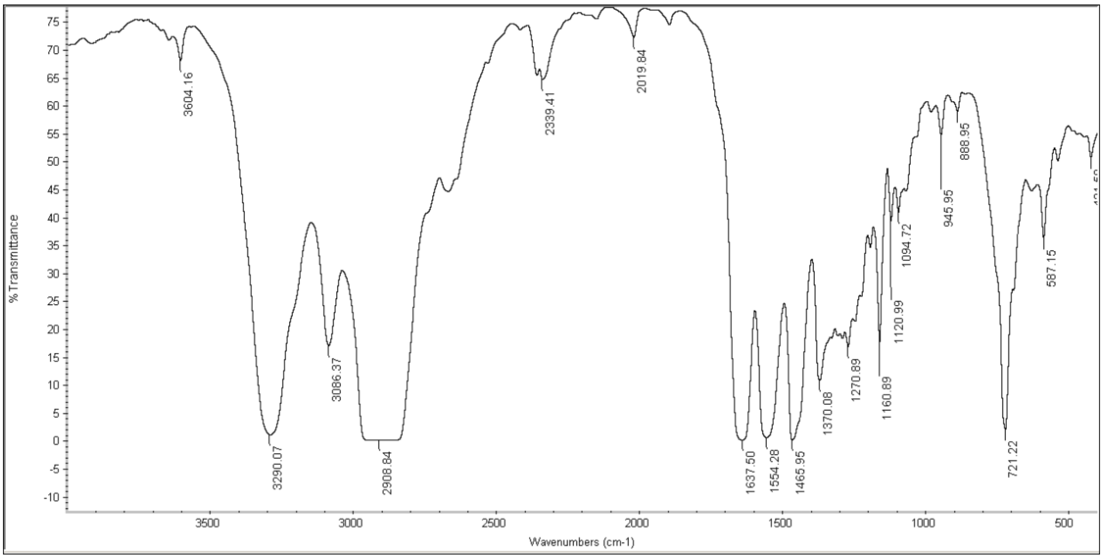


Figure 3.23 Spectrum of PA12 30% (w/w) Set

3.4.2 PA12 40% (w/w) Master Batch Concentrated Master Batch Absorbance Index Values

The following table gives information about absorbance index values of PA12 40% (w/w) master batch (Table 3.8). Same steps were followed with 30% (w/w) concentrated master batch. As it is clearly observed that the absorbance values of this set has higher values than 30% (w/w) master batch which is expected.

Table 3.8 Absorbance Index Values of PA12 40% (w/w) Set

at 1640cm^{-1}	1	2	3	4	5	6	7	8
AI	3.177	4.180	4.173	4.869	3.739	5.198	3.751	6.931

Variation of the absorbance index values are shown in Figure 3.24. The results are between 6.931 and 3.177. As it is recognized the difference between the minimum and maximum value is high. Hence, it is essential to consider the values after taking second deviation to determine the interval for this concentration.

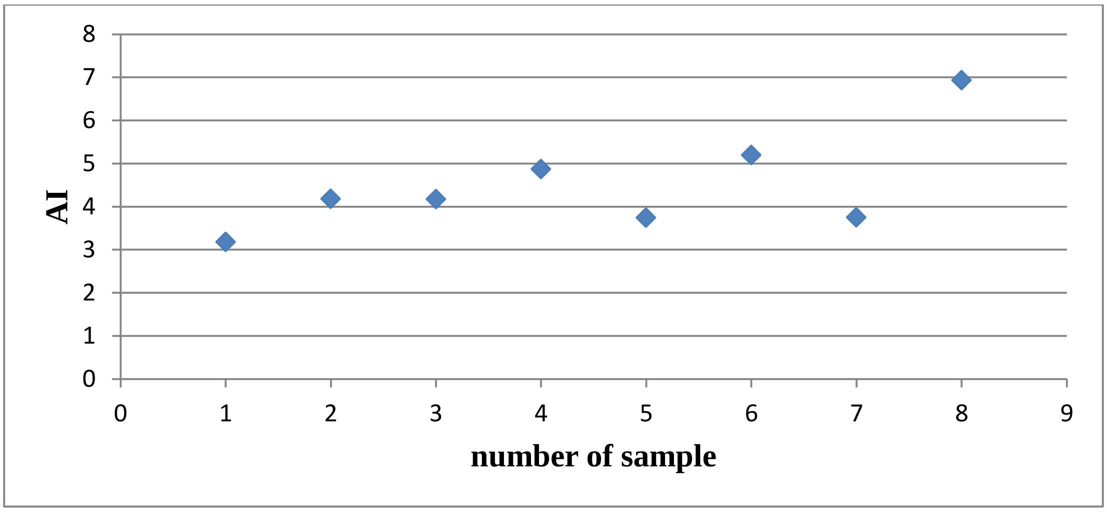


Figure 3.24 Absorbance Index Values of PA12 40% (w/w) with Range [4.502±1.097319]

The values are mostly between 5 and 3 absorbance index values. The last data point is out of this gap. After calculating second deviation, the scattered datum was eliminated to fix the interval for this concentration. Figure 3.25 shows the results after evaluation of seven data points. Although mean value did not change remarkably which was 4.318, standard deviation decreased dramatically.

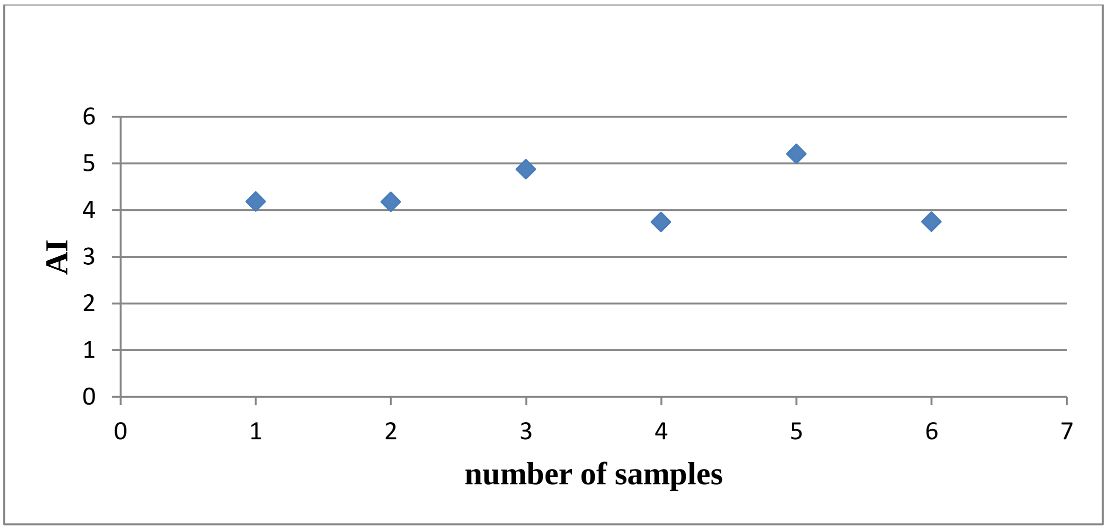


Figure 3.25 Absorbance Index Values of PA12 40% (w/w) Set with Range [4.318±0.596] (second deviation)

3.4.3 PA12 50% (w/w) Master Batch Concentrated Master Batch Absorbance Index Values

This set has the highest PA12 content. The absorbance index values are represented in Table 3.9.

Table 3.9 Absorbance Index Values of PA12 50% (w/w) Set

at 1640cm^{-1}	1	2	3	4	5	6	7	8
AI	4.844	4.709	4.276	3.944	5.337	4.500	5.719	5.069

Absorbance index values for PA12 50% (w/w) are also given in Figure 3.26. Closeness of the data indicates repeatability of the measurement. As it is expected, PA12 50% (w/w) master batch has higher mean value. Mean value and standard deviation value which are 4.799 and 0.575, respectively.

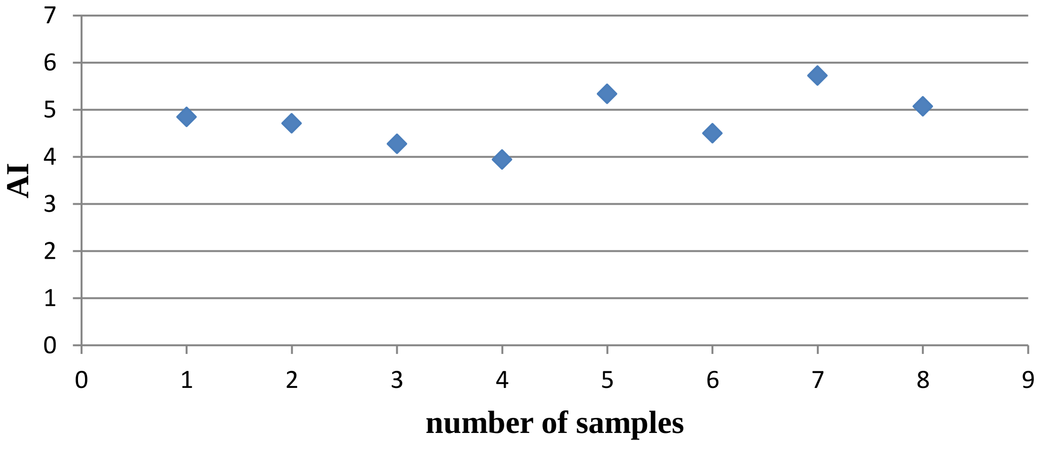


Figure 3.26 Absorbance Index Values of PA12 50% (w/w) Set with Range [4.799±0.575]

3.4.4 Evaluation of the Sets

In figure 3.27, all master batches absorbance index values are compared. It could be emphasized that index data for all concentrations are notable. Higher concentrated master batches which are PA12 50% (w/w) and PA12 40% (w/w) sets gave absorbance index value in the similar interval. However, as it is expected mean value of PA12 50% (w/w) concentrated master batch is the highest. It is possible that as polyamide concentration increases in the master batches, the blend might be mixed at limited level; hence, closeness of absorbance indices of 50% (w/w) and 40% (w/w) could be arose. Moreover, the lowest concentrated master batch which is PA12 30% (w/w) has minimum absorbance index values. In the light of these results, dilute samples are prepared.

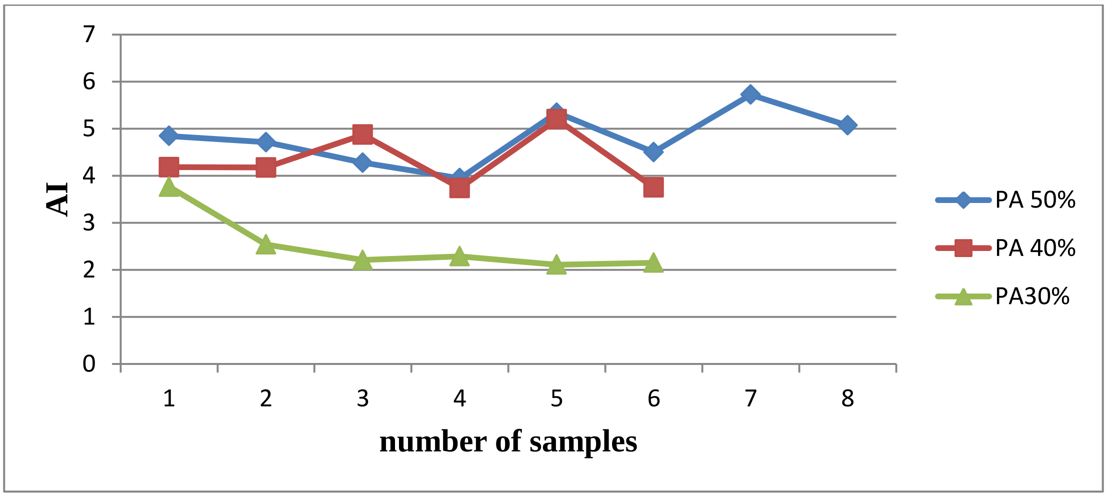


Figure 3.27 Comparison of PA12 Master Batches Absorbance Index Values

3.5 PA12 Master Batches as the Marker

Following samples were prepared in weight ratio 1%, 0.8%, 0.5%, 0.25%, 0.15% and 0.09% PA12 concentration by using extruder. As an oxo-biodegradale pro-oxidant, Fe stearate master batch was added 1% (w/w) ratio. Maximum 1% (w/w), medium 0.5% (w/w) and minimum 0.09% (w/w) concentrated sets are discussed subsequent parts; however, for comparison of sets, other dilute samples also are taken into consideration in order to provide better explanation.

3.5.1 PA12 1% (w/w) Set

This set was prepared by using PA12 50% (w/w) concentrated master batch because mean value of absorbance index values were more or less the same with 40% (w/w) master batch. Absorbance index values of maximum concentrated dilute set which is 1% (w/w), could be seen in Table 3.10. According to these values, it can be clearly said that, visibility of reference peak was sustained.

Table 3.10 Absorbance Index Values of PA12 1% (w/w) Set

at 1640cm^{-1}	1	2	3	4	5	6	7	8
AI x10^{-1}	0.969	1.057	1.454	1.036	1.206	1.014	1.168	0.965

Figure 3.28 reveals distribution of all data. Absorbance index values differ between 0.0965x10^{-1} and 0.1454x10^{-1} with a standard deviation 0.0165 for this set.

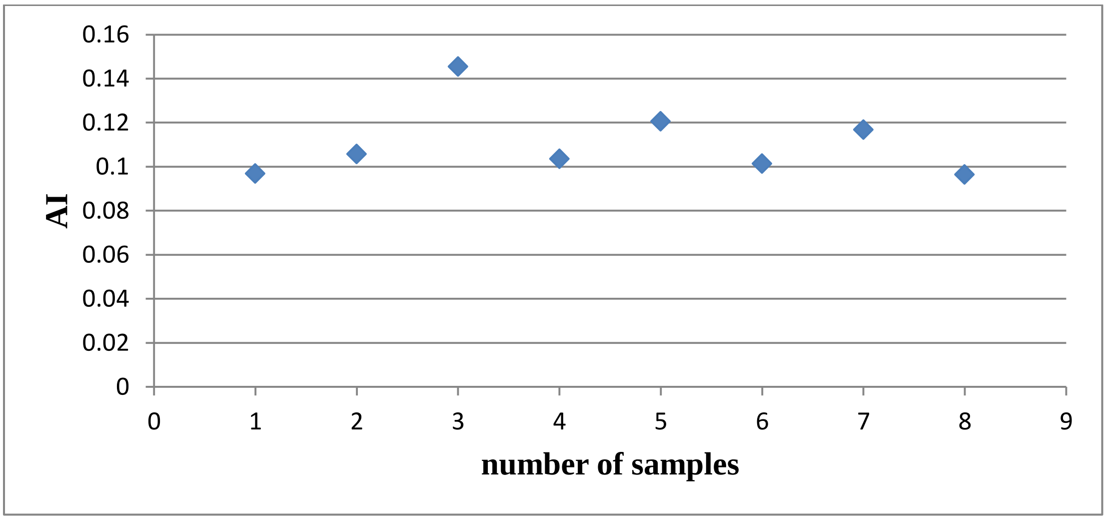


Figure 3.28 Absorbance Index Values of PA12 1% (w/w) Set with Range [0.111±0.016455]

Interior marker peak which is at 1640 cm^{-1} is seen in the sample spectrum (Fig. 3.29). The peak is already recognizable in the spectrum.

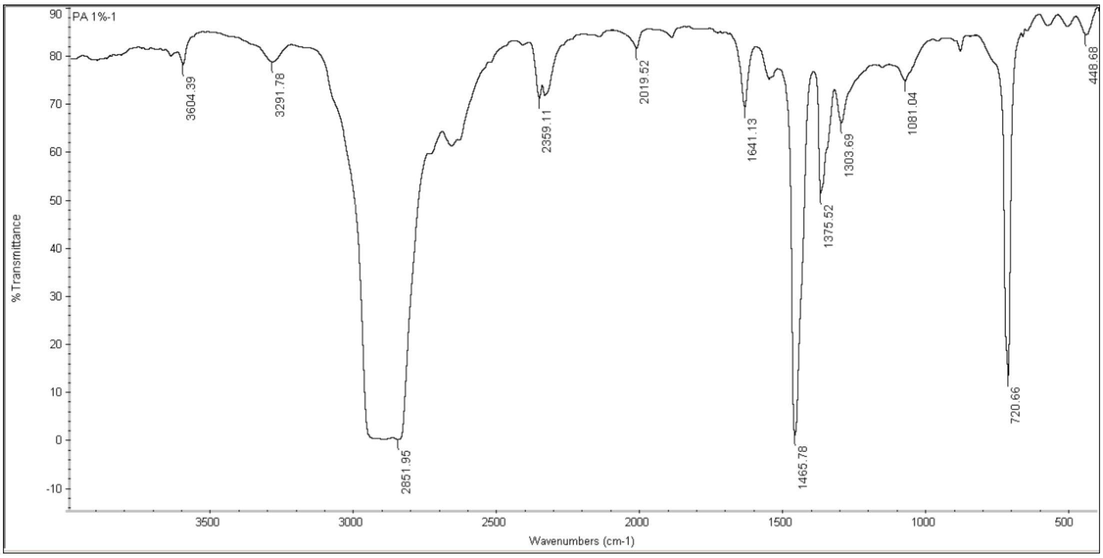


Figure 3.29 Spectrum of PA12 1% (w/w) Sample

Figure 3.30 views comparison of pure PE and 1% (w/w) concentrated polyamide 12 sample. Reference peak is doubtlessly visible in the spectrum as pervious spectrum.

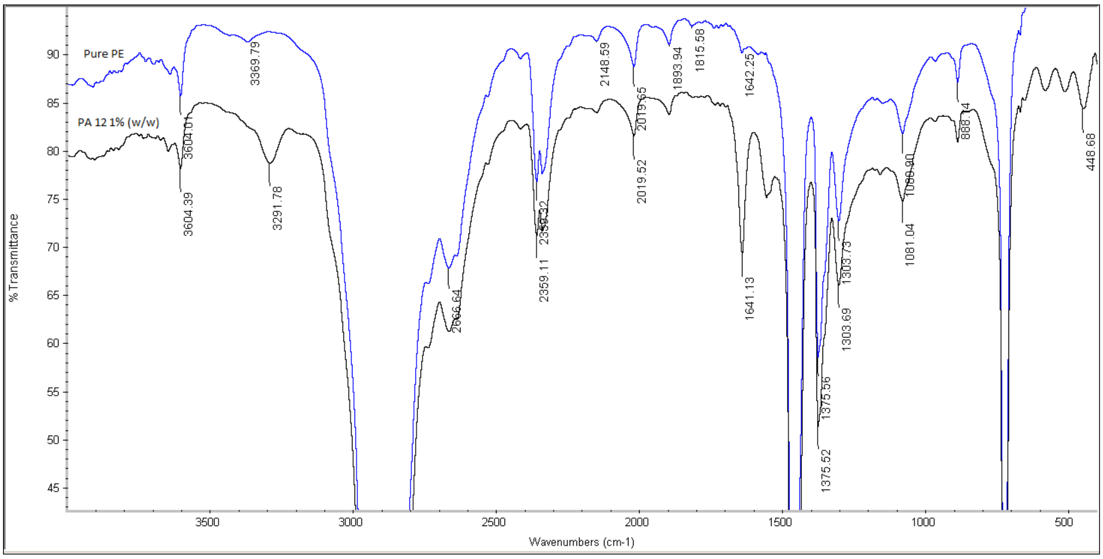


Figure 3.30 Comparison of Pure PE and PA12 1% (w/w) Sample Spectrum

a) Pure PE b) PA12 1% (w/w) Sample

3.5.2 PA12 0.5% (w/w) Set

This set was also prepared by using PA12 50% (w/w) master batch. The absorbance indices of this set could be seen in Table 3.11.

Table 3.11 PA12 0.5% Absorbance Index Values

at 1640 cm^{-1}	1	2	3	4	5	6	7	8
AI $x10^{-2}$	5.810	7.330	7.320	7.740	5.576	7.289	6.953	7.151

Distribution of absorbance indices is represented in Figure 3.31. Absorbance values are in the range of 0.05810 and 0.07740 with standard deviation 0.00778. That refers repeatability is maintained appreciably between data, even in the PA12 50% (w/w) master batch dilution.

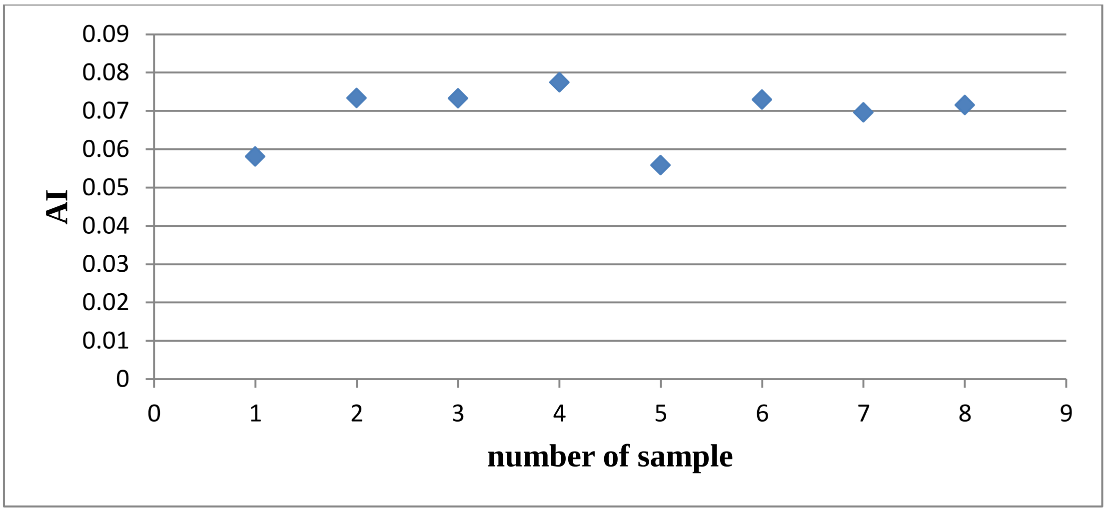


Figure 3. 31 PA12 0.5% (w/w) Absorbance Index Values [0.069±0.00778]

In Figure 3.32, the reference peak is obviously seen in the raw polymeric material spectrum at 1641 cm^{-1}.

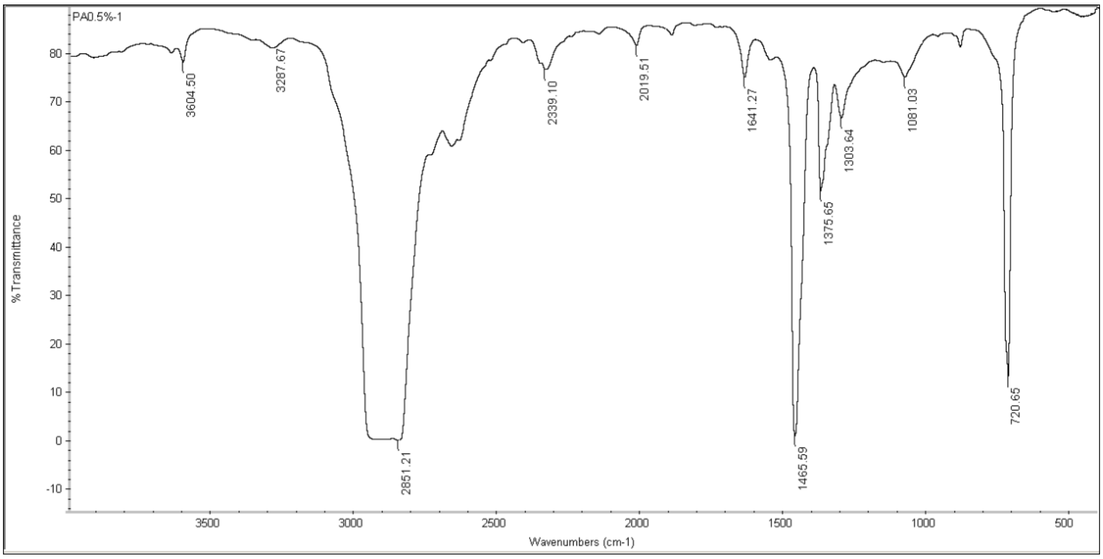


Figure 3.32 Spectrum of PA12 0.5% (w/w) Sample

In Figure 3.33, comparison between pure PE and PA12 0.5% (w/w) sample is shown. Differences between two spectra are easily perceived.

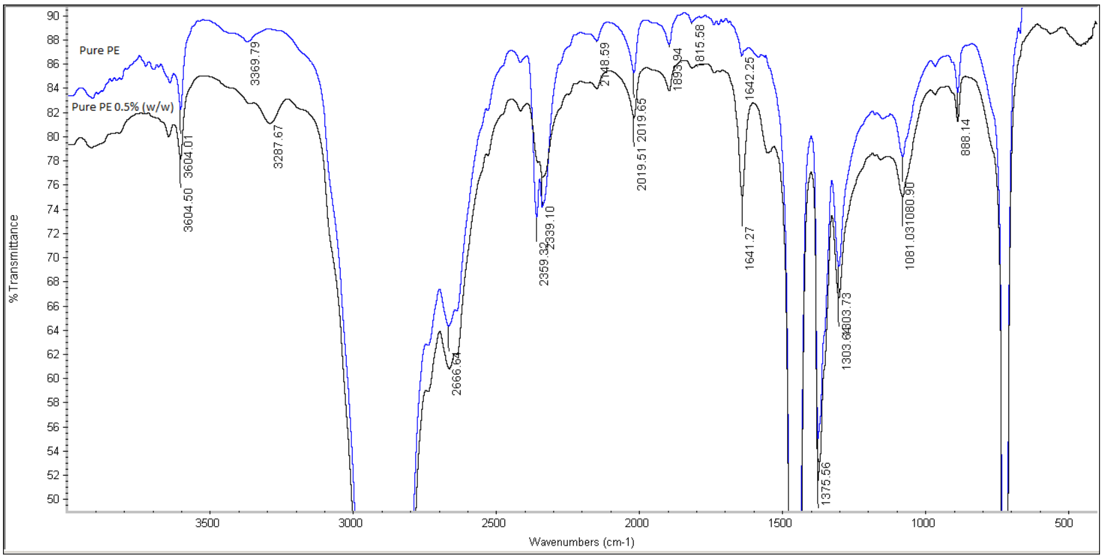


Figure 3.33 Comparison of Pure PE and PA12 0.5% (w/w) Sample Spectrum

a) Pure PE b) PA12 0.5% (w/w) Sample

3.5.3 PA12 0.09% (w/w) Set

PA12 30% (w/w) ratio master batch was used to prepare minimum concentrated interior marker set which is PA12 0.09% (w/w). As it is demonstrated in table 3.12, absorbance index values show a distribution from 2.03×10^{-2} to 3.2×10^{-2}. Moreover, the lowest absorbance index was obtained compare to maximum and medium concentrated dilutes sets.

Table 3.12 Absorbance Index Values of PA12 0.09% (w/w) Set

at 1640cm^{-1}	1	2	3	4	5	6	7	8
AI x10^{-2}	2.03	2.46	3.20	2.76	2.12	2.49	2.49	2.03

Following chart indicates each absorbance index data of this set. Standard deviation is sufficiently small when compare the average absorbance index value of this set. That refers repeatability of the measurement was sustained at acceptable interval.

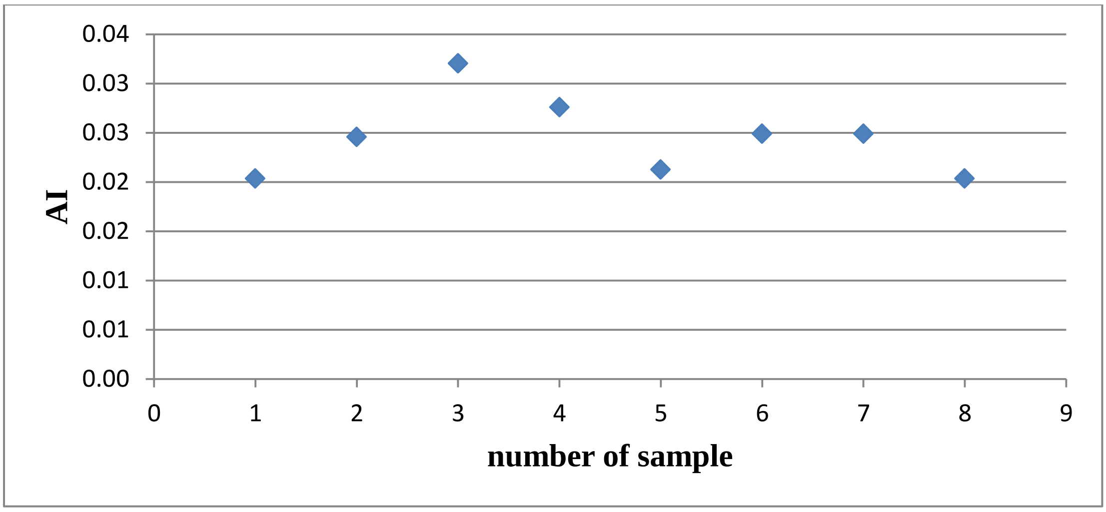


Figure 3.34 Absorbance Index Values of PA12 0.09% (w/w) Set with Range [0.0245±0.0034]

Figure 3.35 is the example spectrum of this set. The lowest absorbance indices were obtained at this concentration but the interior marker peak is easily recognized in the transmittance spectrum.

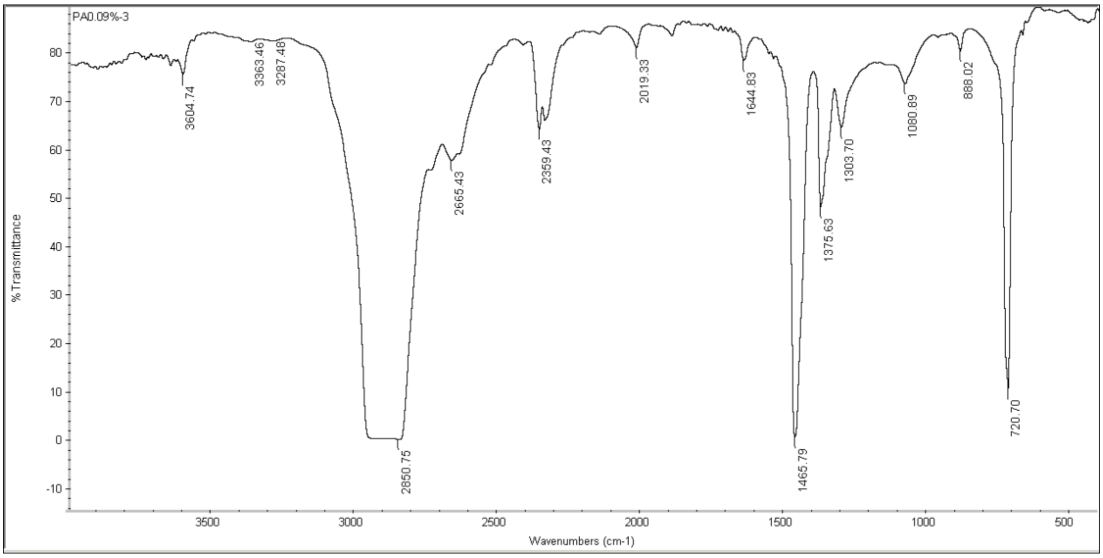


Figure 3.35 Spectrum of PA12 0.09% (w/w) Sample

Next figure contains both pure PE and PA12 0.09% (w/w) transmittance spectrum as expanded form (Fig. 3.36). Comparison between these two spectra provides better visualization about reference peak. Carbonyl peak belonging polyamide is seen definitely.

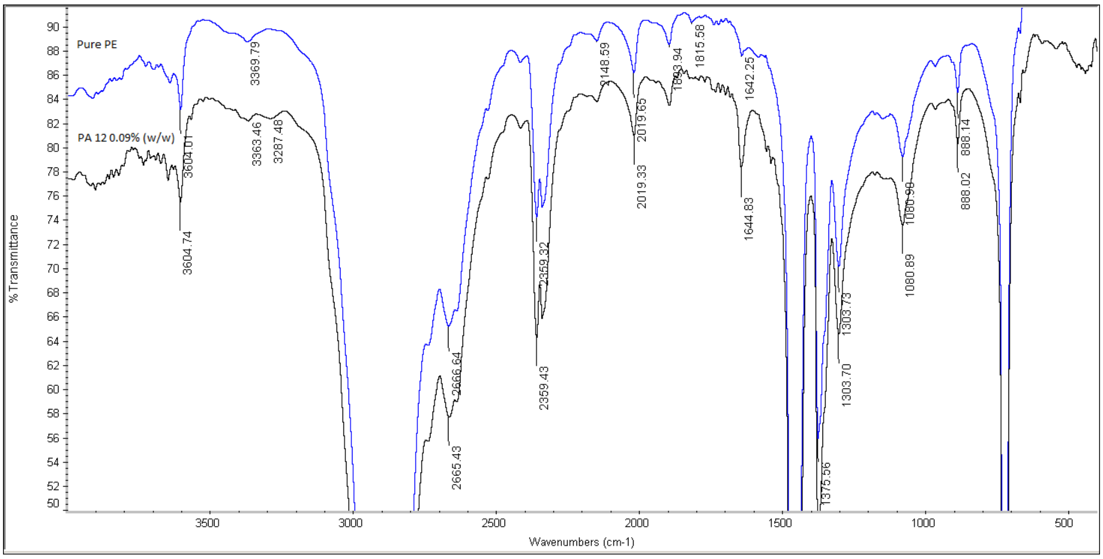


Figure 3.36 Comparison of Pure PE and PA12 0.09% (w/w) Sample Spectrum
a) Pure PE b) PA12 0.09% (w/w) Sample

3.5.4 Evaluation of the Sets

Following figure reveals absorbance indices of all LDPE sets comprising PA12 interior marker polymer (Fig. 3.37). For better understanding, absorbance indices values with means and standard deviations of PA12 0.8%, PA12 0.5% and PA12 0.25% sets can be seen in the Appendix B. Additionally, transmittance spectra of these sets could be checked out in the Appendix C. As it is recognized that higher concentrated dilute sets which are PA12 1%, PA12 0.8% and PA12 0.5% provide consistent results. The closeness between absorbance index results for each set indicates that repeatability of the measurements was successfully achieved. Furthermore, it is evidently seen that as content of PA12 increases, absorbance index values also increase. It is essential to emphasized that medium concentrated set gives medium absorbance index values.

Absorbance indices intervals of PA12 0.25%, PA12 0.15% and PA12 0.09% sets are close to each other. The lower concentrated of PA12 interior marker polymers sets gave similar absorbance index values. These values are the between 0.04 and 0.02 interval. However, it is necessary to point out that mean values of PA12 0.25%, PA12 0.15% and PA12 0.09% are 0.0388, 0.0301 and 0.0245, respectively. That means average mean value of absorbance indices increases.

It is essential to note that there could be alternative way to determine absorbance indices of samples. The regions 3280-3330 cm^{-1} show free N-H stretching vibrations due to free N-H bonds in the PA12 spectrum. The peak at that region could be also used. The peak is seen at 3290 cm^{-1} in the containing interior marker LDPE spectrum which contains PA12 interior marker. However, it would cause some problematical situation since this peak is strongly affected by hydrogen bond in the structure. Consequently, this peak would not provide good consistent data. Additionally, using peak area to obtain absorbance index values could be a way to get rid of thickness differences sample films.

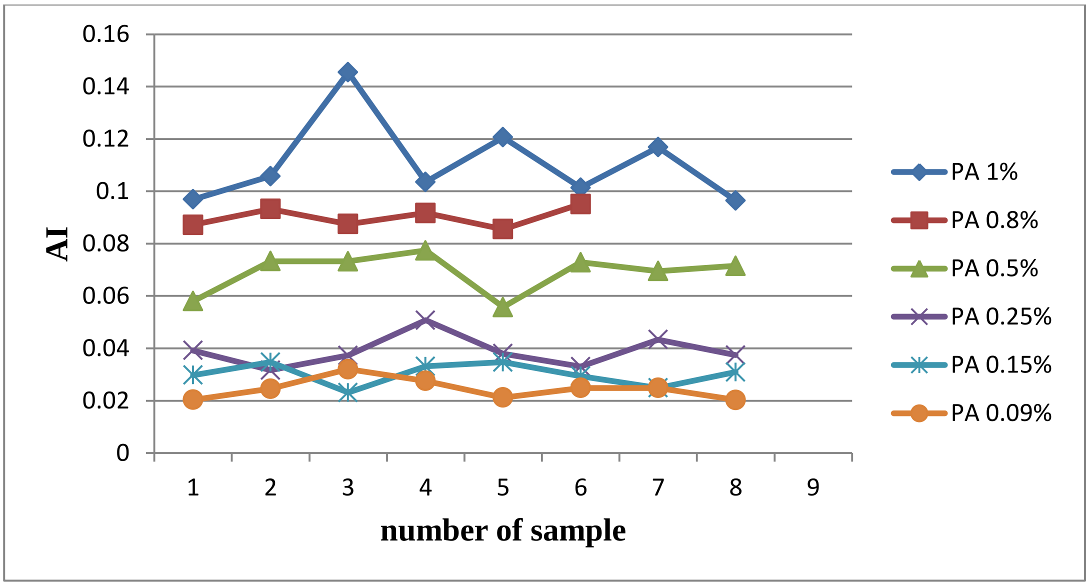


Figure 3.37 Comparison of PA12 Dilute Sets Absorbance Index

As result it is certain that one in all cases, one can follow these marker easily in the spectra. Additionally, PA 0.5% (w/w) ratio set provides not only remarkable absorbance indices but also consistence data.

3.6 IR Spectra of Thermoplastic Polyurethane (TPU) Master Batches

Under the consideration of pure TPU spectrum, the carbonyl peak which is at near 1730 cm^{-1} was preferred as a third interior marker. This peak is not present in the pure PE spectrum. Compatibility of pure PE and TPU could be sustained by soft segments in the TPU backbone. That is why TPU was selected as an interior marking polymer in PE matrix.

3.6.1 TPU 30% (w/w) Concentrated Master Batch Absorbance Index Values

Procedure of NBR and PA12 master batches was also applied for TPU sets. By using Brabender, the blend was prepared which comprises 30% (w/w) TPU content. Four different thin films were used for FTIR analysis. Two sections were taken for each film to form set. Visibility of the peak was detected by using transmittance spectrum and then absorbance values were obtained by using absorbance spectrum of each film. In this case absorbance indices were ratio of absorbance of 1730 cm^{-1} and absorbance of 720 cm^{-1} peak. Consequently, thickness differences among the films were eliminated. Furthermore, interval of absorbance indices for each set was assigned by using mean and standard deviation of absorbance index values. Table 3.13 shows absorbance index values of this set.

Table 3.13 Absorbance Index Values of TPU 30% (w/w) Sets

at 1730cm^{-1}	1	2	3	4	5	6	7	8
AI	3.439	4.018	3.579	7.147	5.387	7.013	7.239	7.730

Figure 3.38 illustrates variation of absorbance index of eight thin films. These values vary between 3.439 and 7.730 with a standard deviation 1.807. It could be mentioned that gap between minimum and maximum absorbance values too high.

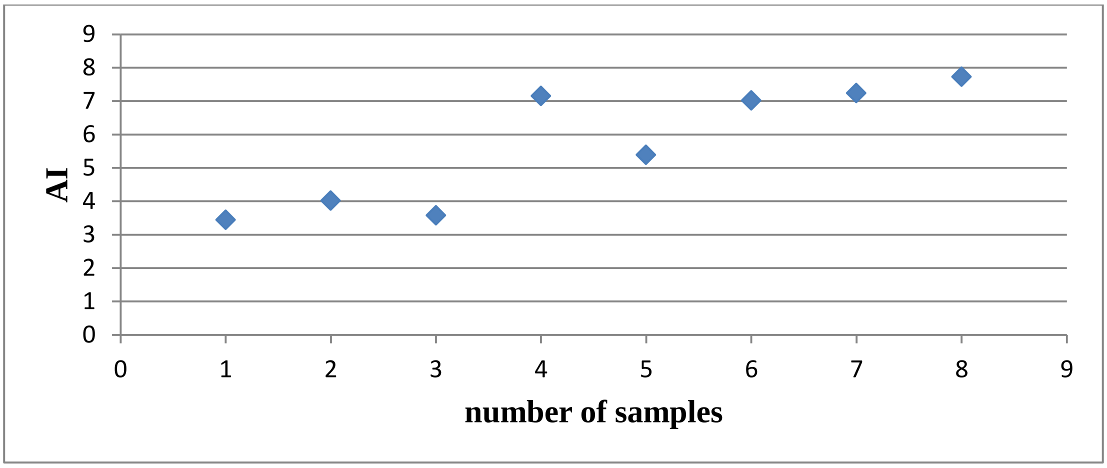


Figure 3.38 Absorbance Index Values of TPU 30% (w/w) Set with Range [5.694±1.807]

Range of absorbance index values could be narrowed to obtaining better estimation about precision of this set. Following sketch contains six sample absorbance indices (Fig. 3.39). Mean and standard deviations are 6.423 and 1.421, respectively. It is obviously seen, mean value increases but standard deviation decreases after taking second deviation. Repeatability is maintained compare to previous figure. It could be said that most probably absorbance indices of TPU 30% (w/w) set would be observed within this interval.

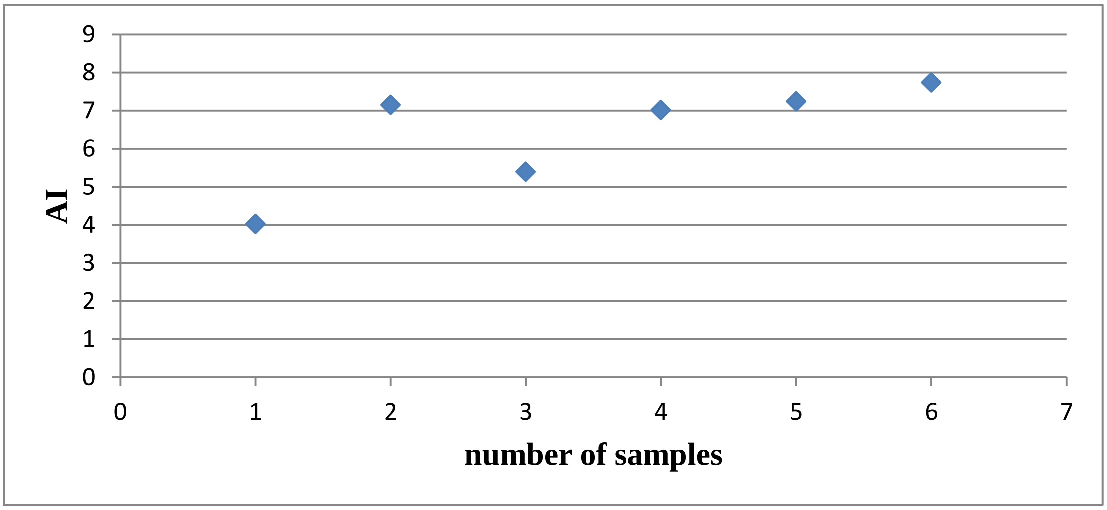


Figure 3.39 Absorbance Index Values of TPU 30% (w/w) Set with Range [6.423±1.421] (second deviation)

Figure 3.40 for the sample of TPU 30% (w/w) concentrated master batch. As estimated there is a strong carbonyl peak in the transmittance spectrum.

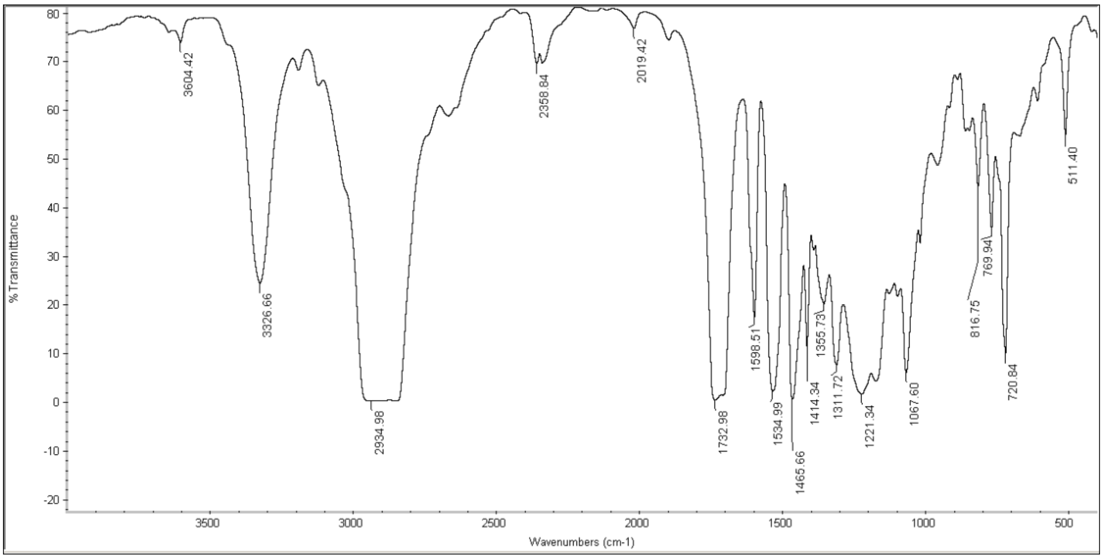


Figure 3.40 Spectrum of TPU 30% (w/w) Sample

3.6.2 TPU 40% (w/w) Concentrated Master Batch Absorbance Index Values

TPU 40% (w/w) was prepared by applying same steps. In Table 3.14, absorbance indices are shown of each sample. According to this table, high absorbance index values were determined compare to former set. These values are distributes between 9.5 and 7.2. This interval could be contracted for a better expression for concentration estimation.

Table 3.14 Absorbance Index Values of TPU 40% (w/w) Set

at 1730cm^{-1}	1	2	3	4	5	6	7	8
AI	6.863	9.151	9.947	9.554	7.306	8.865	7.082	8.882

In figure 3.41, absorbance index of each sample and average of absorbance index values with standard deviation are given. Obtained mean value was satisfactory for a master batch; however, standard deviation which is 1.196 could be revised to obtain acceptable interval.

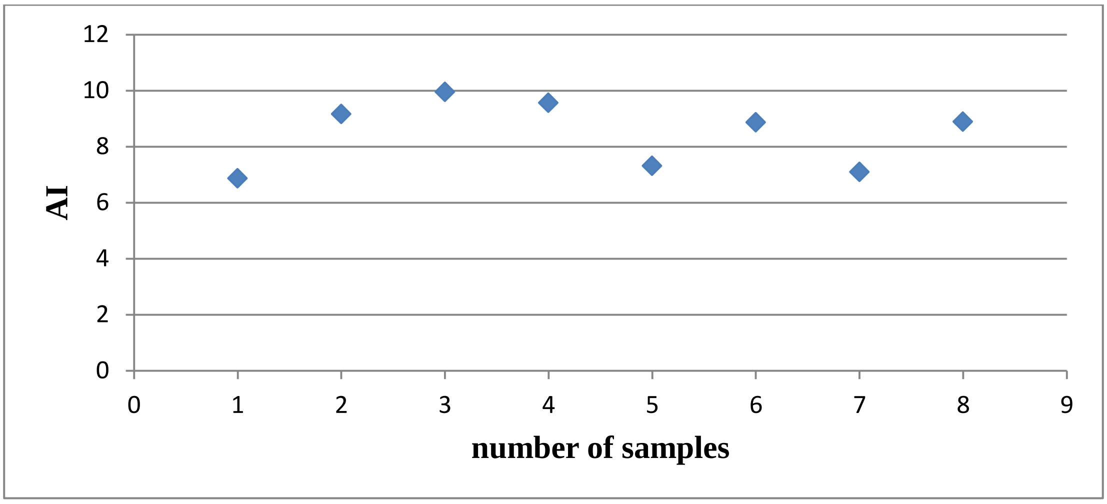


Figure 3.41 Absorbance Index Values of TPU 40% (w/w) Set with Range [8.456±1.196]

Figure 3.42 gives absorbance indices after revision. Two scattered sample points were excluded. In this case, standard deviation is 0.907. Consistency between absorbance index values of samples was acceptable. Consequently, it could be assumed that TPU 40% (w/w) set could mostly gave absorbance index between 10 and 7 interval.

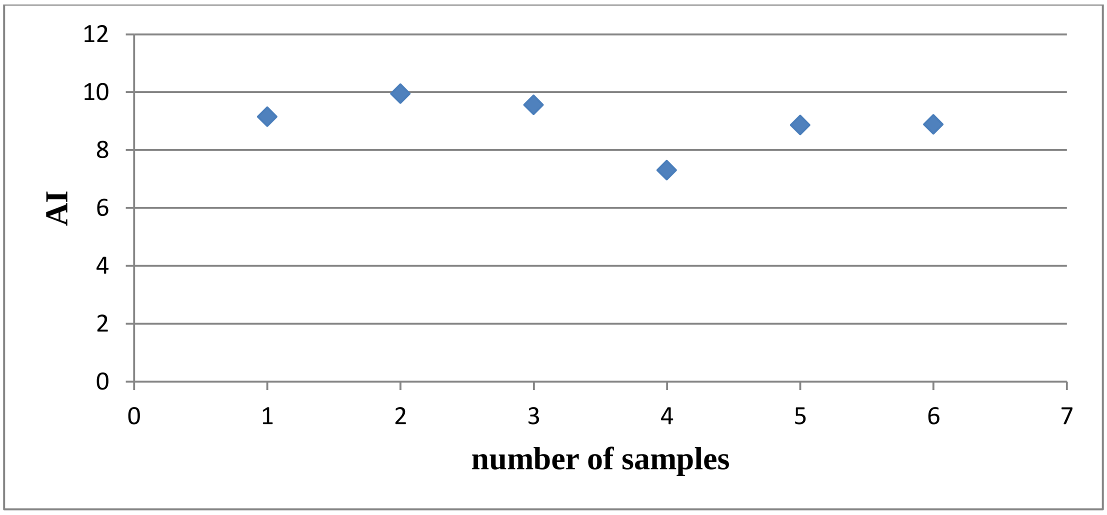


Figure 3.42 Absorbance Index Values of TPU 40% (w/w) Set with Range [8.951±0.907] (second deviation)

3.6.3 TPU 50% (w/w) Concentrated Master Batch Absorbance Index Values

Absorbance index values for TPU 50% (w/w) master batch is seen in the Table 3.15. The mean value is 10.489 with standard deviation 1.443.

Table 3.15 Absorbance Index Values of TPU 50% (w/w) Set

at 1730cm^{-1}	1	2	3	4	5	6	7	8
AI	12.07	10.28	8.522	9.512	11.65	9.241	10.11	12.53

The graph reveals distribution of each sample absorbance index (Fig. 3.43). The gap between maximum and minimum data is a high. Consequently, discarding three highly scattered data gives better information about the interval of absorbance index values.

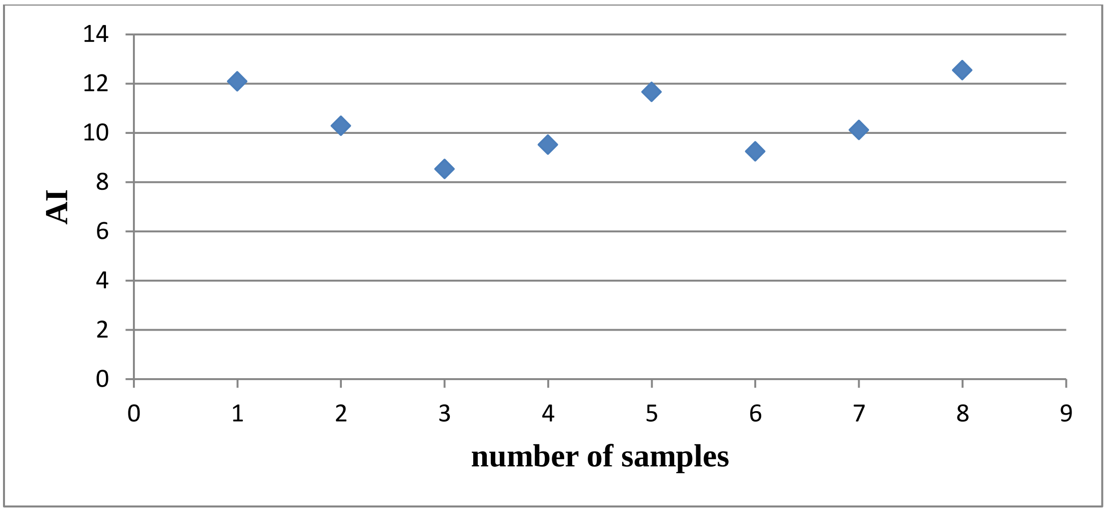


Figure 3.43 Absorbance Index Values of TPU 50% (w/w) with Range [10.489±1.443]

The chart which is below shows distribution of values after taking second deviation study. In this case, the standard deviation is lower than 1. Independent test results were close to each other. Thus, consistent data was observed.

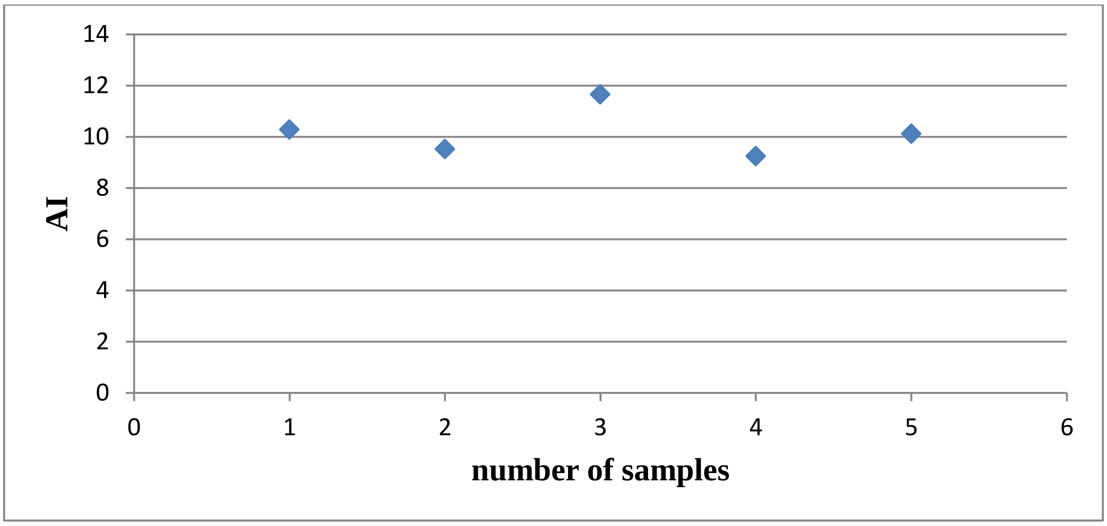


Figure 3.44 Absorbance Index Values of TPU 50% (w/w) Set with Range [10.158±0.935] (second deviation)

3.6.4 Evaluation of the Sets

Figure 3.45 includes comparison between all master batches. The absorbance indices varied between 4 and 12. These absorbance index values are better to follow compare to NBR and PA12 master batches. On the other hand it should be added interval between maximum and minimum values is a bit high for each TPU master batch. Second standard deviation study was carried out to provide better estimation about interval of absorbance index values for the additive marker FTIR controlling. The remaining results provide better information about interval which could include prospective absorbance indices for the master batches. That refers consistent absorbance index values were not obtained at the first place for TPU master batches. Although overlapping is seen some data, it could be underlined absorbance index values increases as content of TPU in the master batches increases.

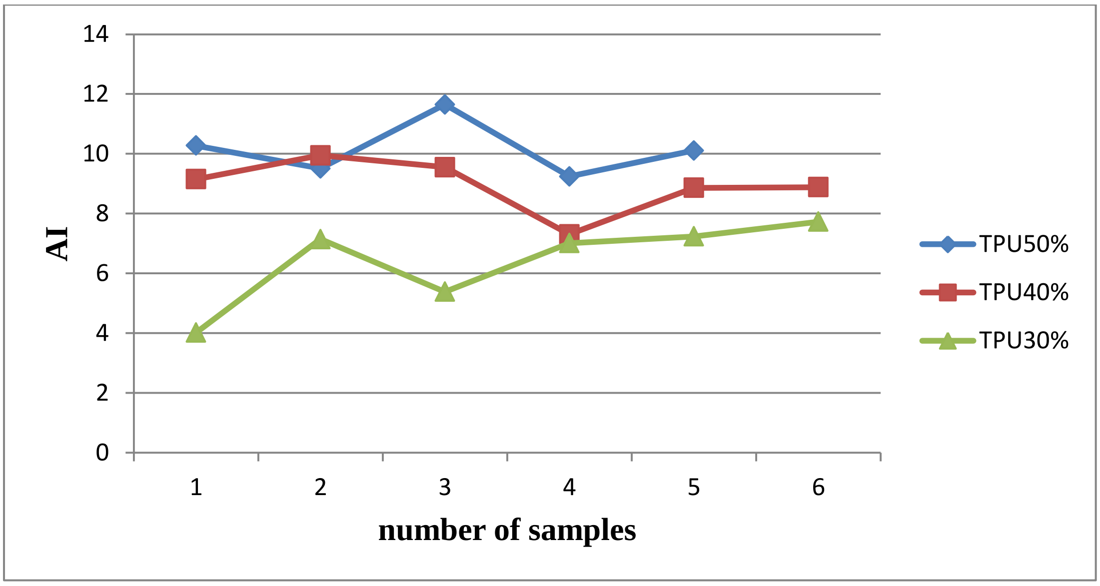


Figure 3.45 Comparison of TPU Master Batches Absorbance Index Values

3.7 TPU Master Batches as the Marker

The third marker concentration in PE matrix varies 1%, 0.8%, 0.5%, 0.25%, 0.15% and to minimum 0.09% weight to weight ratio concentration. The same procedure was applied as mentioned in the previous master batches. Fe stearate master batch was added 1% (w/w) ratio to the degradable of LDPE. The selected which are 1% (w/w), 0.5% (w/w) and 0.09% (w/w) concentrated samples are handled.

3.7.1 TPU 1% (w/w) Set

In this part, absorbance indices of LDPE samples containing maximum concentrated interior marker polymer was discussed. The set was prepared by using TPU 50% (w/w) concentrated set. In Table 3.16, absorbance values are shown. These values are change between 3.6 and 12.5. The gaps between these values are a bit large.

Table 3.16 Absorbance Index Values of TPU 1% (w/w) Set

at 1730cm^{-1}	1	2	3	4	5	6	7	8
AI x10^{-2}	8.251	11.84	8.102	6.805	3.682	7.484	12.54	11.25

In the Figure 3.46, variation of absorbance indices is revealed. The mean value of the set is 0.08 with a standard deviation 0.02. According to mean value it could be said that standard deviation is slightly high.

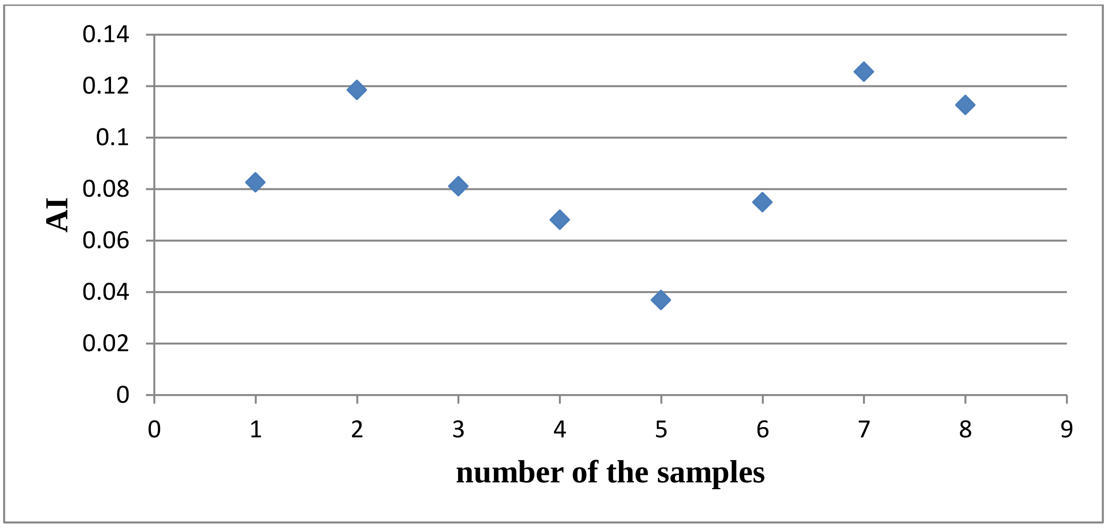


Figure 3.46 Absorbance Index Values of TPU 1% (w/w) Set with Range [0.087±0.0297]

The second deviation of the results were taken to define interval for prospective absorbance index values for TPU 1% (w/w) concentrated interior marker set (Fig. 3.47). After this step, about repeatability of results was observed clearly. The mean value did not change considerably but standard deviation decreased dramatically from 0.02 to 0.007.

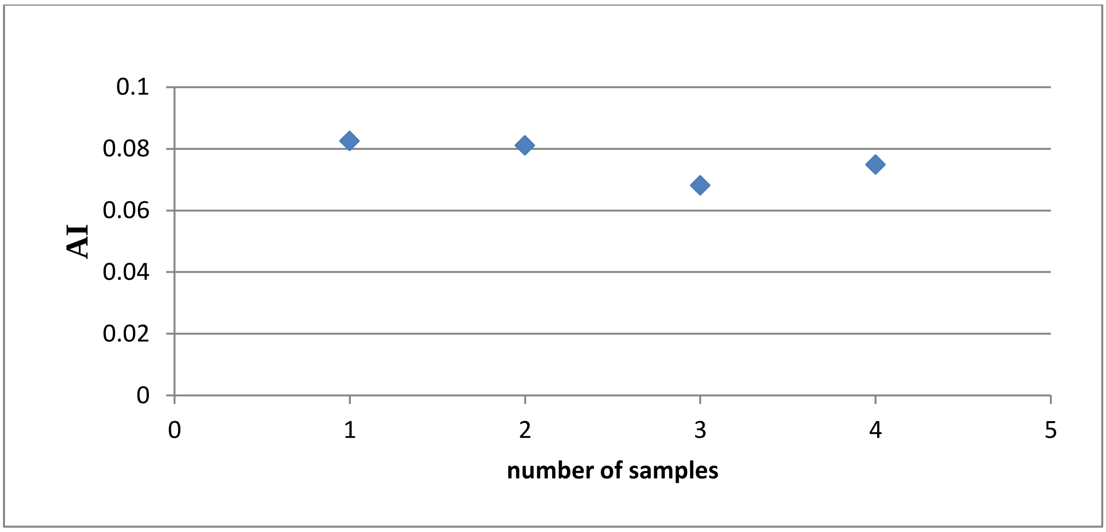


Figure 3.47 Absorbance Index Values of TPU 1% (w/w) Set with Range [0.077±0.007] (second deviation)

Following image displays an example of transmittance spectrum belonging to maximum concentrated set. Selected peak as a reference is realized at near the 1730 cm^{-1} (Fig. 3.48).

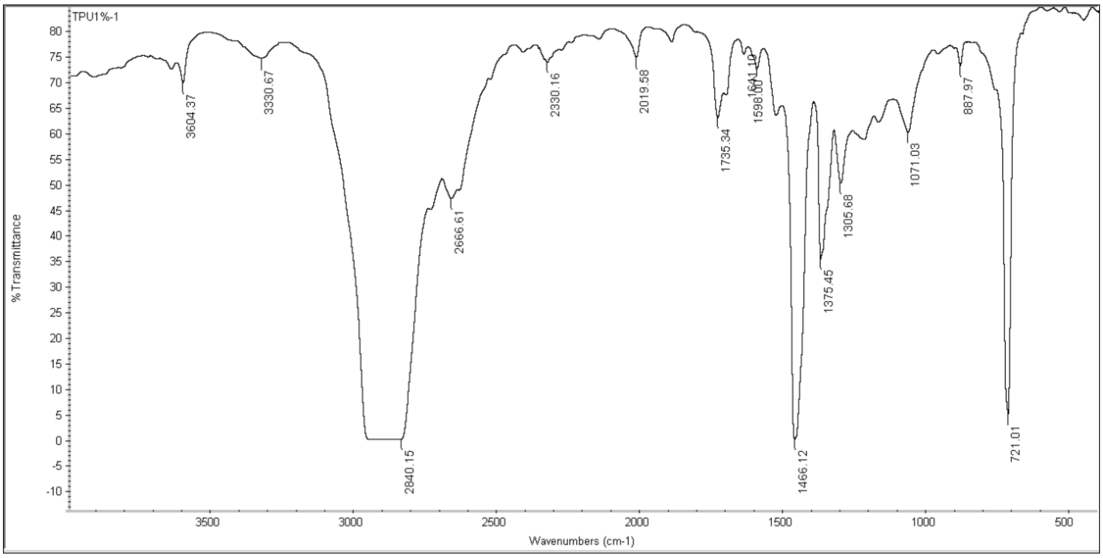


Figure 3.48 Spectrum of TPU 1% (w/w) Sample

Additionally, comparison between pure PE and the sample of this set could be seen in Figure 3.49. The carbonyl peak in the TPU polymer is definitely observed.

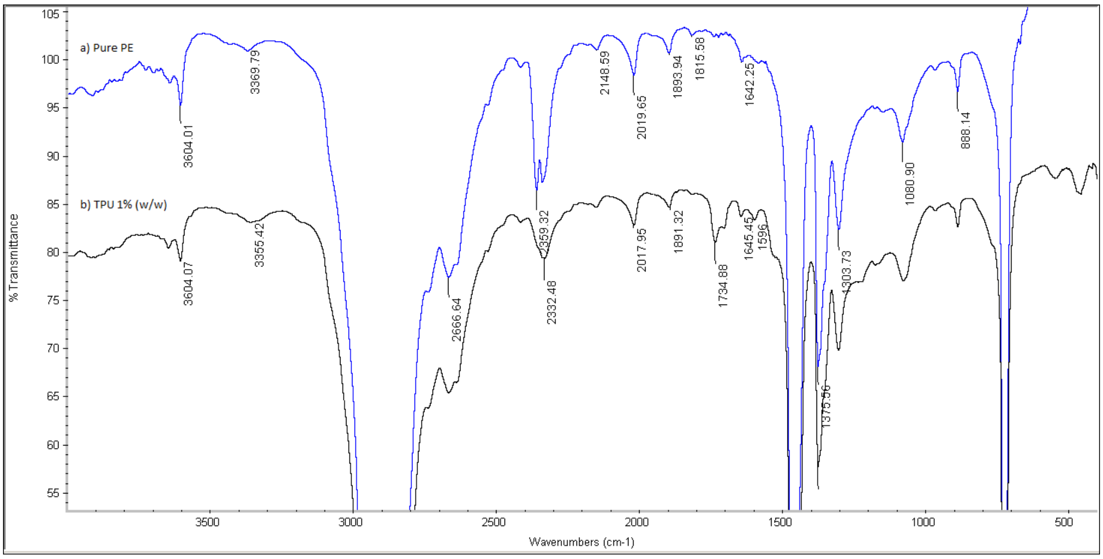


Figure 3.49 Comparison of Pure PE and TPU 1% (w/w) Sample Spectrum
a) Pure PE b) TPU 1% (w/w) Sample

3.7.2 TPU 0.5% (w/w) Set

In this part medium concentrated sample is handled. This set was also obtained by using 50% (w/w) master batch. Six samples were used to observe the variation of absorbance index values. The values are seen in the table 3.17.

Table 3.17 TPU 0.5% (w/w) Absorbance Index Values

at 1730cm^{-1}	1	2	3	4	5	6
AI x10^{-2}	7.577	4.627	7.749	6.506	4.917	4.919

Distribution of mentioned values is drawn in Figure 3.50. The absorbance index values are within the range from 7.7 x10^{-2} to 4.6 x10^{-2}. Also, standard deviation was calculated which is 0.0142. Standard deviation value indicates gap between maximum and minimum values is a bit high.

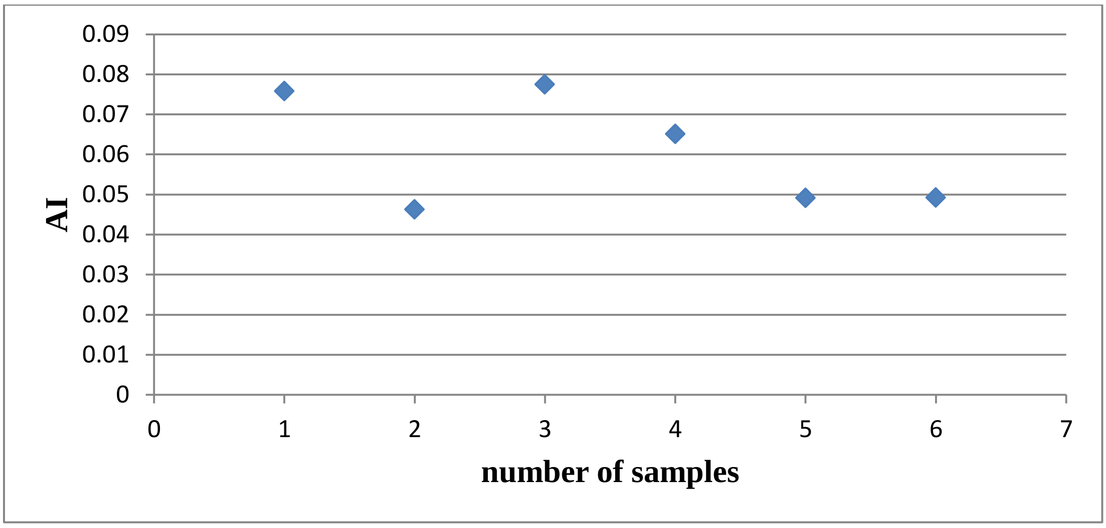


Figure 3.50 Absorbance Index Values of TPU 0.5% (w/w) Set with Range [0.061±0.014]

Gap between highest and lowest absorbance index values was narrowed to decide reasonable interval for this set (Fig. 3.51). Repeatability of measurements was examined after taking second deviation. In this case, standard deviation is 0.008. The mean value decreases from 0.06 to 0.05. The mean value does not change dramatically.

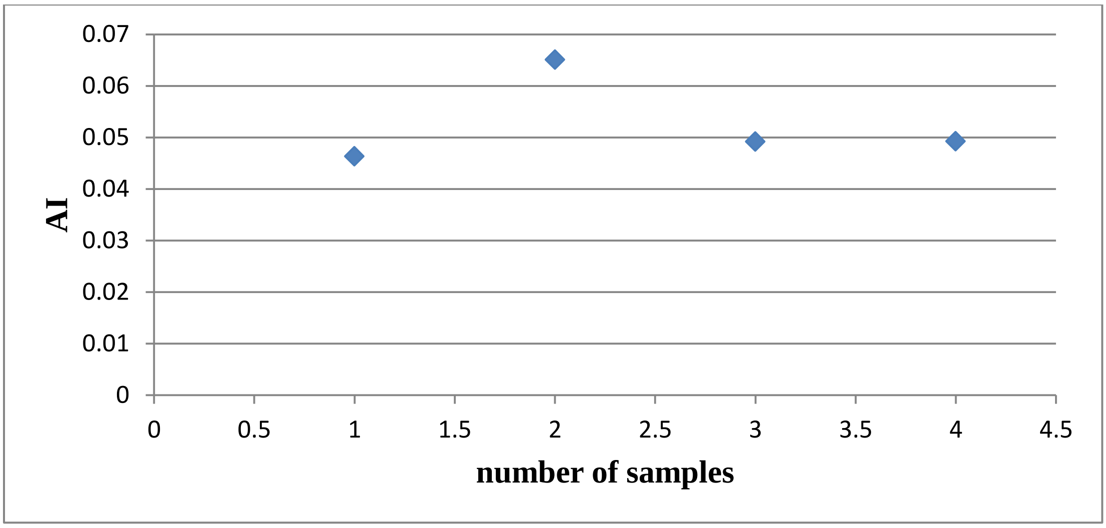


Figure 3.51 Absorbance Index Values of TPU 0.5% (w/w) with Range [0.052±0.0085] (second deviation)

Next transmittance spectrum belongs to TPU 0.5% (w/w) concentrated dilute set. Carbonyl peak is seen definitely in the spectrum (Fig. 3.52).

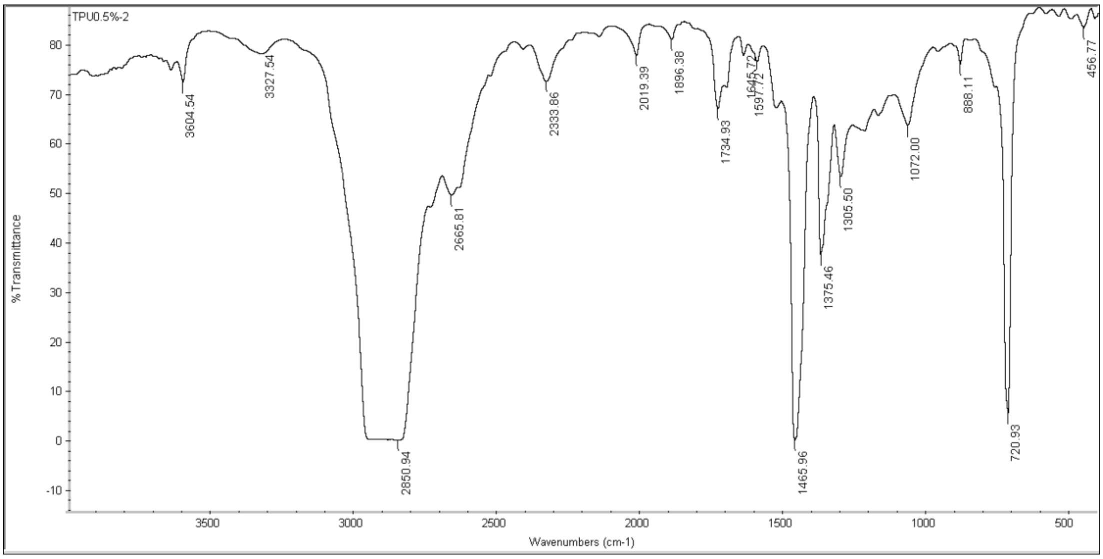


Figure 3.52 Spectrum of TPU 0.5% (w/w) Sample

Comparative spectra could be checked below (Fig. 3.53). The difference between medium concentrated set and pure PE in the carbonyl peak region is seen certainly.

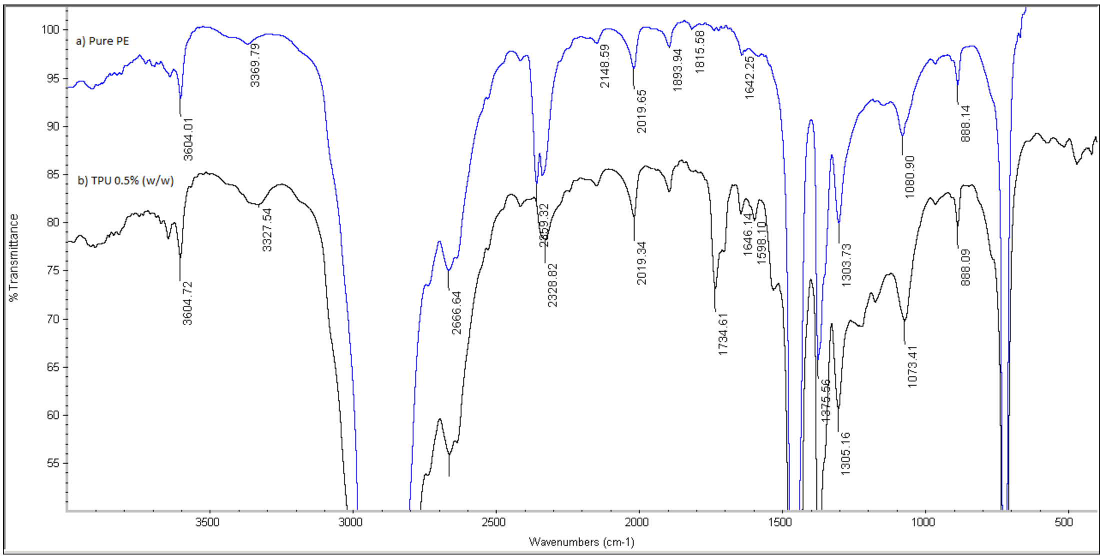


Figure 3.53 Comparison of Pure PE and TPU 0.5% (w/w) Sample Spectrum

a) Pure PE b) TPU 0.5% (w/w)

3.7.3 TPU 0.09% (w/w) Set

TPU 0.09% (w/w) set was prepared by using TPU 30% (w/w) master batch. In that case eight samples were used to determine absorbance index values. In Table 3.18, absorbance index values of each sample are given.

Table 3.18 Absorbance Index Values of TPU 0.09% (w/w)

at 1730cm^{-1}	1	2	3	4	5	6	7	8
AI x10^{-2}	1.452	1.483	1.505	1.429	1.046	0.935	1.163	1.046

In Figure 3.54, variation between absorbance indices is demonstrated. Mean values of the data is 0.013. Additionally, standard deviation is 0.00234. This result shows that agreement between replicated results of this set is quite good since standard deviation is sufficiently smaller than average value of the set. Hence, it is expected that absorbance index data is mostly observed between 0.015 and 0.009.

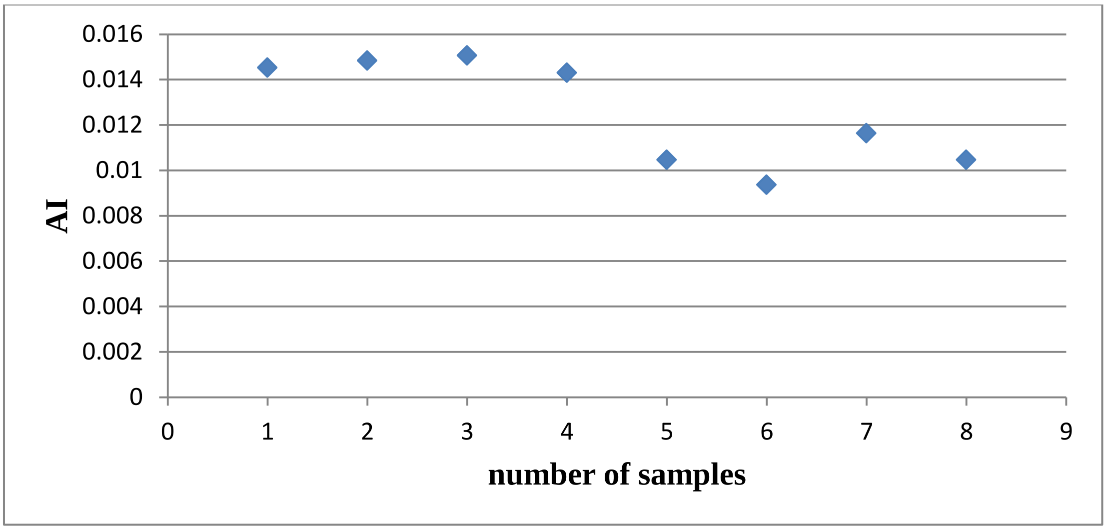


Figure 3.54 Absorbance Index Values of TPU 0.09% (w/w) Sample with Range [0.013±0.00234]

Following transmittance spectrum belongs to minimum concentrated set (Fig.3.55). Presence of reference peak is slightly seen at near 1730. This spectrum is as pure PE spectrum at the first view.

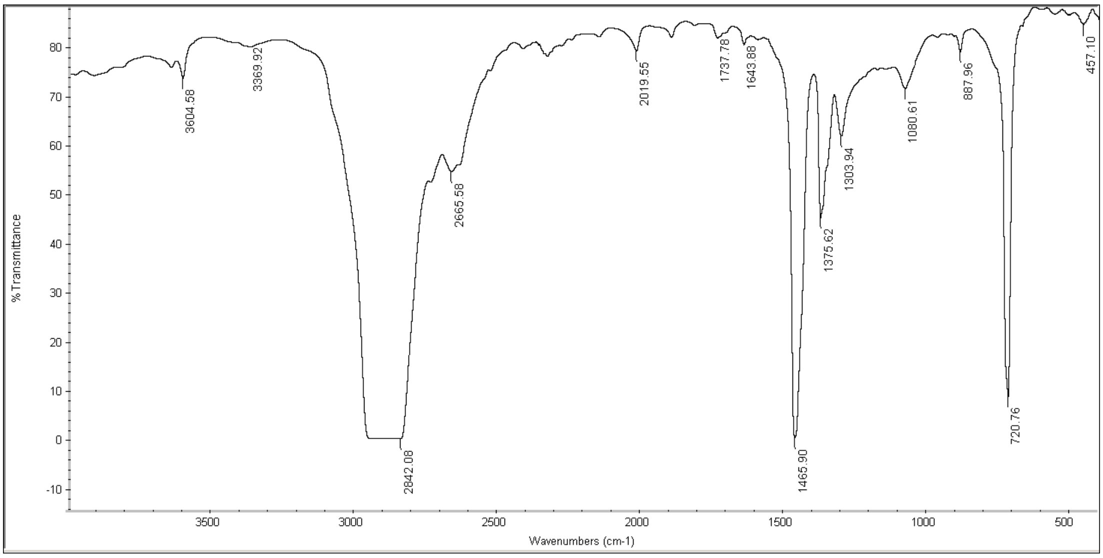


Figure 3.55 Spectrum of TPU 0.09% (w/w) Sample

Following image displaces comparison between pure PE and TPU 0.09% (w/w) concentrated set (Fig. 3.56). Interior marker peak is clearly observed in the spectrum but it is relatively small when compare to previous discussed sets.

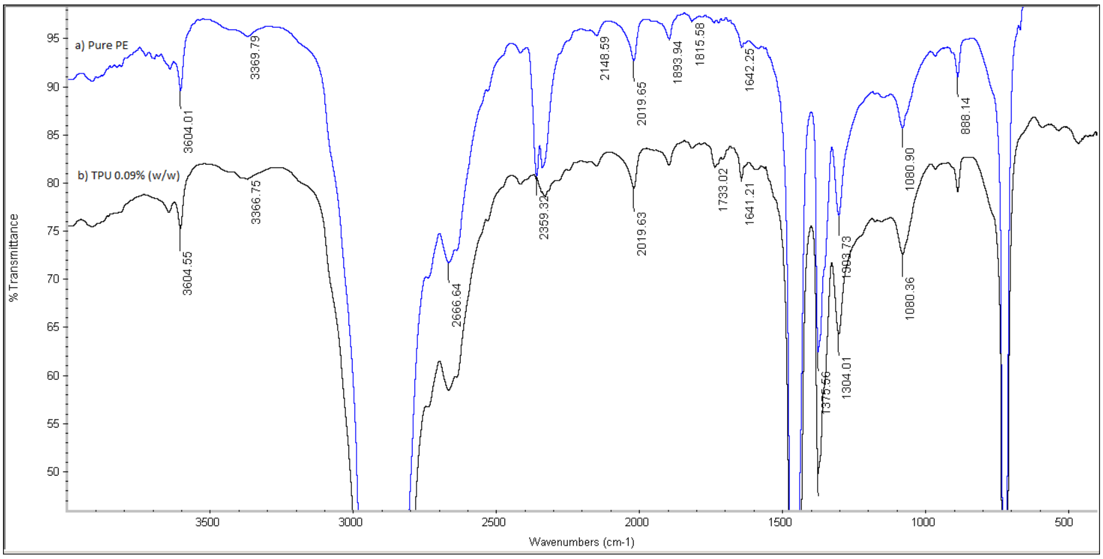


Figure 3.56 Comparison of Pure PE and TPU 0.09% (w/w) Sample

a) Pure PE b) TPU 0.09% (w/w)

3.7.4 Evaluation of the Sets

Maximum (1% w/w), medium (0.5 w/w) and minimum (0.09% w/w) concentrated sets were discussed. The following chart includes all dilute set together for a better explanation about TPU as an interior marker in PE matrix (Fig. 3.57).

TPU 1% (w/w) reveals the highest absorbance indices. Second deviation was taken in order to get better explanation about interval of absorbance index values. Additionally, TPU 0.8% ratio concentrated set was formed six samples. Second deviation was also calculated for this set. Consistent data was attained after this step. Furthermore, 0.5% (w/w) concentrated set gave medium absorbance index value by considering absorbance indices of all set. However, it is essential to add that agreement between the data was provided after ignoring scattered data. It could be concluded precision of the measurement a bit low when compare to NBR and PA12 sets. The reason why these situations might occur is the presence both hard and soft segments. Incompatibility between hard and soft segments cause phase separation in the structure. Owing to capability to form hydrogen bonding in the urethane part, hard segments could form local crystallization in the soft segment matrix [52]. Therefore, it could be also possible that in some parts in the film, hard segments may aggregate. Thus, incident radiation might come across to the region and gives higher absorbance index. Therefore, consistency between data was not achieved at desirable level

It is evidently observed in the graph absorbance index values for the lower concentrated sets are close to each other except 0.25% (w/w) set. The sets which are 0.15% (w/w) and 0.09% concentrated gave absorbance index values within the similar interval.

In addition to all of this, by using N-H bond in the urethane which is seen at near the 3325 cm^{-1} might be selected as reference peak. However, it is possible to encounter sensitivity issue due to presence of hydrogen bonding in the structure. Also, usage of peak area could be a way to obtain alternative absorbance index values of sets.

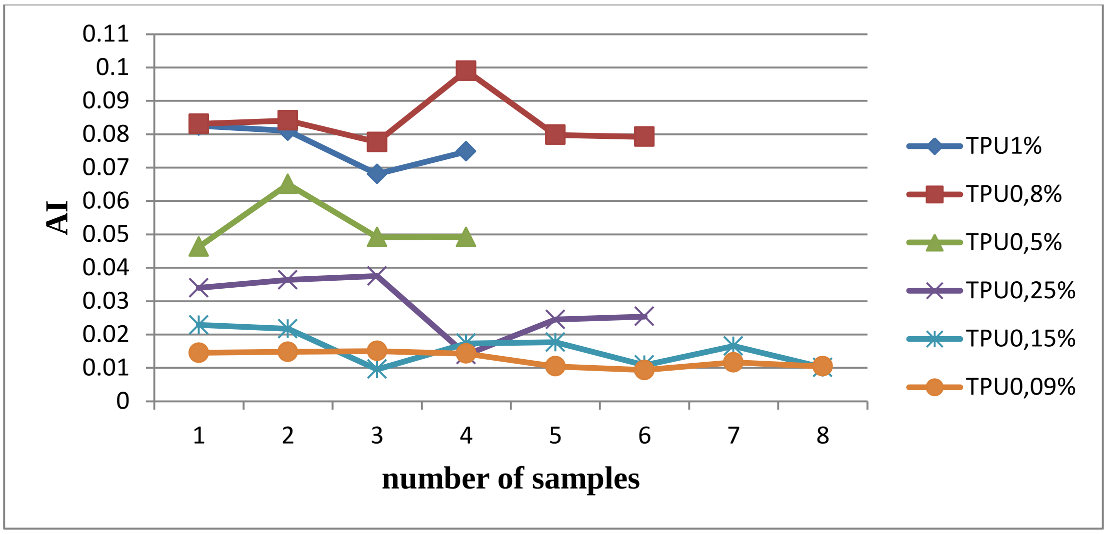


Figure 3.57 Comparison of TPU Dilute Sets Absorbance Index Values

3.8 Mechanical Testing

In this thesis, universal mechanical testing was carried out to observe mechanical property of polymer matrix. In the light of ultimate tensile strength, stress at yield and percentage strain at break values, the effect of interior marking polymers in the LDPE matrix was investigated.

Firstly, pure polyethylene was prepared as thin films cut into dog bone shapes. Five samples were prepared and the thickness of these samples was around 600 μ. The sample films were prepared thicker on purpose to overcome difficulty of handling the testing samples. Mechanical testing was performed to sketch stress versus percentage strain plot (Fig. 3.58). Under consideration this graph, ultimate tensile strength, stress at yield and percentage strain at break results obtained. The values were obtained by taking mean values of five samples results (Table 3.19).

Same procedure was applied for LDPE sets containing three interior marking polymers. The maximum (1% w/w), medium (0.5% w/w) and minimum (0.09%

w/w) concentrated samples were prepared as dog bone shaped and they were used to compare pure PE mechanical characteristics.

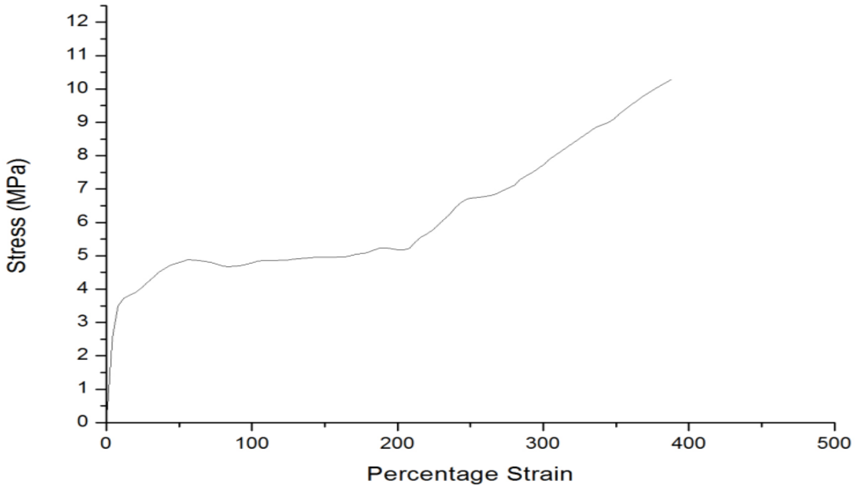


Figure 3.58 Stress versus Percentage Strain Curve of Pure PE

3.8.1 1% (w/w) Concentrated Interior Marker Polymers Sets

Mean thickness value of NBR 1% (w/w) set was measured as 540 μ. The thickness values for PA12 (1% w/w) and TPU (1% w/w) were around 400μ and 200μ, respectively.

Table 3.19 shows each interior marker polymers mechanical characteristics and pure PE characteristics.

The closest ultimate strength value belongs to acrylonitrile sets. It is necessary to point out that percentage strain of this set is the highest compare to both pure PE and other sets. The reason why this situation is it could be elastomeric characteristic of NBR. However, it could be emphasized that percentage strain values of each group are close to each other. Stress at yield values of maximum concentrated sets varies between 5.2 MPa and 6.4 MPa . Hence, 1% (w/w) interior marker containing sets showed slightly different ultimate mechanical properties than pure PE.

Table 3.19 Mechanical Properties of 1% (w/w) Sets

	NBR mean	PA12 mean	TPU mean	PE mean
Ultimate Tensile Strength (MPa)	11.8	10.9	9.9	12.1
Stress at Yield (MPa)	5.9	6.4	5.2	7.0
Percentage Strain at Break	405	350	350	380

In figure 3.59, stress percentage versus percentage strain of all sets with pure PE is given together for better comprehension. As it is seen, the curves are not much different from each other. This situation is expected since the concentration of marker polymer is small in the polymer matrix; thus, mechanical property of LDPE does not change significantly.

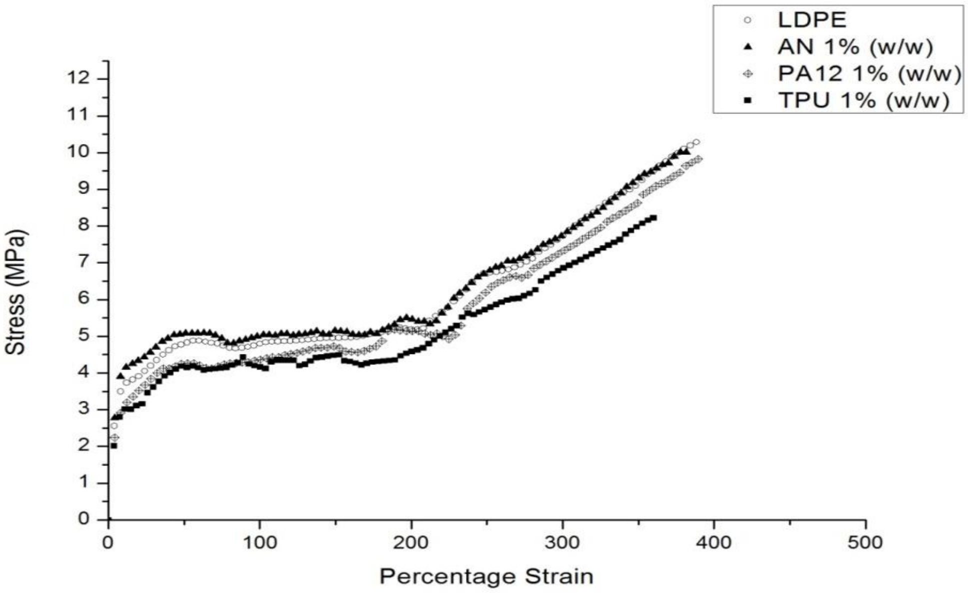


Figure 3.59 Stress- Percentage Strain Curve of Interior Marker Polymer (1 % w/w) and LDPE

3.8.2 0.5% (w/w) Concentrated Interior Marker Polymers Sets

The same procedure also was applied for this set. Dog bone shaped, five samples were used to obtain desired mechanical features. Comparison is done between pure polymer and 0.5 (w/w) concentrated sets which could be seen in table 3.20. Five samples were used for each set. The mean values of thickness for NBR set was 475 µ. The thinner thicknesses of films belong to TPU sets and the mean value of it was 190 µ. Also, the thickness of PA12 samples varies between 440 µ and 330 µ.

Table 3.20 Mechanical Properties of 0.5% (w/w) Sets

	NBR mean	PA12 mean	TPU mean	PE mean
Ultimate Tensile Strength (MPa)	12.1	10.9	11	12.1
Stress at Yield (MPa)	6.2	6.7	6.4	7.0
Percentage Strain at Break	385	330	350	380

In figure 3.60, stress versus percentage stress curves is illustrated for all sets. Consistency was provided at reasonable level.

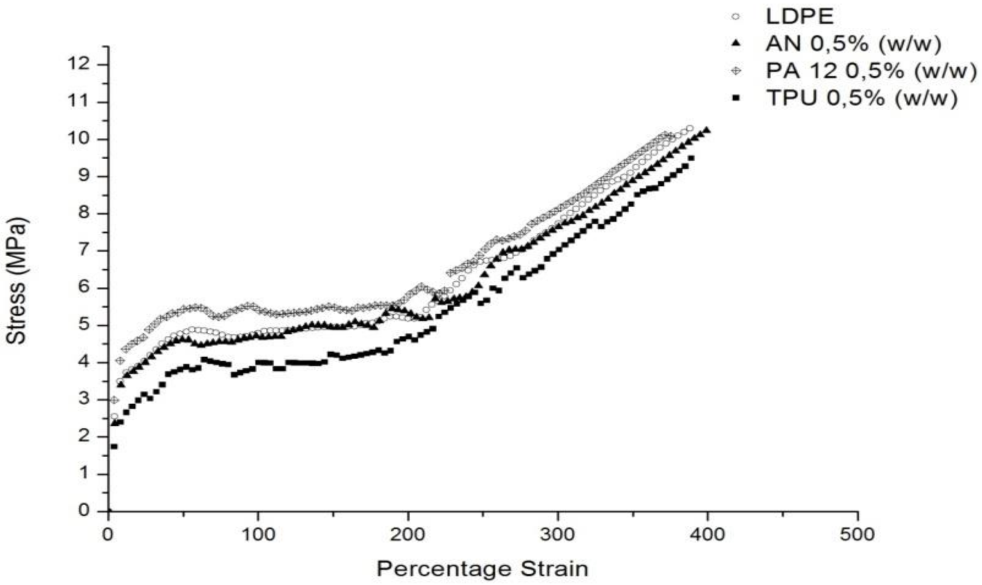


Figure 3.60 Stress- Percentage Strain Curve of Interior Marker Polymer (0.5 % w/w) and LDPE

3.8.3 0.09% (w/w) Concentrated Interior Marker Polymers Sets

In this case, oxo-biodegradable LDPE sets contain minimum concentrated interior marker polymer. These sets were exposed to mechanical testing. Thicknesses of NBR films were around 600 µ; also, PA12 films were thicker than 750 µ. Additionally, mean of thicknesses values was 180 µ for TPU sets.

Table 3.21 includes 0.09% concentrated samples mechanical properties. As it is shown regardless of interior marker type, mechanical properties values are almost equal

Table 3.21 Mechanical Properties of 0.09% (w/w) Sets

	NBR mean	PA12 mean	TPU mean	PE mean
Ultimate Tensile Strength (MPa)	12.3	11.9	10.7	12.1
Stress at Yield (MPa)	6.3	7.0	5.7	7.0
Percentage Strain at Break	495	365	335	380

The figure which is demonstrated below provides better understanding consistency of curves. Curves of the sets overlap each other. It means mechanical characteristics of interior marker containing sets do not show any significant change (Fig. 3.61).

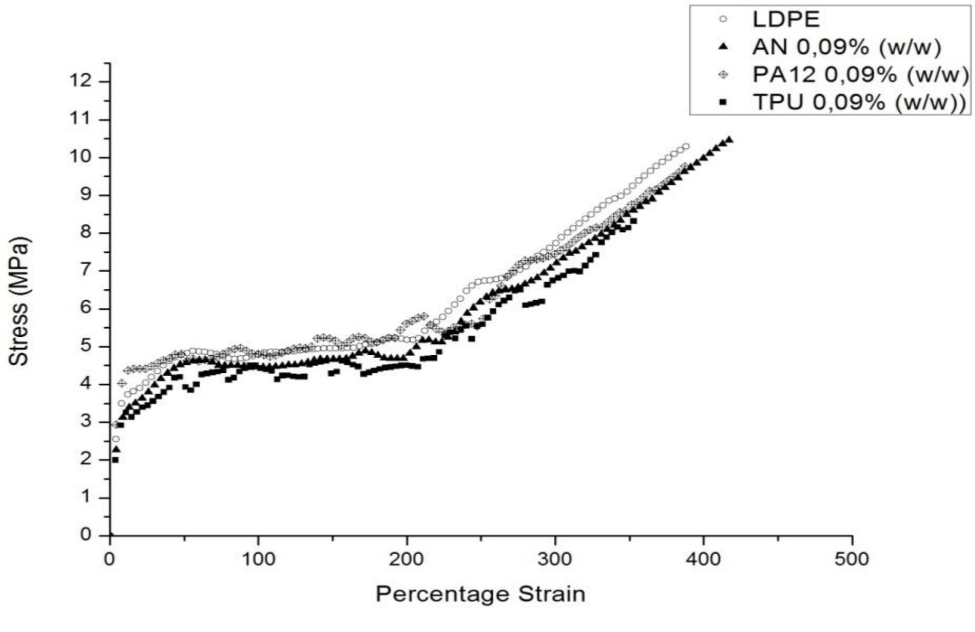


Figure 3.61 Stress- Percentage Strain Curve of Interior Marker Polymer (0.09% w/w) and LDPE

As a result, three different interior marker polymers which were 1% (w/w), 0.5% (w/w) and 0.09% (w/w) concentrated were subjected mechanical testing. The consequences indicate that the interior marker polymers do not have any significant effect on PE matrix. This result was expected because concentrations of markers are too small in order to influence on mechanical properties on PE.

3.9 Thermal Analysis of Samples

In this thesis project, in addition to mechanical testing, differential scanning calorimetry (DSC) was also carried out in order to check thermal stability of PE matrix. Pure PE NBR 1% (w/w), PA12 1% (w/w) and TPU 1% (w/w) samples were analyzed for thermal analysis. DSC analysis was undergone for temperature range from 25°C to 200°C at heating rate of 20°C/min. Finally, isothermal process was performed at 200°C for one hour.

DSC is widely used to determine crystalline melting temperature (T_m) and glass transition temperature T_g. T_m is the temperature at which crystalline part of the polymers melts. Furthermore, T_g is the transition temperature which cause immediate change in amorphous part of the polymer from glassy state (brittle) to rubbery state (elastic). DSC shows reflection to change in heat capacity of a sample as a function of temperature by measuring the heat flow required to maintain a zero temperature differential between an inert reference materials [53].

T_m is observed in pure PE matrix at 112.8°C due to semi-crystal structure of it. The onset temperature which is temperature to start melting is 96.51°C. As it is recognized from thermogram melting temperature is seen at 113°C (Fig. 3.62).

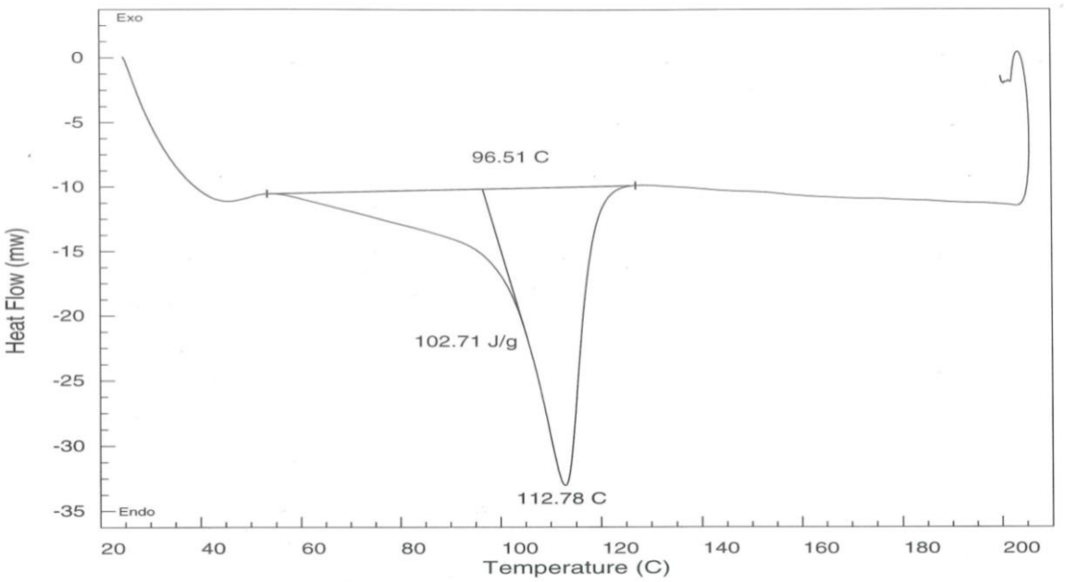


Figure 3.62 Pure PE Thermogram

Pure PE sample was also subjected to isothermal process for one hour. The thermogram was sketched by using heat flow and time data (Fig. 3.63). During first five minutes, sample was taken sufficient heat to melt. After then isothermal process was started at 200°C in order to observe stability of polymer matrix. The reason of applying isothermal process on the polymer is that observing stability against to permanent high temperature. During that time interval, endothermic or exothermic reactions would be occurred. This situation shows instability of polymer matrix which could be observed clearly on the thermogram.

It is evidently recognized that heat flow value did not change during isothermal process. That means, characteristic properties of PE matrix was protected during the process.

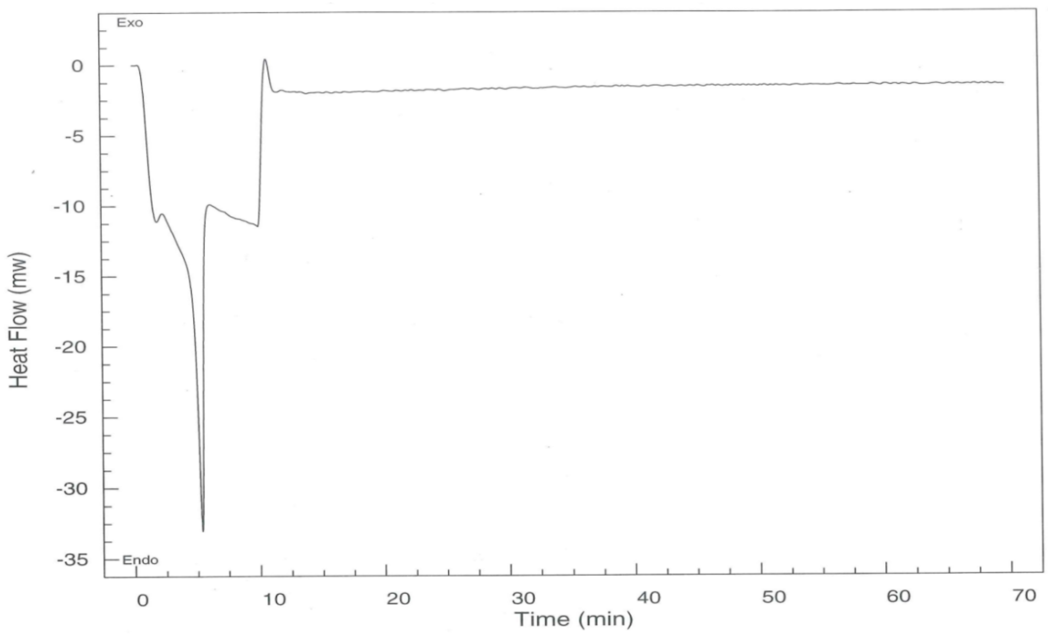


Figure 3.63 Isothermal Treatment of Pure PE at 200°C for 1 Hour

The example figure which is seen below belongs to NBR 1% (w/w) concentrated LDPE set (Fig. 3.64). The thermogram contains approximately same data with pure PE matrix. The onset temperature and T_m value of this set 97.28 °C and 111.55°C, respectively. This result proves that there is a consistency between sets in terms of thermal characteristics.

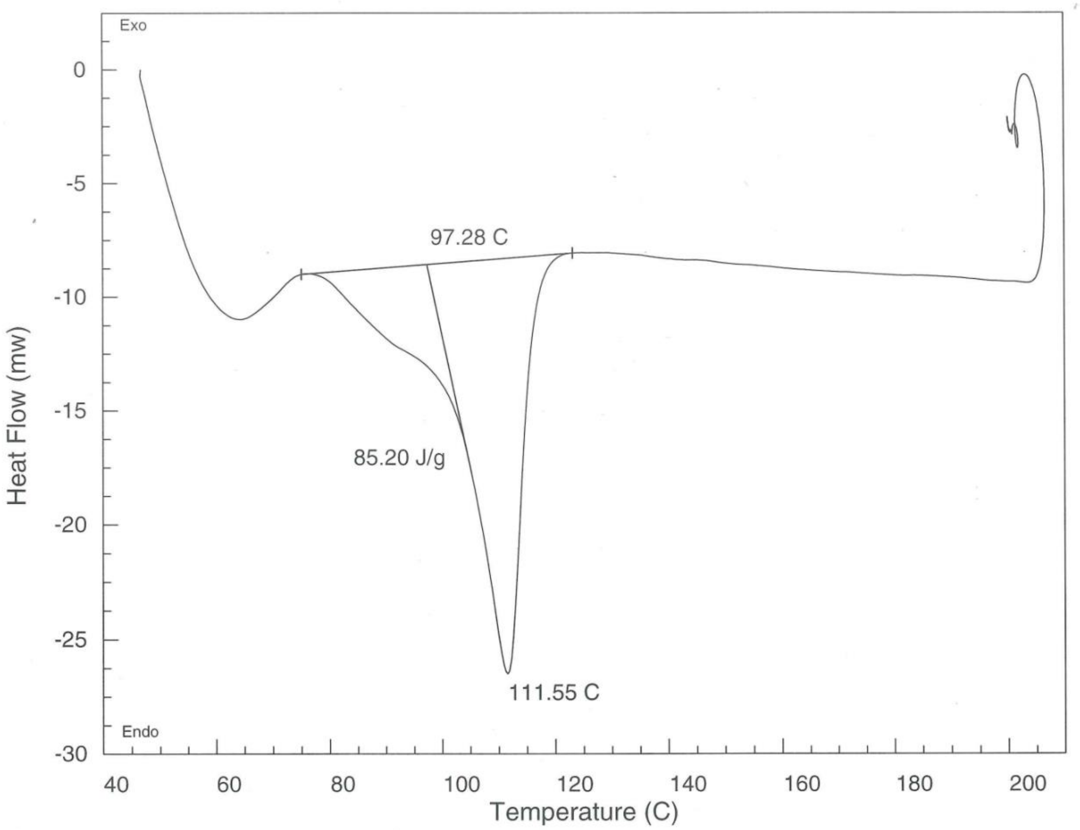


Figure 3.64 NBR 1% (w/w) Sample Thermogram

The sample was also exposed to isothermal process at 200°C for one hour since there was a necessity to maintain of same environmental condition in order to get efficient comparison between PE matrix and NBR 1% (w/w) matrix. The Figure 3.65 shows melting process was completed in first ten minutes. After that isothermal process was started. It is necessary to point out that heat flow value does not display any discrepancy. That means thermo oxidation reaction did not occur. Therefore, it can be said that stability of polymer matrix was preserved like pure PE. The LDPE set containing maximum concentrated marker polymer possess similar characteristic with pure PE at desirable level.

This process was also carried out for the other two interior marker polymers. These sets were contain 1% (w/w), 0.5% (w/w), 0.09% (w/w) interior marker. The only one example is revealed in this part. The thermogarms which belongs to PA12 and TPU could be seen in the Appendix D. The stability of PA12 and TPU was also verified.

Under the light of this information It could be concluded that working conditions for processes were set properly since application of suitable temperature, pressure and speed of process is vital and influences final product features. Consequently, any instability was not observed on the thermograms.

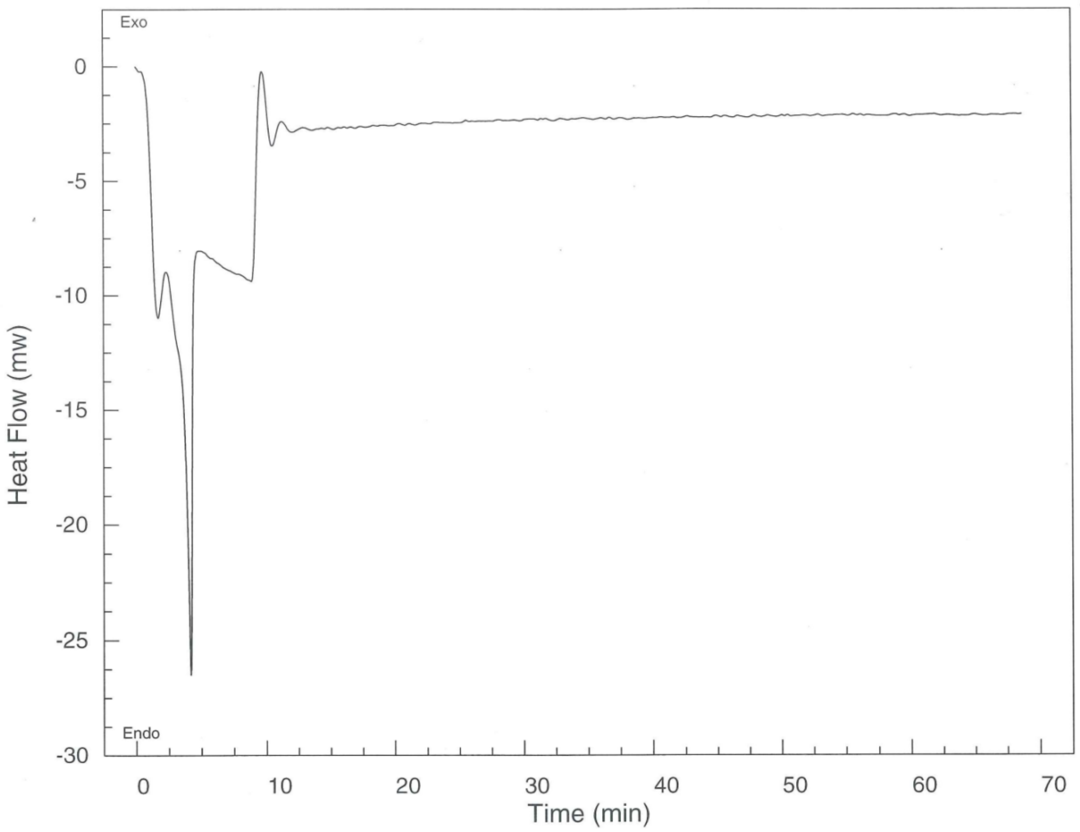


Figure 3.65 Isothermal Treatment of NBR 1% (w/w) at 200°C for 1 Hour

CHAPTER 4

CONCLUSIONS

Three different interior markers were used for LDPE shopping bag containing oxo-biodegradable pro-oxidant. These were NBR, PA12 and TPU. The polymers were preferred for being compatible, nontoxic, nonvolatile, cheap and available.

For each type of polymer, weight ratios of 30%, 40% and 50% concentrated master batches were analyzed by ATR FTIR technique. The marker peaks of master batches were assigned by using transmittance spectrum. Absorbance index values were obtained to prove existence of interior marker. The marker peaks were chosen as a reference peak which did not overlap any PE peaks. The other reference peak was chosen as 720 cm^{-1} of LDPE. Absorbance index values were obtained by dividing absorbance of interior marker reference peak into absorbance of PE reference peak.

ATR-FTIR technique was used to assess presence of these markers. Additionally, universal mechanical testing was applied to obtain mechanical properties weight ratios for 1%, 0.5% and 0.09% and DSC studies were also carried out to obtain T_m values for the same concentrated samples. Moreover, these samples were exposed to isothermal process at 200°C for one hour to observe stability of marker containing polymer matrix.

Nitrile peak at 2238 cm^{-1} was used as good interior marker in nitrile rubber. Absorbance indices of master batches were remarkable. The NBR at low concentrations is compatible with PE and repeatable results were obtained at acceptable level. Furthermore, that interior marker was detectable in the transmittance spectra of samples even low concentration.

Carbonyl group of PA12 at 1640 cm^{-1} was used reference peak as a second interior marker. PA12 master batches provided high absorbance indices. Moreover, high absorbance index values were obtained even in the dilute sets. Results of measurements were consistent. The peak of marker polymer in the sample spectrum is observed clearly.

The carbonyl part of TPU gives peak at 1730 cm^{-1}. This peak was selected as an interior marker. The highest absorbance indices were obtained among all master batches but consistencies of absorbance indices were limited. Interior marker peak belonging TPU polymer was recognized easily in the transmittance spectra. However, agreement between absorbance index values was limited.

Furthermore, when compare to master batches of three different polymers, TPU master batches provides the maximum absorbance index values for each concentration. However, the repeatability of the measurements was weaker when compare to NBR and PA12 master batches. Besides, the lowest absorbance index values were seen in NBR master batches but precision of measurements was acceptable level. Master batches which were produced by using PA12 provided both remarkable mean values and consistent absorbance values.

It is necessary to mention that interior marker peak was detectable in the spectra of PA12 and TPU dilute sets at the first place. However, NBR interior marker peak was observed clearly when transmittance spectra extended along y axis. Dilute sample sets which constitute PA12 possessed the highest absorbance index values than NBR and TPU sets. Consistent results were also obtained. The reference peak was seen as a weak peak in the transmittance spectra. The reference peak of TPU interior marker polymer was visible in the transmittance spectra even low concentration but precision of measurement was limited.

In addition to all of these, universal mechanical testing and differential scanning calorimetry were carried out for selected samples to check stability of polymer matrix. According to these measurements, the sample sets which included interior markers did not show any significant diverse effect on PE matrix.

In this thesis, three different interior markers were placed in LDPE shopping bag matrix including pro-oxidant. The interior markers were used to assessment the presence of prodegradant additives in oxo-biodegradable plastic PE shopping bags by using ATR-FTIR technique. The purpose of this study was that proceeding confidence level of usage pro-oxidant additives in PE shopping bags by improving an interior marker in PE. ATR-FTIR method was chosen as an instrument type since it is commonly used in industry gives fast, the cheapest and reliable result. Consequently, it could be used for industrial application.

REFERENCES

[1] Sudhakar, M.; Doble, M.; Murthy, P.; Venkatesan, R. *International Biodeterioration & Biodegradation* 2007, *61*, 203-213.

[2] Ołdak, D.; Kaczmarek, H.; Buffeteau, T.; Sourisseau, C. *J Mater Sci* 2005, *40*, 4189-4198.

[3] Ojeda, T.; Freitas, A.; Birck, K.; Dalmolin, E.; Jacques, R.; Bento, F.; Camargo, F. *Polymer Degradation and Stability* 2011, *96*, 703-707.

[4] Klein, J. M., Ramos, G. R., Coulon Grisa, A. M., Brandalise, R. N., & Zeni, M. *Progress In Rubber, Plastics & Recycling Technology*, 2012, *29*(1), 39-54.

[5] Mark, J. *Polymer Data Handbook*; Oxford University Press: Oxford, 1999.

[6] Hamid, S. *Handbook of Polymer Degradation*; Marcel Dekker: New York, 1992

[7] Reddy, M.; Gupta, R.; Gupta, R.; Bhattacharya, S.; Parthasarathy, R. *Journal of Polymers and the Environment* 2008, *16*, 27-34.

[8] Koutny, M.; Lemaire, J.; Delort, A. *Chemosphere* 2006, *64*, 1243-1252.

[9] Chiellini, E.; Corti, A.; Swift, G. *Polymer Degradation and Stability* 2003, *81*, 341-351.

[10] Smith, R. *Biodegradable Polymers for Industrial Applications*; Woodhead: Cambridge, 2005.

[11] Ojeda, T.; Dalmolin, E.; Forte, M.; Jacques, R.; Bento, F.; Camargo, F. *Polymer Degradation and Stability* 2009, *94*, 965-970.

[12] Siracusa, V.; Rocculi, P.; Romani, S.; Rosa, M. *Trends in Food Science & Technology* 2008, *19*, 634-643.

[13] Ammala, A.; Bateman, S.; Dean, K.; Petinakis, E.; Sangwan, P.; Wong, S.; Yuan, Q.; Yu, L.; Patrick, C.; Leong, K. *Progress in Polymer Science* 2011, *36*, 1015-1049.

[14] Abrusci, C.; Pablos, J.; Marín, I.; Espí, E.; Corrales, T.; Catalina, F. *International Biodeterioration & Biodegradation* 2013, *83*, 25-32.

[15] Jakubowicz, I.; Yarahmadi, N.; Petersen, H. *Polymer Degradation and Stability* 2006, *91*, 1556-1562.

[16] Scott G. Polymer compositions. Pat US4121025, assigned to Scott G; 1978.

[17] Newland GC, Greear GR, Tamblin JW. Polyolefin Compositions and Degradable Films Made Therefrom. Pat US3454510, assigned to Eastman Kodak Co.; 1969.

[18] Gho JG, Garcia RA. Degradable/Compostable Concentrates, Process for Making Degradable/Compostable Packaging Materials and the Products Thereof. Pat US5854304, assigned to EPI Environmental Products Inc.; 1998.

[19] Peng C. A Degradable Polyolefin Resin and Process for Making same. Pat WO2008020752, assigned to Gain Mark Technology Ltd.; 2008.

[20] Graziani, M.; Fornasiero, P. *Renewable Resources and Renewable Energy*; CRC Press: Boca Raton, 2007.

[21] Swanholm CE, Caldwell RG. Photodegradable Polyolefins Containing an Aromatic Ketone, Ferric Stearate and a Pigment. Pat US4038227, assigned to Bio-degradable Plastics Inc.; 1977.

[22] Lambert B. Photodegradable Polyolefins. Pat US3679777, assigned to Ethylene Plastique; 1972.

[23] Fox RC. Photodegradability of Plastic Polyolefins. Pat US4197375, assigned to Chevron Research Co.; 1980.

[24] Richter E, Kling R. Peroxide Containing Active Ingredient Composition for Targetted Scission or Crosslinking Reactions in Plastics. Pat WO2008037398, assigned to Clariant International Ltd.; 2008.

[25] Sala M, Gardi S, Schlingloff G. Degradable Polymer Article. Pat WO2007028731, assigned to Ciba Specialty Chemicals Holding Inc.; 2007.

[26] Cichy, B.; Kwiecień, J.; Piątkowska, M.; Kużdżał, E.; Gibas, E.; Rymarz, G. *Polish Journal of Chemical Technology* 2010, *12*.

[27] Lucas, N.; Bienaime, C.; Belloy, C.; Queneudec, M.; Silvestre, F.; Nava-Saucedo, J.*Chemosphere* 2008, *73*, 429-442.

[28] Benítez, A.; Sánchez, J.; Arnal, M.; Müller, A.; Rodríguez, O.; Morales, G. *Polymer Degradation and Stability* 2013, *98*, 490-501.

[29] Fontanella, S.; Bonhomme, S.; Koutny, M.; Husarova, L.; Brusson, J.; Courdavault, J.; Pitteri, S.; Samuel, G.; Pichon, G.; Lemaire, J.; Delort, A. *Polymer Degradation and Stability* 2010, *95*, 1011-1021.

[30] Busfield, W.; Taba, P. *Polymer Degradation and Stability* 1996, *51*, 185-196.

[31] Koutny, M.; Sancelme, M.; Dabin, C.; Pichon, N.; Delort, A.; Lemaire, J. *Polymer Degradation and Stability* 2006, *91*, 1495-1503.

[32] Scott, G.; Wiles, D. *Biomacromolecules* 2001, *2*, 615-622.

[33] Mannle F, Rodseth KR, Kleppe EA, Hauge RP. Thermoplastic Materials with Adjustable Useful Lifetime, Method for their Manufacture and Products thereof. Pat WO2006043827, assigned to NOR-X Industries; 2006.

[34] Tobias JW, Taylor LJ. Photodegradable Polymer Compositions. Pat US4360606, assigned to Owens-Illinois Inc.; 1982.

[35] Mannle F, Beylich J, Lecerf N, Olafsen K, Hauge R, Roedseth KR, Kleppe EA. Additive for Thermoplastics, Use of and Method for its Manufacture. Pat WO2004094516, assigned to NOR-X Ind; 2004.

[36] Akovalı, G. *Advances in Polymer Coated Textiles*; Smithers Rapra Technology Ltd.: Shrewsbury, United Kingdom, 2012.

[37] Visakh, P. *Advances in Elastomers*; Springer: Heidelberg [etc.], 2013.

[38] McKeen, L. *Film Properties of Plastics and Elastomers*; William Andrew: [S.l.], 2012.

[39] Gao, F. *Advances in Polymer Nanocomposites - Types and Applications*. Woodhead Publishing, 2014.

[40] Dodiuk, H., Goodman Sidney, H. *15. Biobased Thermosets*. Elsevier, 2014.

[41] Petkim Petrokimya Holding A.Ş. Product Specifications Page. https://app.petkim.com.tr/web/urun/ToPdf.ashx?fn=UR.12-SD-U1231.0_9.xls&l=tr&fl=urunler (accessed July 21, 2015)

[42] Rilsamide by Arkema Product Specifications Page. http://www.materialdatacenter.com/ms/it/tradenames/Rilsamid/ARKEMA/Rilsamid%C2%AE+AESN+NOIR+P201+TL/708507db/6604 (accessed July 21, 2015)

[43] Merquinsa Product Specifications Page. http://www.merquinsa.com/p_info/pdf/ECO%20D12T85.pdf (accessed July 21, 2015)

[44] Henniker, J. *Infrared Spectrometry of Industrial Polymers*; Academic Press: London, 1967.

[45] Koenig, J. *Spectroscopy of Polymers*; American Chemical Society: Washington, DC, 1999.

[46] Gulmine, J.; Janissek, P.; Heise, H.; Akcelrud, L. *Polymer Testing* 2002, *21*, 557-563.

[47] Avram, M.; Mateescu, G. *Infrared Spectroscopy: Applications in Organic Chemistry*; Wiley-Interscience: New York, 1972.

[48] Chakraborty, S.; Bandyopadhyay, S.; Ameta, R.; Mukhopadhyay, R.; Deuri, A. *Polymer Testing* 2007, *26*, 38-41.

[49] Seehra, M.; Yalamanchi, M.; Singh, V. *Polymer Testing* 2012, *31*, 564-571.

[50] Sidwell, J. *The Rapra Collection of Infrared Spectra of Rubbers, Plastics, and Thermoplastic Elastomers*; Rapra Technology Ltd.: Shrewsbury, Shropshire, U.K., 1997.

[51] Alves, P.; Coelho, J.; Haack, J.; Rota, A.; Bruinink, A.; Gil, M. *European Polymer Journal* 2009, *45*, 1412-1419.

[52] Pielichowski, K., Njuguna, J. *Thermal Degradation of Polymeric Materials*. Shawbury: Rapra Technology Ltd, 2005.

[53] Odian, G. *Principles of Polymerization*, John Wiley & Sons, Inc., New Jersey, 2004.

APPENDICES

A. ABSORBANCE INDICES DATA

Table A.1 NBR 30% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI x 10^{-1}	3.975	4.657	4.322	4.691	4.136	4.515	4.197	4.063
A 2238 cm^{-1}	0.161	0.468	0.268	0.455	0.249	0.475	0.191	0.18
A 720 cm^{-1}	0.405	1.005	0.62	0.97	0.602	1.052	0.455	0.443

Table A.2 NBR 40% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI x10^{-1}	4.357	4.816	6.159	5.425	5.699	6.084	5.781	5.911
A 2238 cm^{-1}	0.299	0.21	0.393	0.236	0.277	0.376	0.322	0.467
A 720 cm^{-1}	0.686	0.436	0.638	0.435	0.486	0.618	0.557	0.79

Table A. 3 NBR 50% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7
AI	1.0647	1.0903	1.053	0.9739	1.0205	1.0151	0.9808
A 2238 cm^{-1}	0.493	0.748	0.715	0.261	0.398	0.403	0.564
A 720 cm^{-1}	0.463	0.686	0.679	0.268	0.39	0.397	0.575

Table A. 4 NBR 1% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI x10^{-3}	7.466	6.269	10	9.146	7.509	11.57	5.964	7.208
A 2238 cm^{-1}	0.0056	0.004	0.01	0.009	0.006	0.01	0.0047	0.0063
A 720 cm^{-1}	0.75	0.638	1	0.984	0.799	0.864	0.788	0.874

Table A. 5 NBR 0.8% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7
AIx10^{-3}	7.335	5.977	6.161	9.594	8.343	10.76	5.907
2238cm^{-1}	0.0049	0.0063	0.0052	0.009	0.007	0.0091	0.007
720cm^{-1}	0.668	1.054	0.844	0.938	0.839	0.845	1.185

Table A. 6 NBR 0.5% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI x10^{-3}	4.948	5.995	5.326	5.599	5.533	5.917	6.289	6.698
A 2238 cm^{-1}	0.0048	0.005	0.0049	0.005	0.007	0.006	0.006	0.007
A 720 cm^{-1}	0.97	0.834	0.92	0.893	1.265	1.014	0.954	1.045

Table A. 7 NBR 0.25% (w/w) Set Absorbance Data

1	1	2	3	4	5	6	7
AI x10^{-3}	3.722	4.113	3.395	2.898	3.389	2.352	3.349
A 2238cm^{-1}	0.003	0.0039	0.0038	0.0028	0.004	0.002	0.0034
A 720cm^{-1}	0.806	0.948	1.119	0.966	1.18	0.85	1.015

Table A. 8 NBR 0.15% (w/w) Set Absorbance Data

1	1	2	3	4	5	6	7
AI x10^{-3}	2.387	2.699	1.862	2.73	3.617	3.135	2.895
A 2238cm^{-1}	0.0026	0.0026	0.0016	0.0021	0.0034	0.0027	0.0028
A 720cm^{-1}	1.089	0.963	0.859	0.769	0.94	0.861	0.967

Table A. 9 NBR 0.09% (w/w) Set Absorbance Data

	1	2	3	4	5	6
AI x10^{-3}	3.715	2.232	3.094	2.789	2.378	2.86
A 2238cm^{-1}	0.0034	0.0019	0.0032	0.0027	0.0025	0.0027
A 720cm^{-1}	0.915	0.851	1.034	0.968	1.051	0.944

Table A. 10 PA12 30% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI	4.496	4.518	3.764	2.539	2.208	2.287	2.109	2.15
A 1640cm^{-1}	5.566	5.525	5.45	3.021	2.672	2.388	2.912	2.773
A 720cm^{-1}	1.238	1.223	1.448	1.19	1.21	1.044	1.381	1.29

Table A. 11 PA12 40% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI	3.177	4.18	4.173	4.869	3.739	5.198	3.751	6.931
A 1640cm^{-1}	3.298	5.371	5.366	5.458	5.399	5.489	5.341	5.545
A 720cm^{-1}	1.038	1.285	1.286	1.121	1.444	1.056	1.424	0.8

Table A. 12 PA12 50% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI	4.844	4.709	4.276	3.944	5.337	4.5	5.719	5.069
A 1640cm^{-1}	5.386	5.387	5.324	5.265	5.433	5.396	5.376	5.414
A 720cm^{-1}	1.112	1.144	1.245	1.335	1.018	1.199	0.94	1.068

Table A. 13 PA12 1% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI x10^{-1}	0.969	1.057	1.454	1.036	1.206	1.014	1.168	0.965
A 1640cm^{-1}	0.078	0.083	0.147	0.102	0.12	0.096	0.125	0.071
A 720cm^{-1}	0.805	0.785	1.011	0.985	0.995	0.947	1.07	0.736

Table A. 14 PA12 0.8% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AIx10^{-2}	8.719	7.814	9.324	8.748	11.423	9.168	8.553	9.512
A 1640cm^{-1}	0.096	0.084	0.102	0.095	0.11	0.076	0.078	0.074
A 720cm^{-1}	1.101	1.075	1.094	1.086	0.963	0.829	0.912	0.778

Table A. 15 PA12 0.5% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI x10^{-2}	5.81	7.33	7.32	7.74	5.576	7.289	6.953	7.151
A 1640cm^{-1}	0.0477	0.056	0.056	0.063	0.061	0.075	0.055	0.062
A 720cm^{-1}	0.821	0.764	0.765	0.814	1.094	1.029	0.791	0.867

Table A. 16 PA12 0.25% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI x10^{-2}	3.916	3.169	3.731	5.073	3.798	3.3	4.333	3.738
A 1640cm^{-1}	0.0309	0.034	0.025	0.038	0.0324	0.363	0.432	0.04
A 720cm^{-1}	0.789	1.073	0.67	0.749	0.853	1.1	0.997	1.07

Table A. 17 PA12 0.15% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI x10^{-2}	2.976	3.473	2.309	3.312	3.469	2.942	2.489	3.09
A 1640cm^{-1}	0.0289	0.0322	0.0206	0.031	0.04	0.0253	0.0277	0.033
A 720cm^{-1}	0.971	0.927	0.892	0.936	1.153	0.86	1.113	1.068

Table A. 18 PA12 0.09% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI x10^{-2}	2.03	2.46	3.2	2.76	2.12	2.49	2.49	2.03
A 1640cm^{-1}	0.0143	0.024	0.029	0.0287	0.018	0.0271	0.021	0.014
A 720cm^{-1}	0.703	0.977	0.906	1.041	0.848	1.09	0.844	0.689

Table A. 19 TPU 30% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI	3.4387	4.0184	3.5787	7.147	5.3873	7.0133	7.2393	7.7297
A 1730cm^{-1}	2.5	2.829	2.319	5.782	5.716	5.779	5.777	7.7297
A 720 cm^{-1}	0.727	0.704	0.648	0.809	1.061	0.824	0.798	0.729

Table A. 20 TPU 40% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI	6.8629	9.151	9.9465	9.5544	7.3056	8.8646	7.0821	8.8815
A 1730 cm^{-1}	5.71	5.756	5.769	5.79	5.713	5.762	5.687	5.773
A 720 cm^{-1}	0.477	0.555	0.667	0.599	0.493	0.617	0.562	0.458

Table A. 21 TPU 50% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI	12.0733	10.2756	8.5217	9.5125	11.649	9.2414	10.1103	12.5283
A 1730 cm^{-1}	5.759	5.703	5.684	5.698	5.743	5.702	5.682	5.738
A 720 cm^{-1}	0.477	0.555	0.667	0.599	0.493	0.617	0.562	0.458

Table A. 22 TPU 1% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI $x10^{-2}$	8.251	11.835	8.102	6.805	3.682	7.484	12.542	11.254
A 1730 cm^{-1}	0.1	0.129	0.076	0.072	0.0246	0.072	0.11	0.114
A 720 cm^{-1}	1.212	1.09	0.938	1.058	0.668	0.962	0.877	1.013

Table A. 23 TPU 0.8% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI $x10^{-2}$	8.31	8.41	7.766	9.902	7.981	4.14	7.921	10.204
A 1730 cm^{-1}	0.089	0.081	0.081	0.121	0.083	0.032	0.072	0.08
A 720 cm^{-1}	1.071	0.953	1.043	1.222	1.04	0.773	0.909	0.784

Table A. 24 TPU 0.5% (w/w) Set Absorbance Data

	1	2	3	4	5	6
AI $x10^{-2}$	7.577	4.627	7.749	6.506	4.917	4.919
A 1730 cm^{-1}	0.091	0.046	0.073	0.065	0.053	0.055
A 720 cm^{-1}	1.201	0.994	0.942	0.999	1.078	1.149

Table A. 25 TPU 0.25% (w/w) Set Absorbance Data

	1	2	3	4	5	6
AI(x10^{-2})	3.397	3.635	3.753	1.395	2.446	2.541
A 1730 cm^{-1}	0.034	0.043	0.037	0.0142	0.0228	0.031
A 720 cm^{-1}	1.001	1.183	0.017	1.018	0.932	1.22

Table A. 26 TPU 0.15% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI(x10^{-2})	2.286	2.172	0.958	1.785	1.766	1.083	1.655	1.013
A 1730 cm^{-1}	0.038	0.042	0.0097	0.019	0.024	0.0106	0.019	0.0144
A 720 cm^{-1}	1.662	1.934	1.012	1.095	1.359	1.001	1.148	1.422

Table A. 27 TPU 0.09% (w/w) Set Absorbance Data

	1	2	3	4	5	6	7	8
AI(x10^{-2})	1.452	1.483	1.505	1.429	1.046	0.935	1.163	1.046
A 1730 cm^{-1}	0.0124	0.0155	0.011	0.0141	0.0115	0.013	0.0123	0.011
A 720 cm^{-1}	0.854	1.045	0.731	0.987	1.099	1.391	1.058	1.052

B. ABSORBANCE INDICES FIGURES

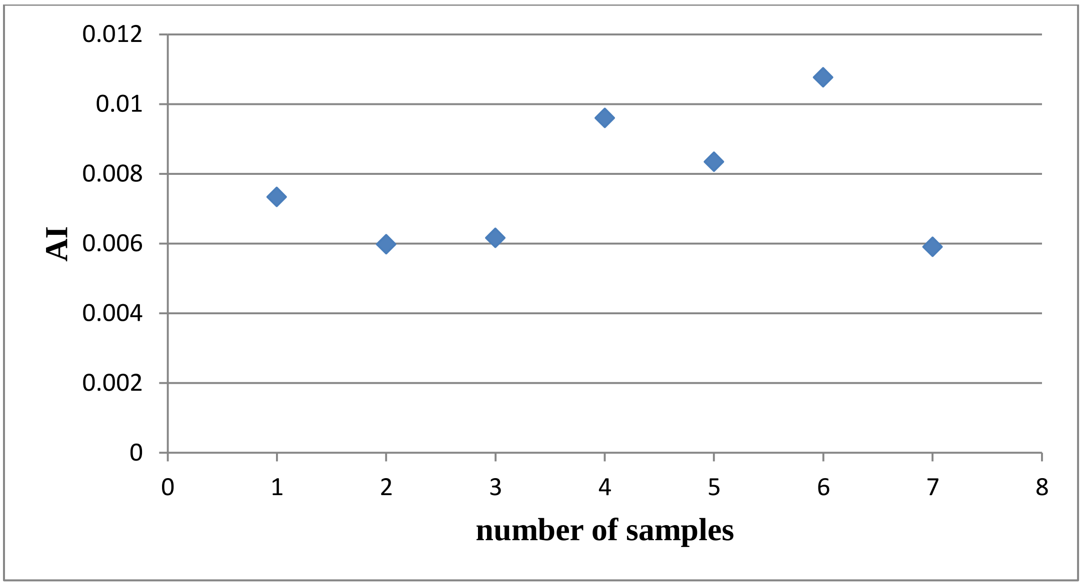


Figure B. 1 Absorbance Index Values of NBR 0.8% (w/w) Set with Range [0.0073±0.001917]

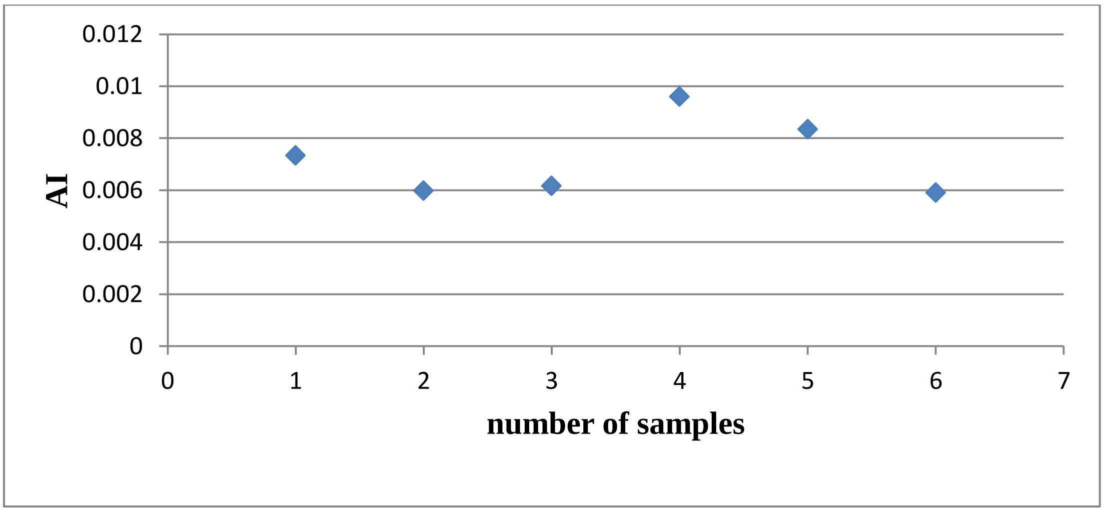


Figure B. 2 Absorbance Index Values of NBR 0.8% (w/w) Set with Range [0.0072±0.0015] (second deviation)

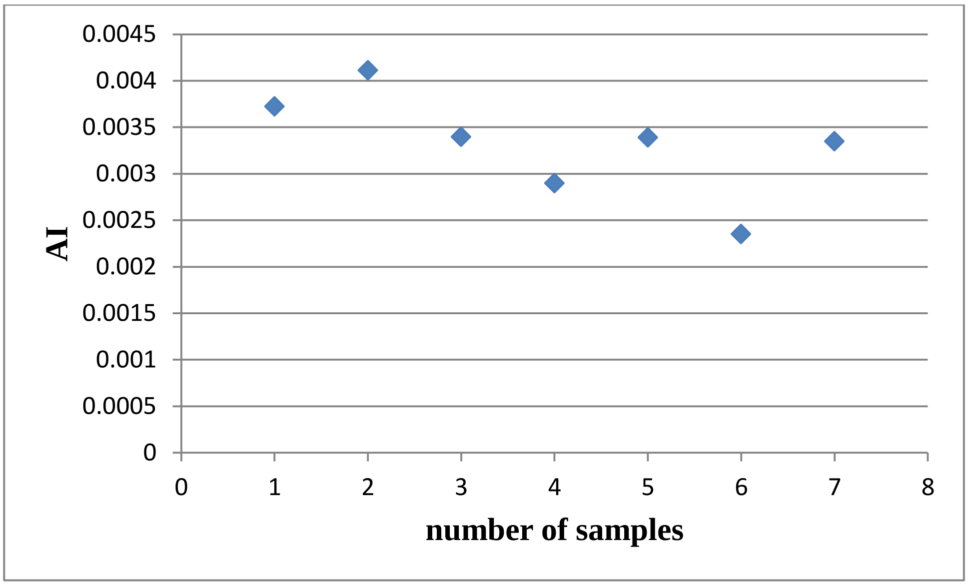


Figure B. 3 Absorbance Index Values of NBR 0.25% (w/w) Set with Range [0.0033±0.00057]

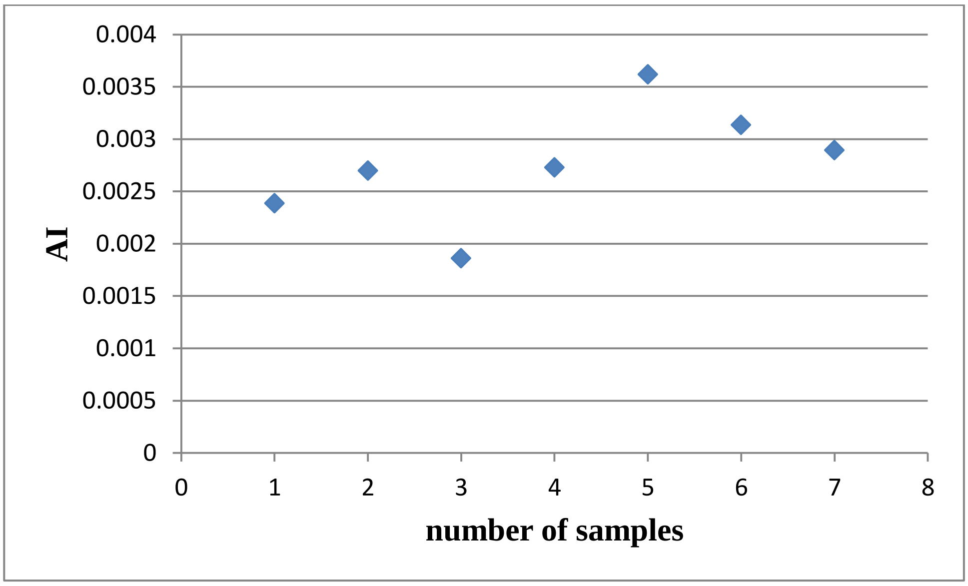


Figure B. 4 Absorbance Index Values of NBR 0.15% (w/w) Set with Range [0.0027±0.00055]

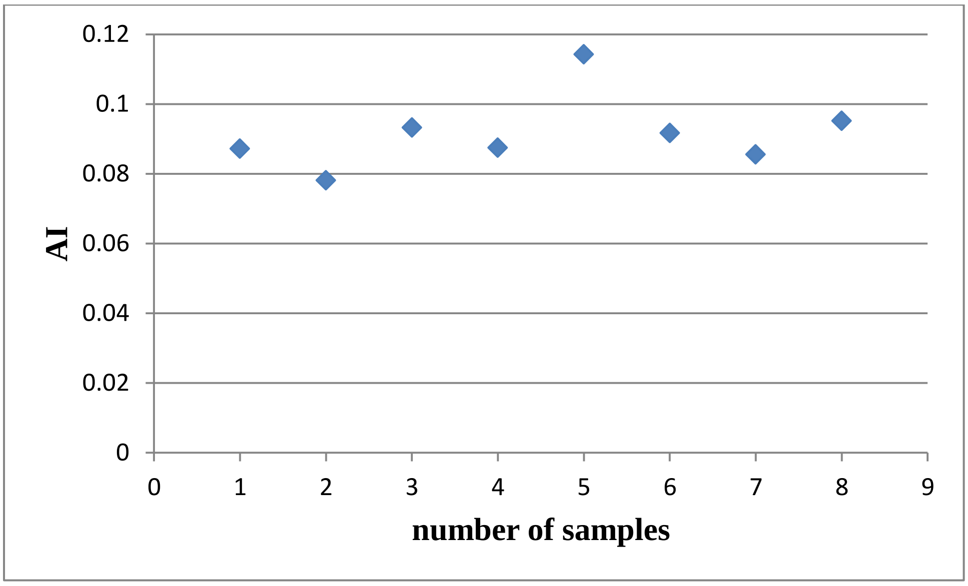


Figure B. 5 Absorbance Index Values of PA12 0.8% (w/w) Set with Range [0.092±0.0106]

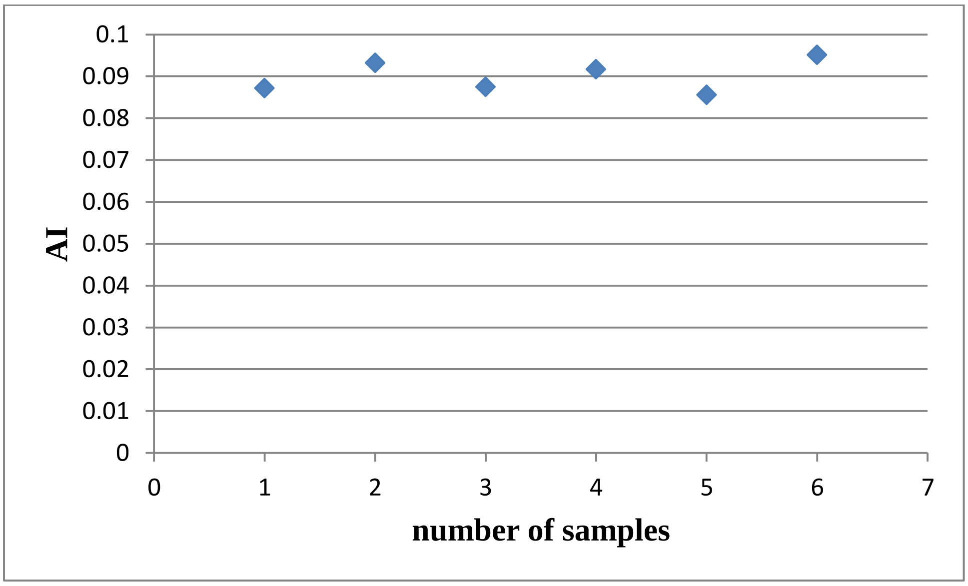


Figure B. 6 Absorbance Index Values of PA12 0.8% (w/w) Set with Range [0.09±0.0038] (second deviation)

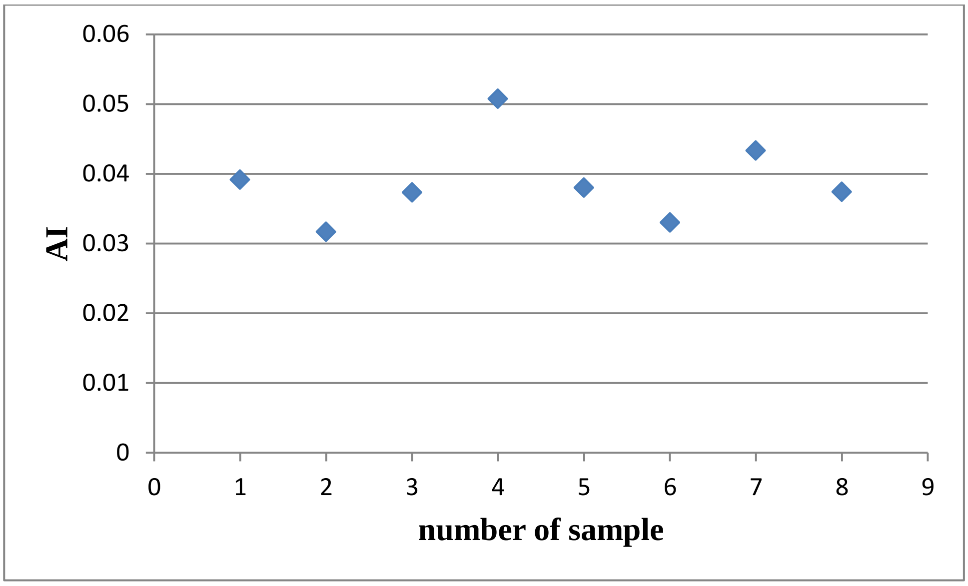


Figure B. 7 Absorbance Index Values of PA12 0.25% (w/w) Set with Range [0.039±0.0060]

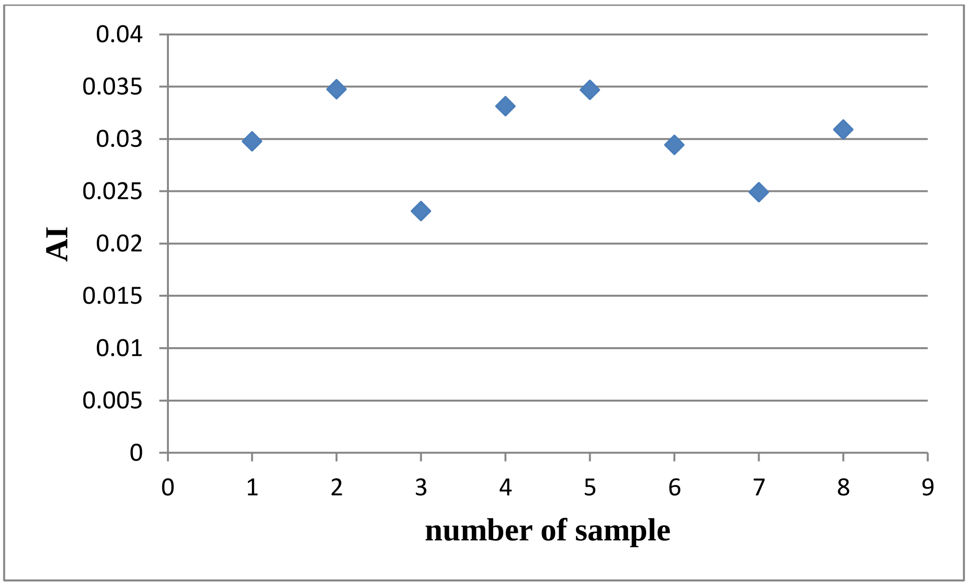


Figure B. 8 Absorbance Index Values of PA12 0.15% (w/w) Set with Range [0.03±0.0043]

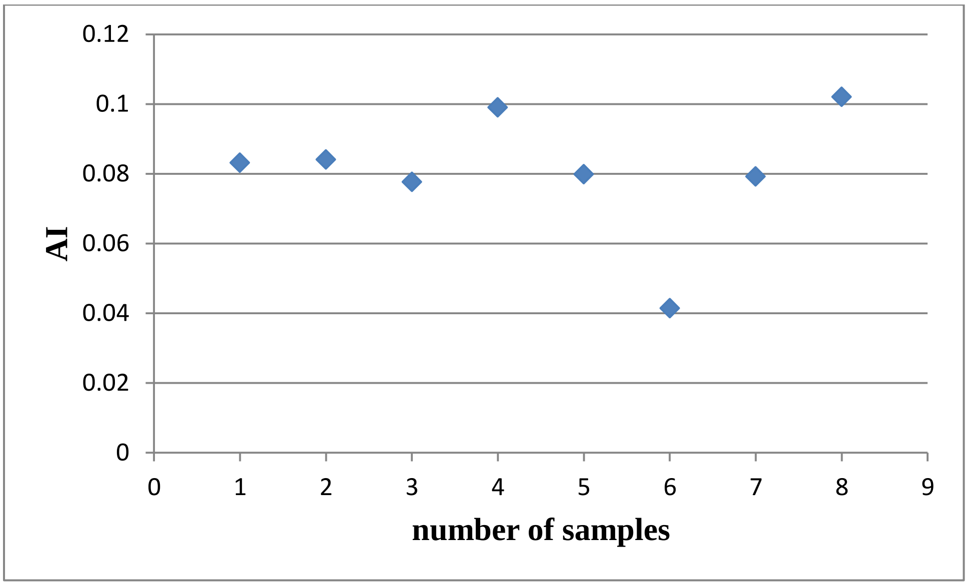


Figure B. 9 Absorbance Index Values of TPU 0.8% (w/w) Set with Range [0.081±0.018]

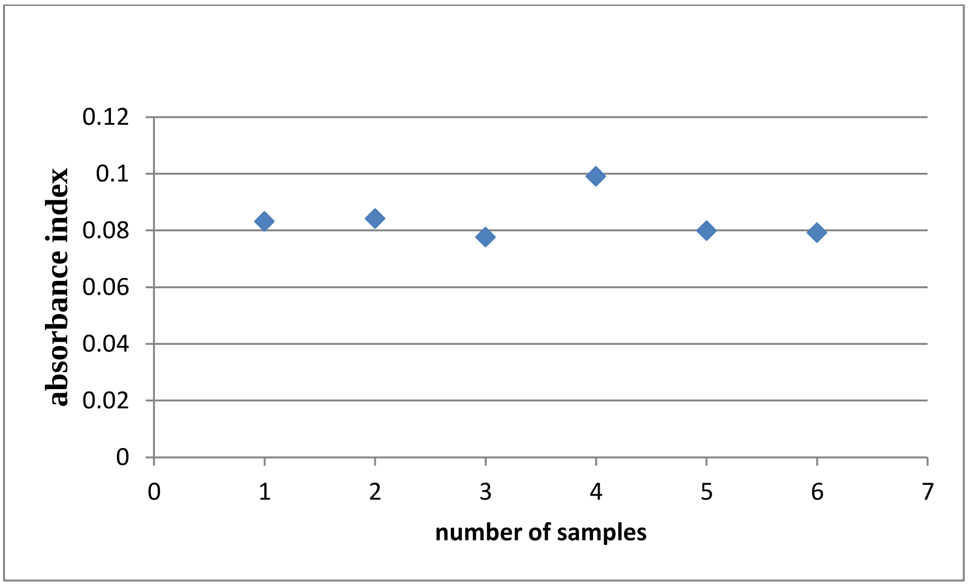


Figure B. 10 Absorbance Index Values of TPU 0.8% (w/w) Set [0.084±0.0078] (second deviation)

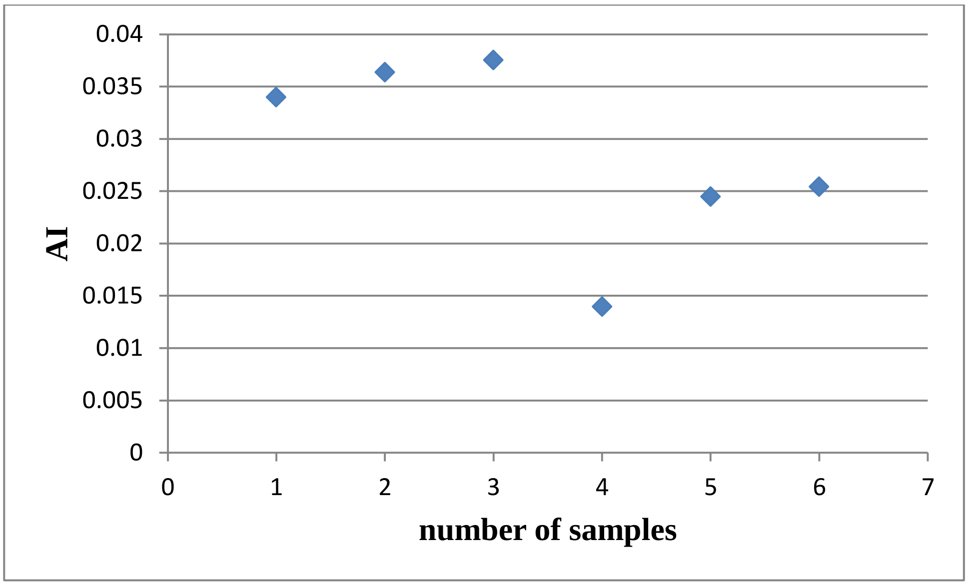


Figure B. 11 Absorbance Index Values of TPU 0.25% (w/w) Set with Range [0.029±0.0091]

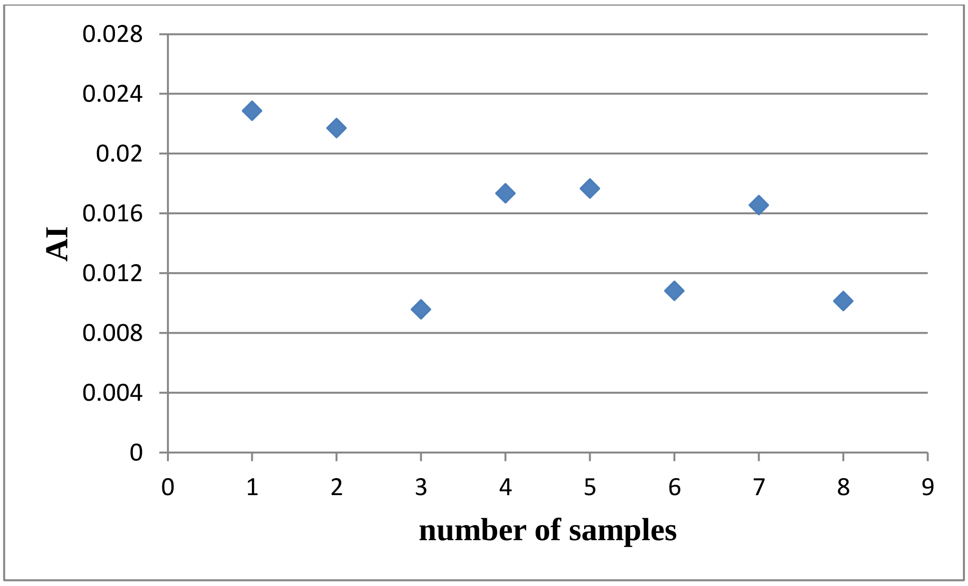


Figure B. 12 Absorbance Index Values of TPU 0.15% (w/w) Range with [0.016±0.0052]

C. INTERIOR MARKER SPECTRA

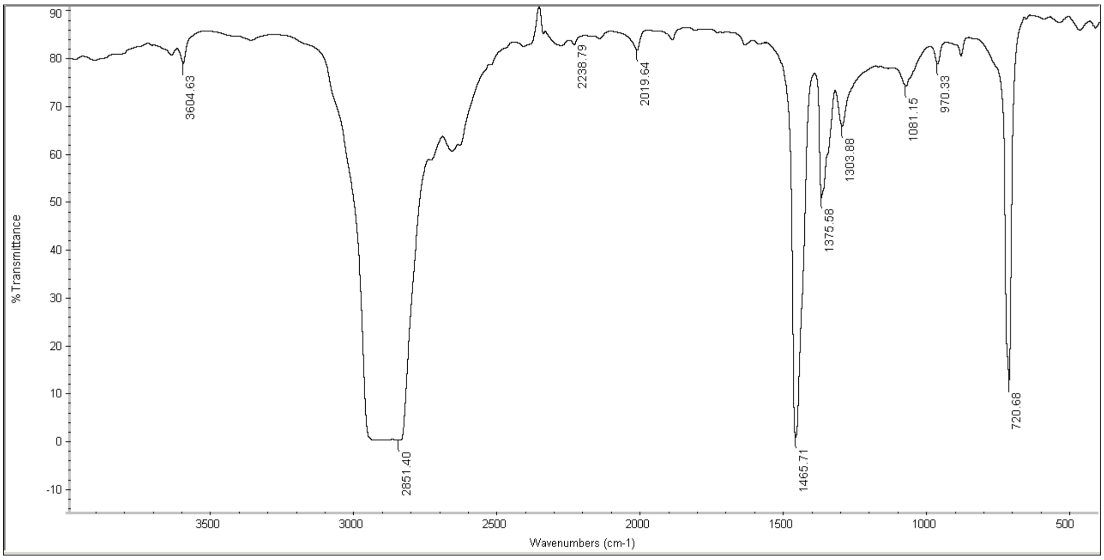


Figure C. 1 NBR 0.8% (w/w) Sample Spectrum

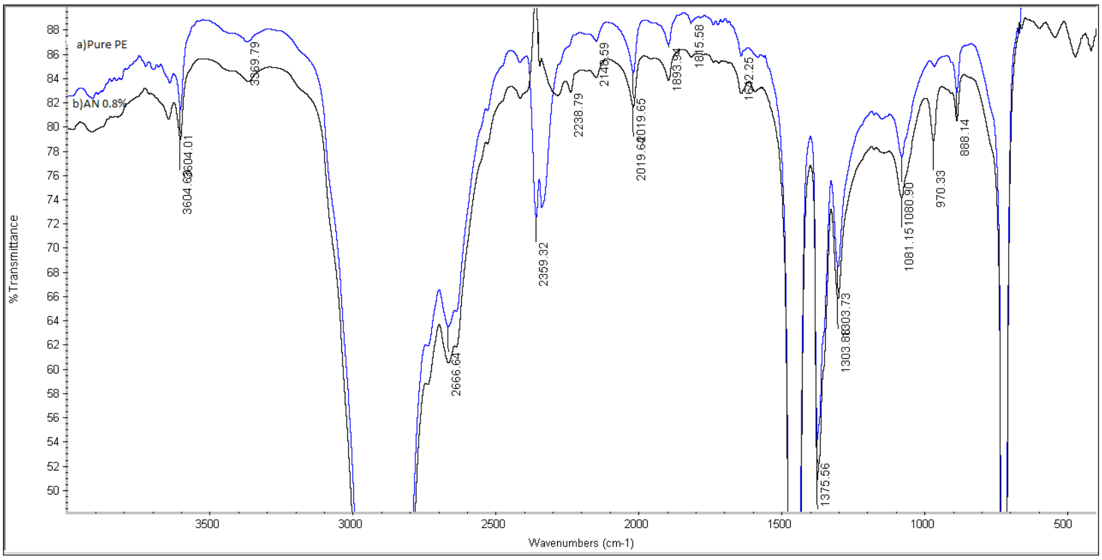


Figure C. 2 NBR 0.8% (w/w) Sample and Pure PE Comparison

a) Pure PE b) Sample

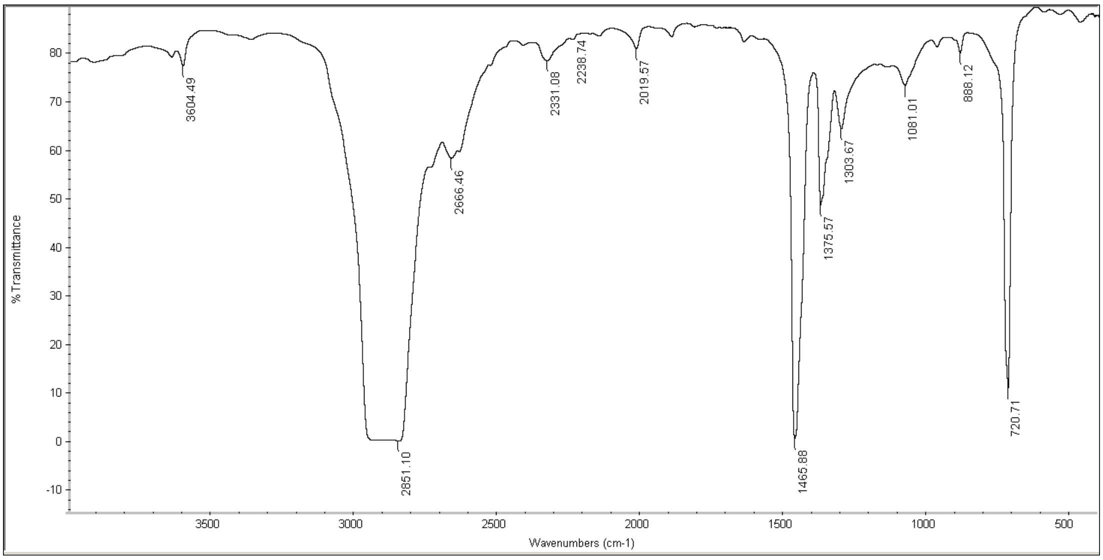


Figure C. 3 NBR 0.25% (w/w) Sample Spectrum

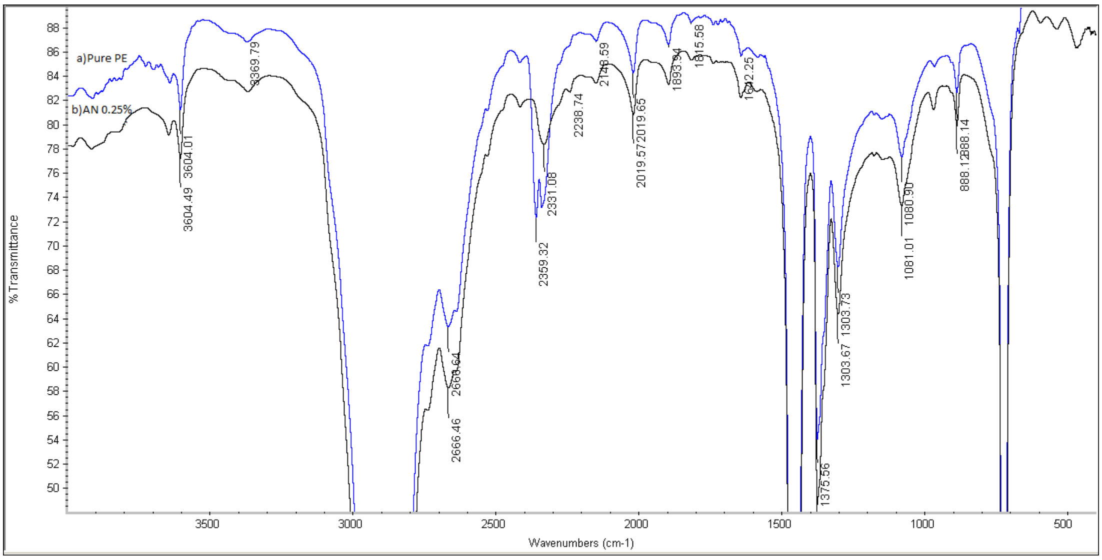


Figure C. 4 NBR 0.25% (w/w) Sample and Pure PE Comparison

a)Pure PE b) Sample

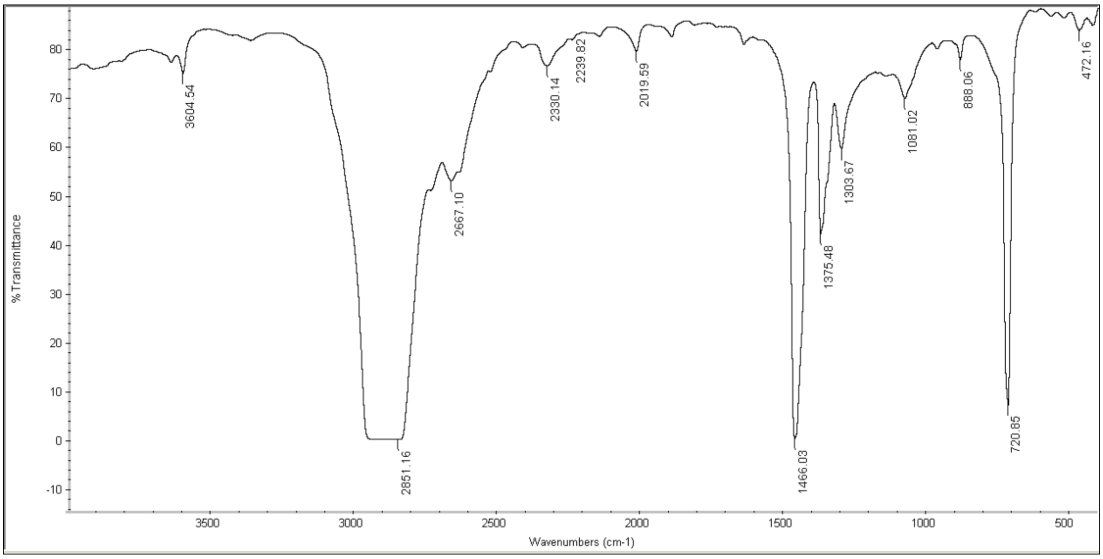


Figure C. 5 NBR 0.15% (w/w) Sample Spectrum

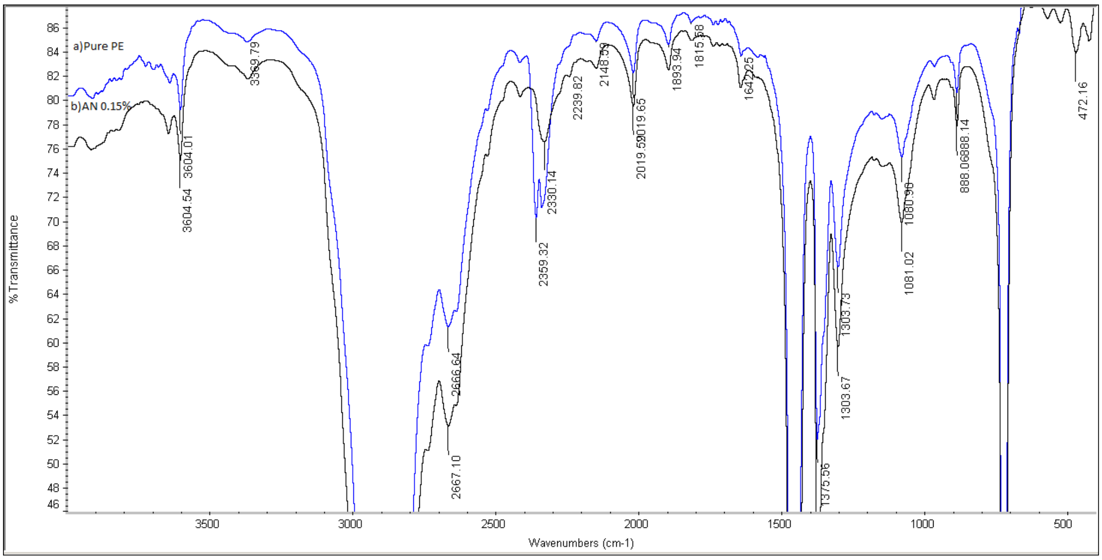


Figure C. 6 NBR 0.15% (w/w) Sample and Pure PE Comparison

a) Pure PE b) Sample

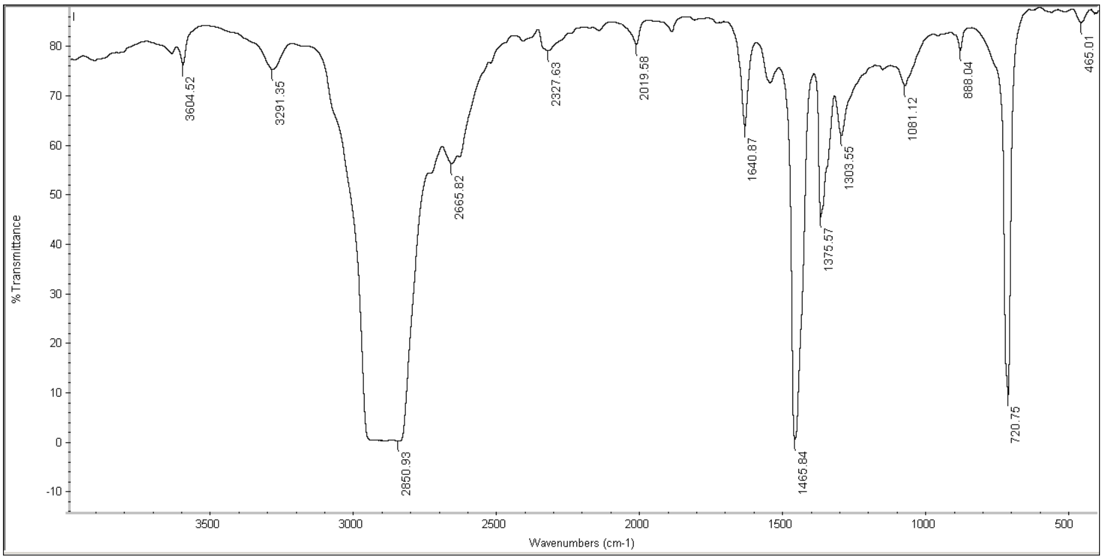


Figure C. 7 PA12 0.8% (w/w) Sample Spectrum

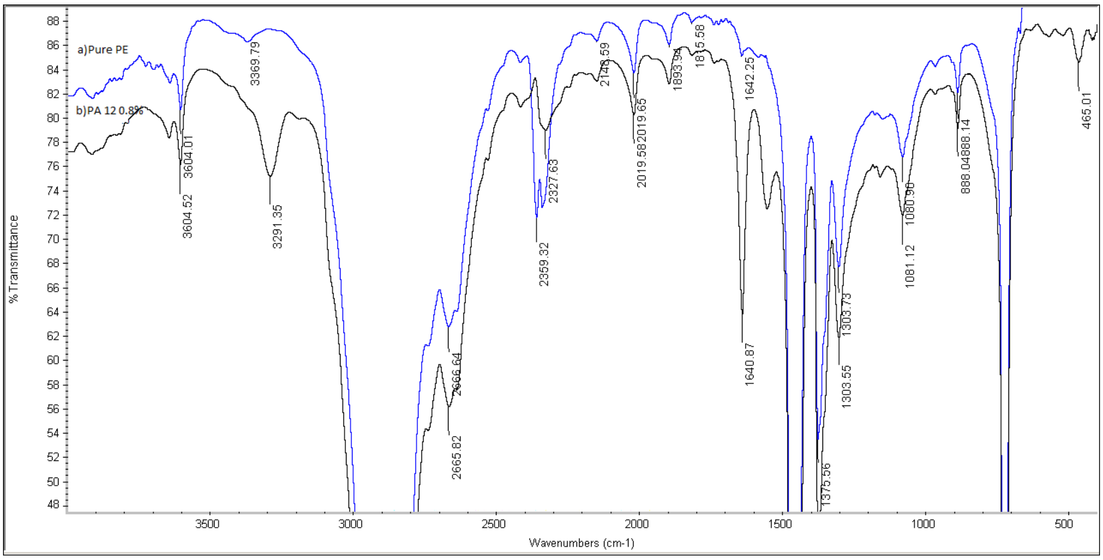


Figure C. 8 PA12 0.8% (w/w) Sample and Pure PE Comparison

a)Pure PE b) Sample

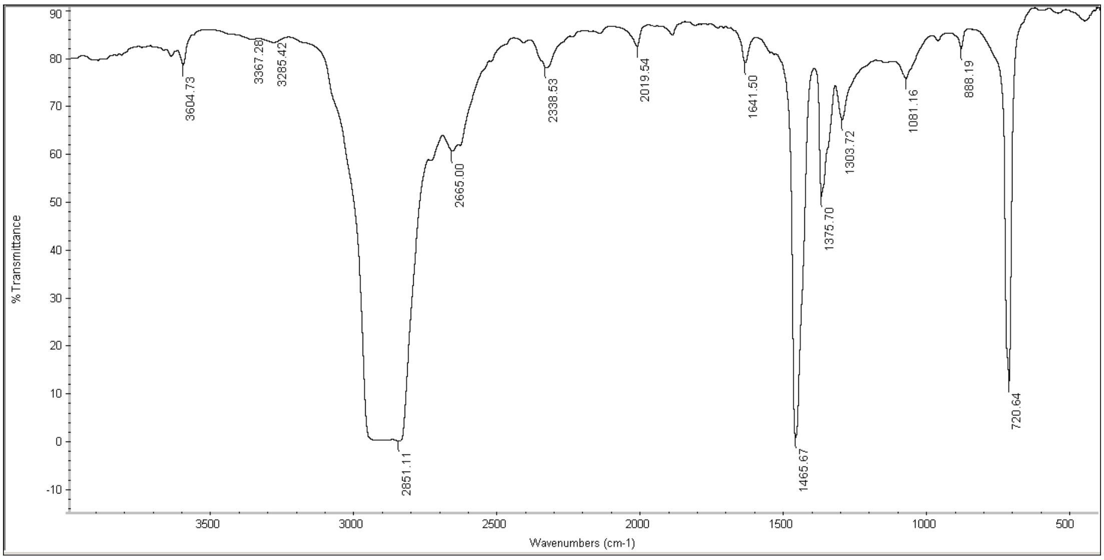


Figure C. 9 PA12 0.25% (w/w) Sample Spectrum

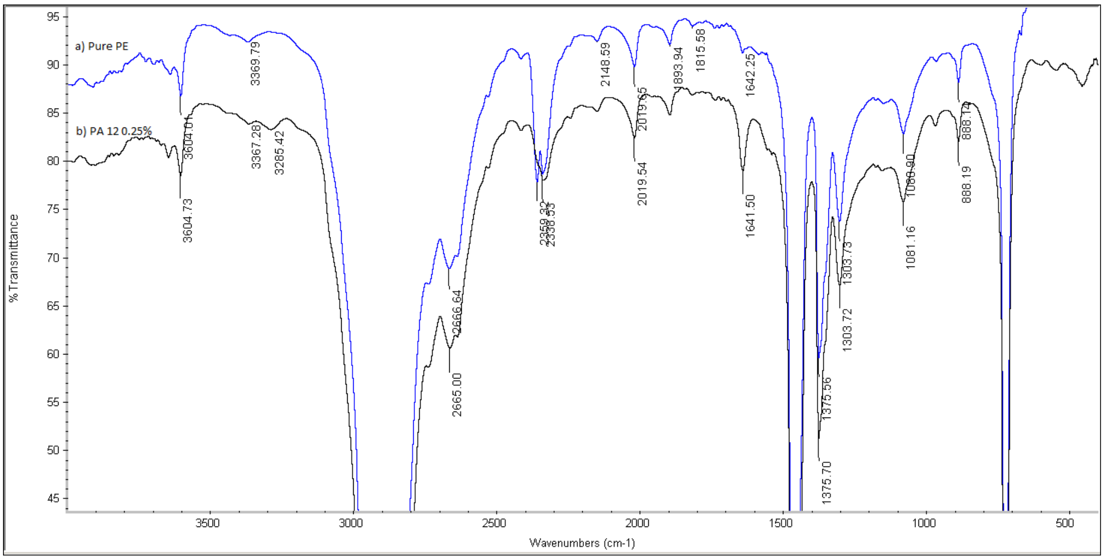


Figure C. 10 PA12 0.25% (w/w) Sample and Pure PE Comparison

a)PurePE b) Sample

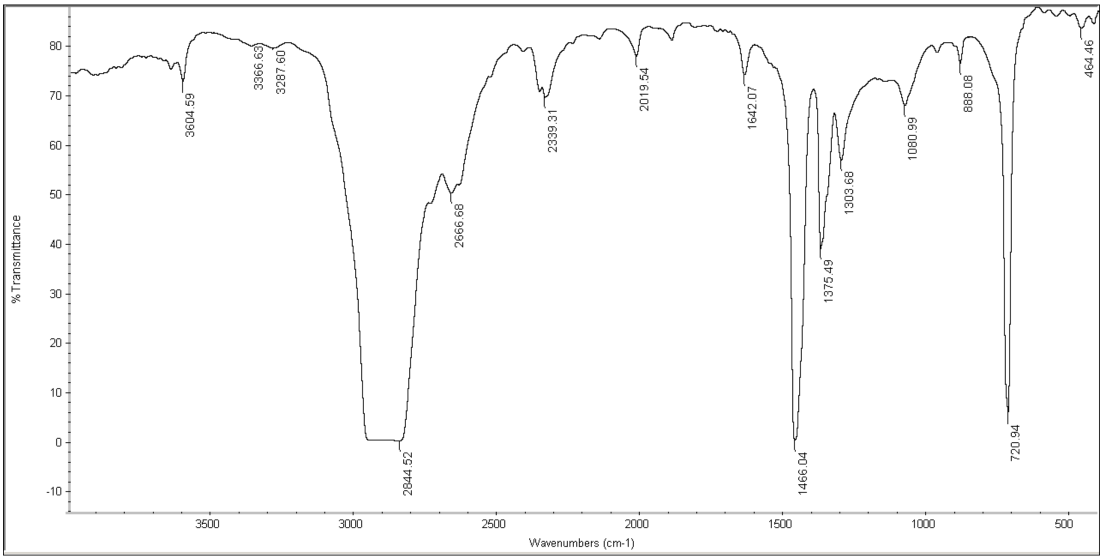


Figure C. 11 PA12 0.15% (w/w) Sample Spectrum

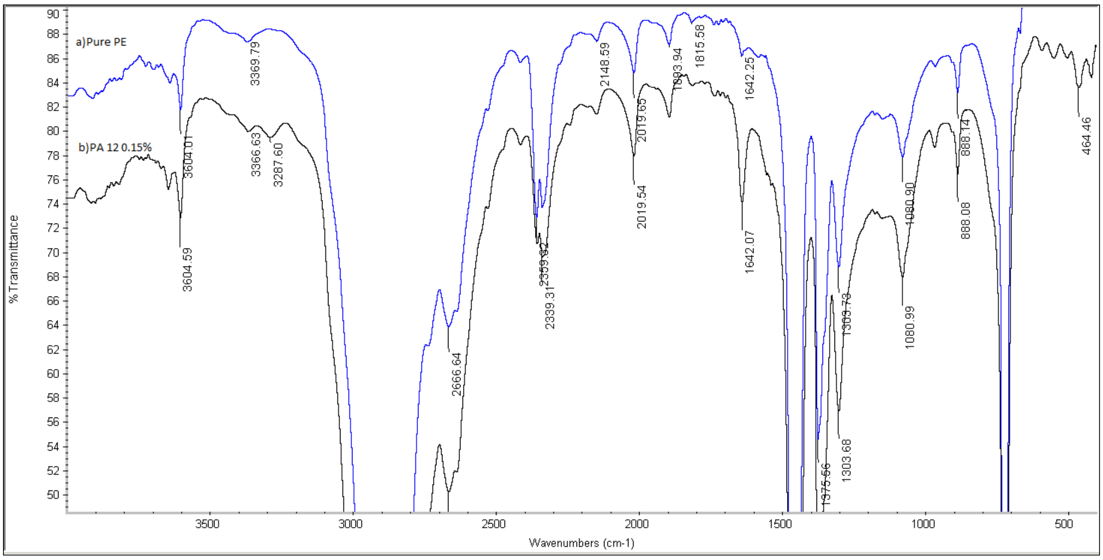


Figure C. 12 PA12 0.15% (w/w) Sample and Pure PE Comparison a)PurePE b) Sample

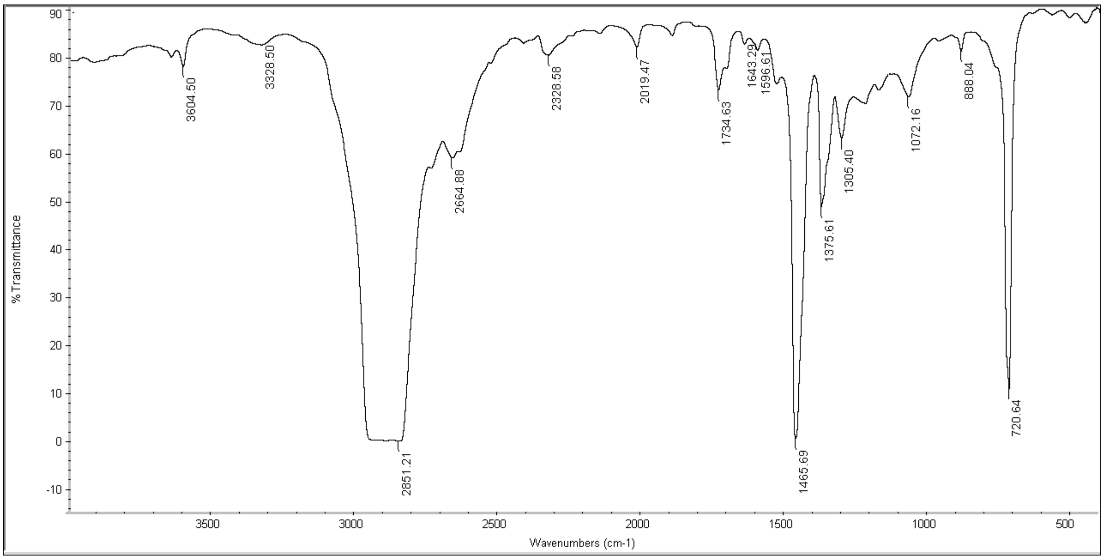


Figure C. 13 TPU 0.8% (w/w) Sample Spectrum

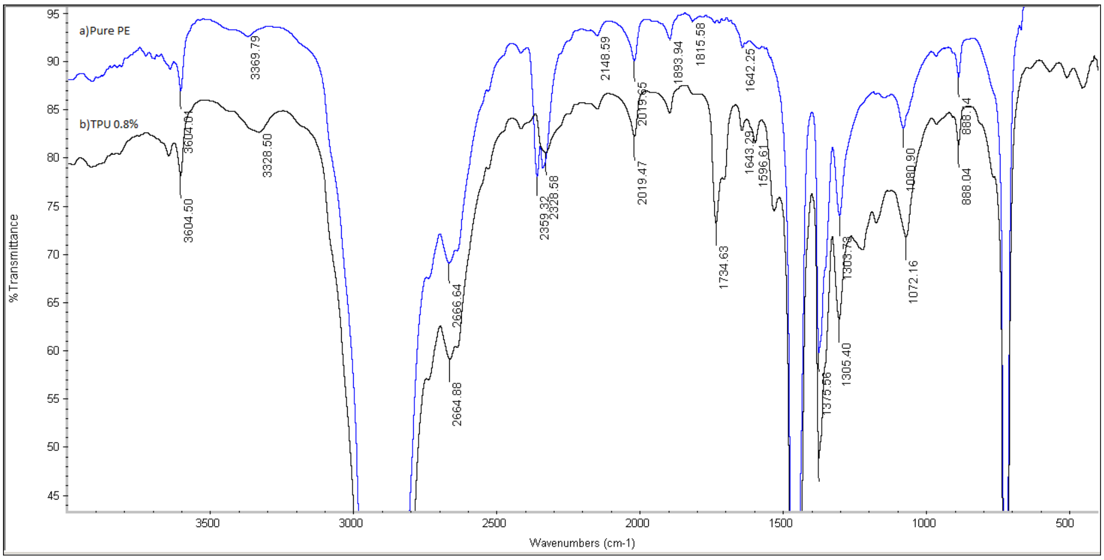


Figure C. 14 TPU 0.8% (w/w) Sample and Pure PE Comparison

a)PurePE b) Sample

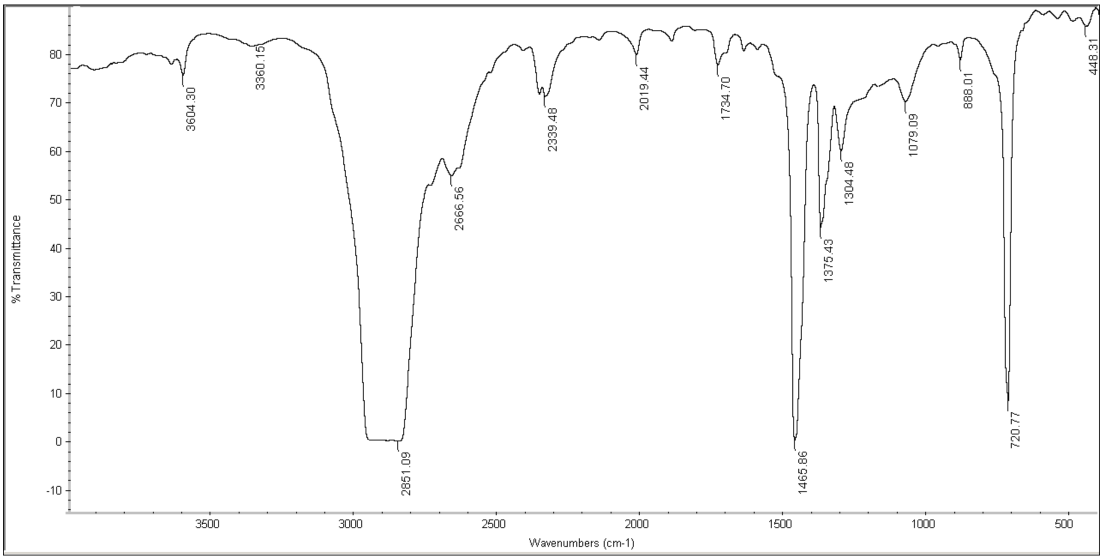


Figure C. 15 TPU 0.25% (w/w) Sample Spectrum

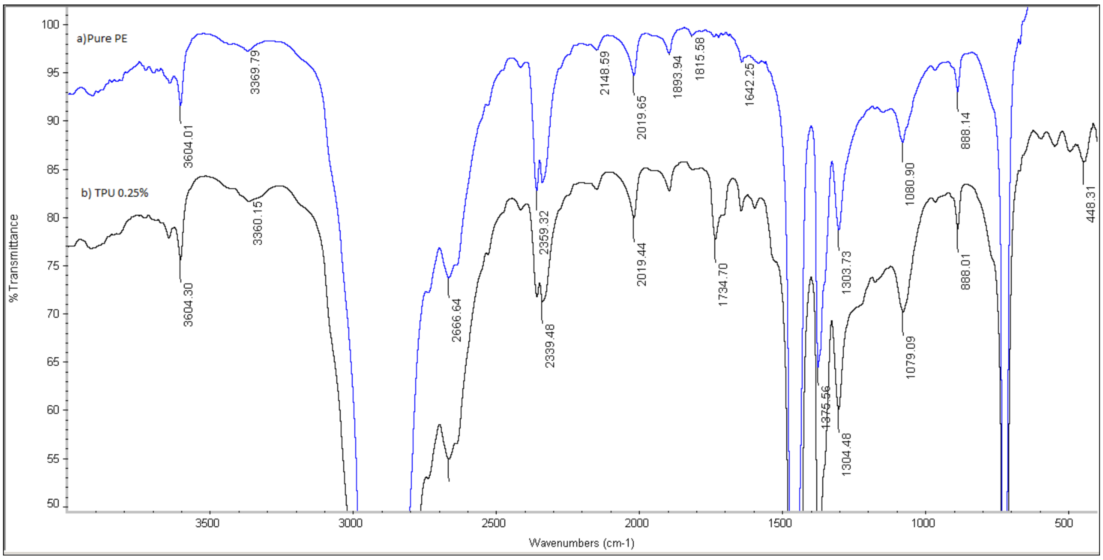


Figure C. 16 TPU 0.25% (w/w) Sample and Pure PE Comparison

a)PurePE b) Sample

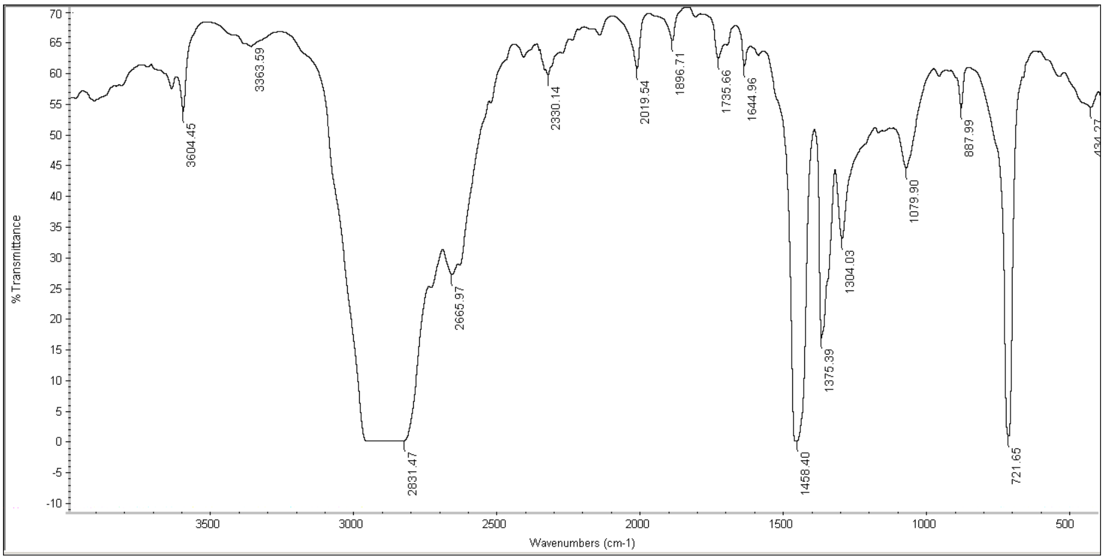


Figure C. 17 TPU 0.15% (w/w) Sample Spectrum

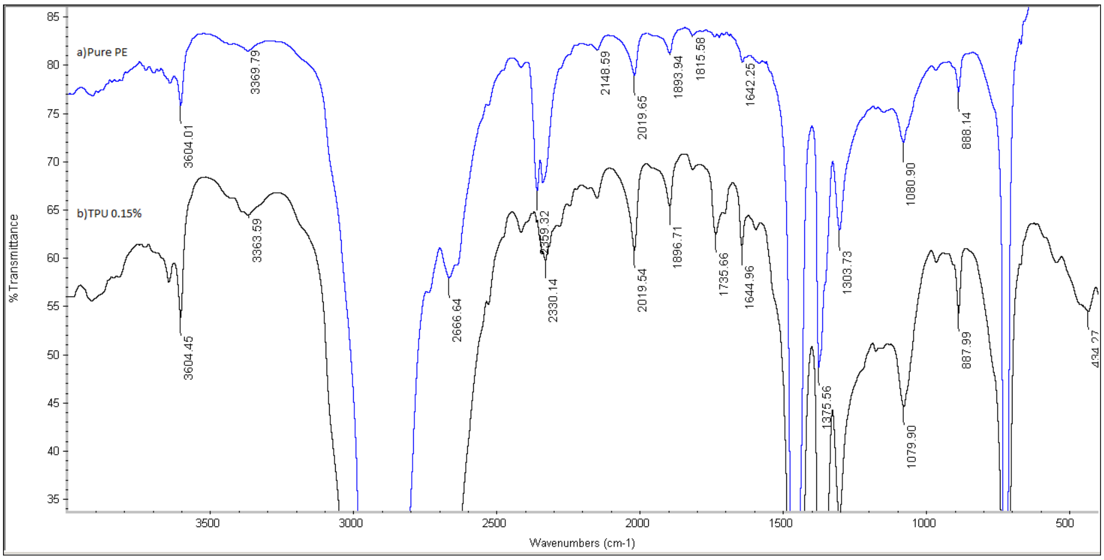


Figure C. 18 TPU 0.15% (w/w) Sample and Pure PE Comparison

a)Pure PE b) Sample

D. DSC THERMOGRAMS

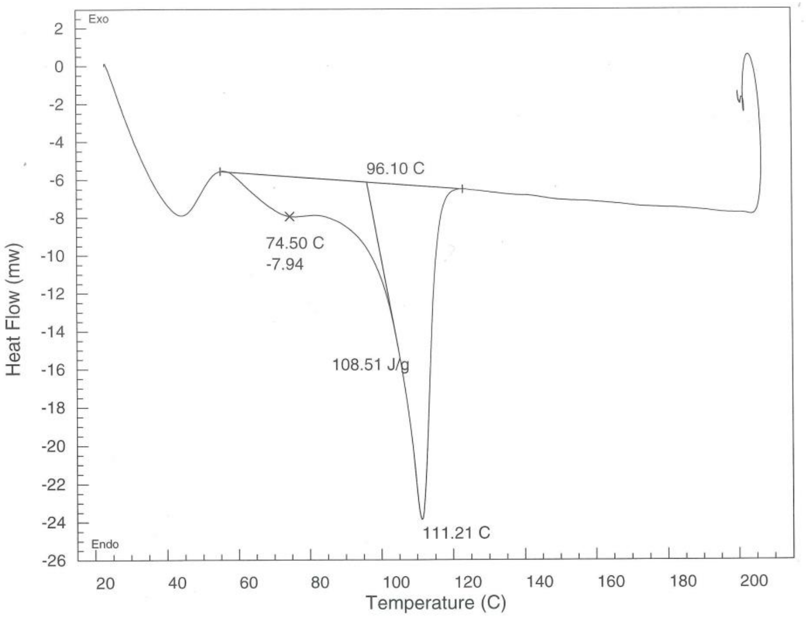


Figure D. 1 NBR 0.5% (w/w) Sample Thermogram

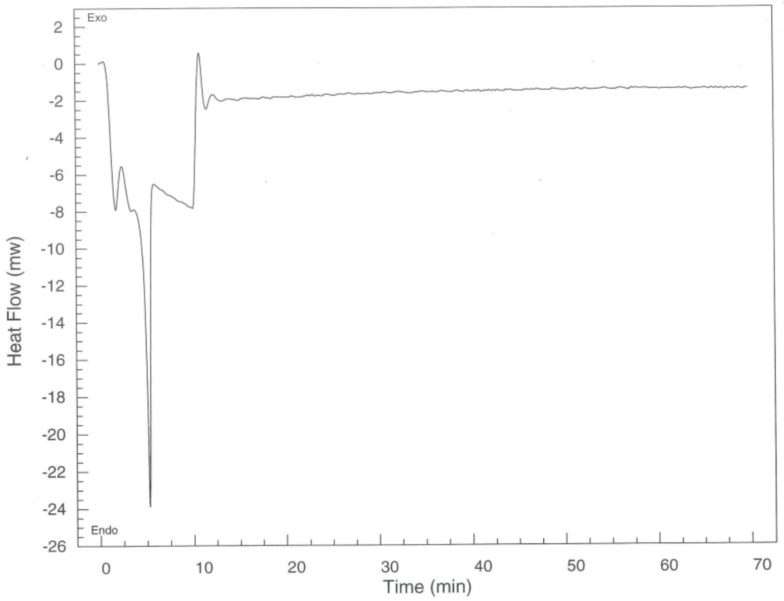


Figure D. 2 Isothermal Treatment of NBR 0.5% (w/w) at 200°C for 1 Hour

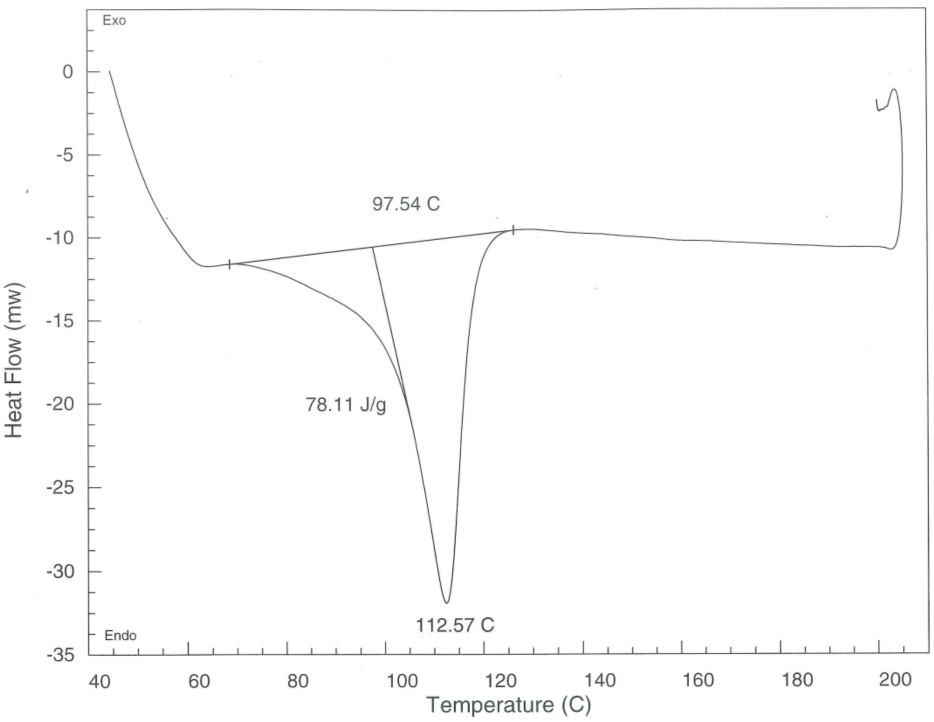


Figure D. 3 NBR 0.09% (w/w) Sample Thermogram

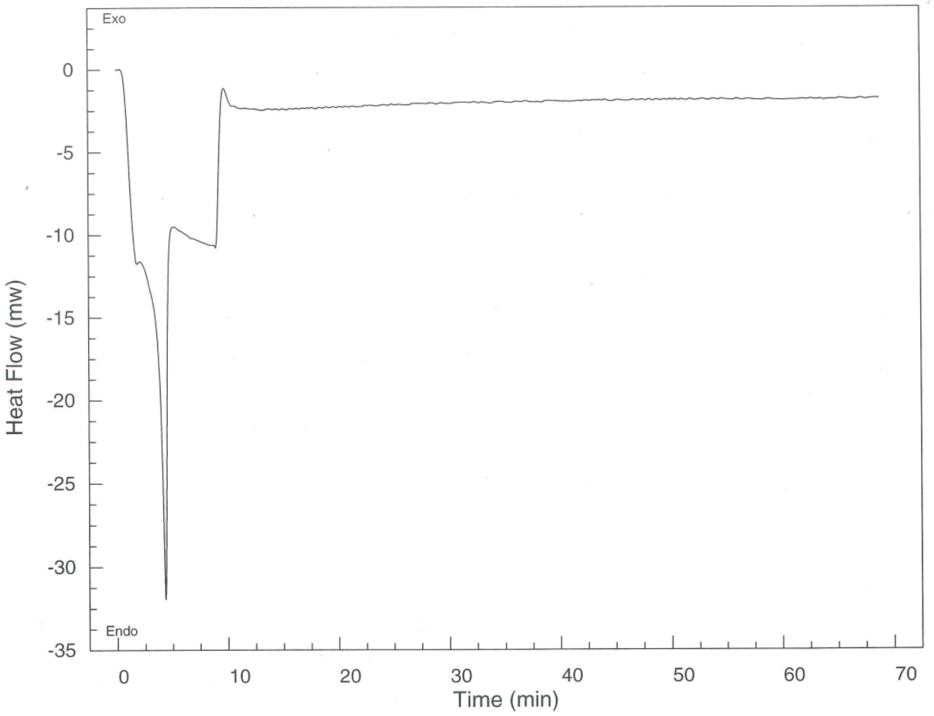


Figure D. 4 Isothermal Treatment of NBR 0.09% (w/w) at 200°C for 1 Hour

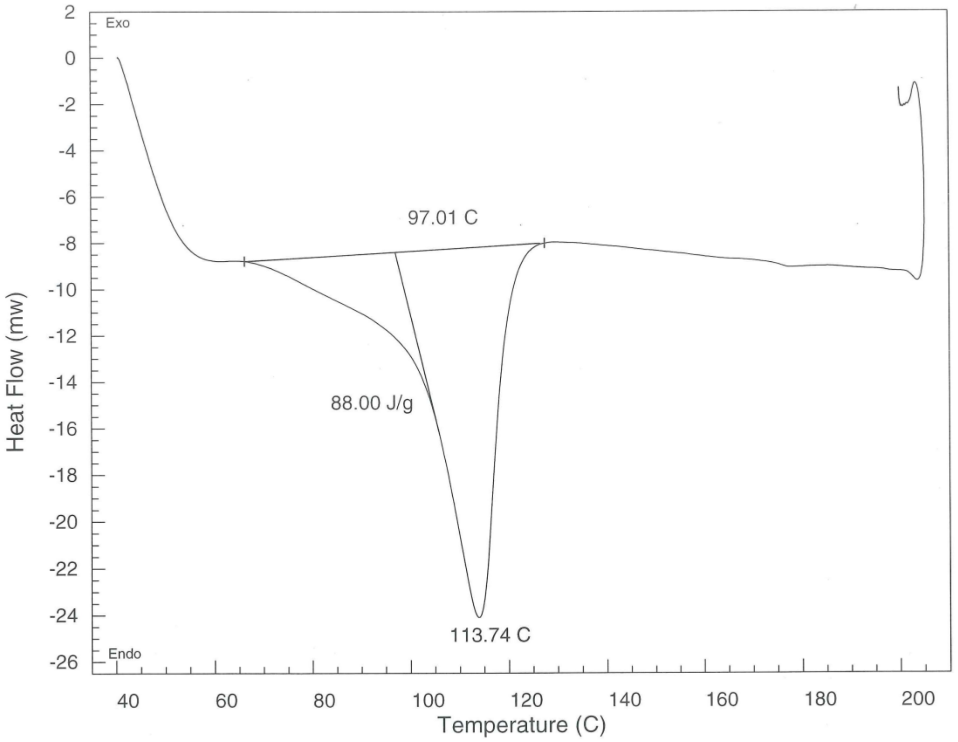


Figure D. 5 PA12 1% (w/w) Sample Thermogram

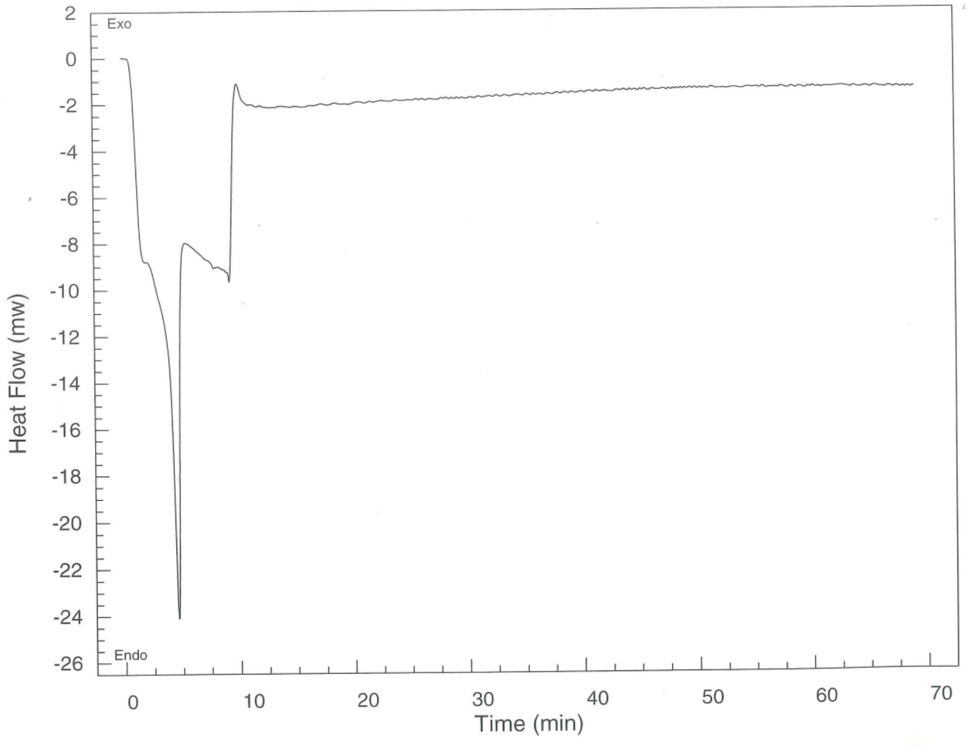


Figure D. 6 Isothermal Treatment of PA12 1% (w/w) at 200°C for 1 Hour

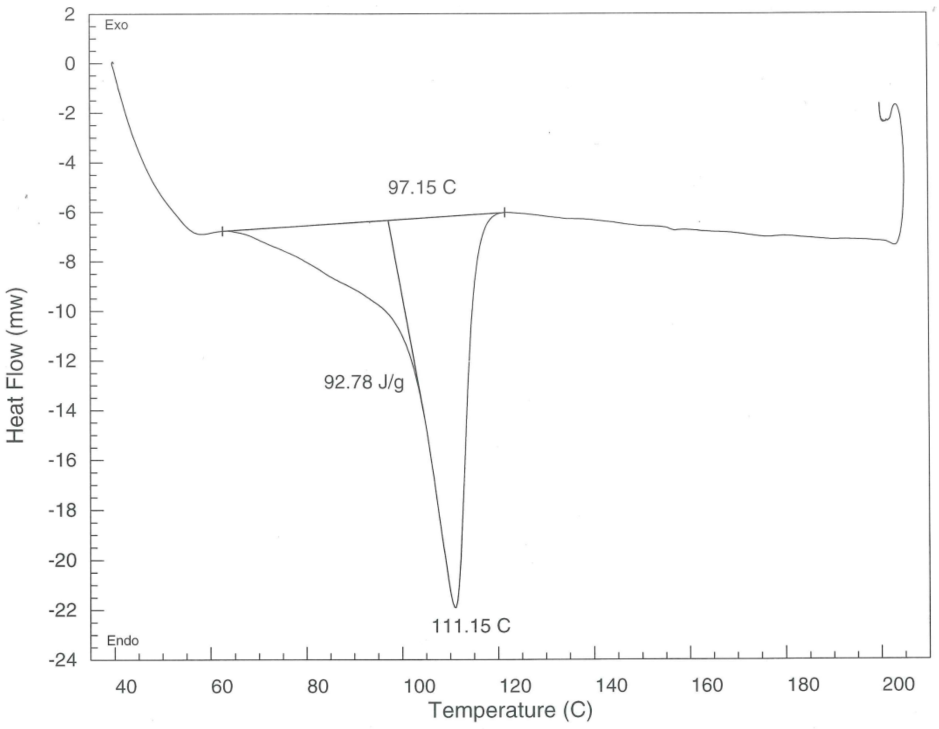


Figure D. 7 PA12 0.5% (w/w) Sample Thermogram

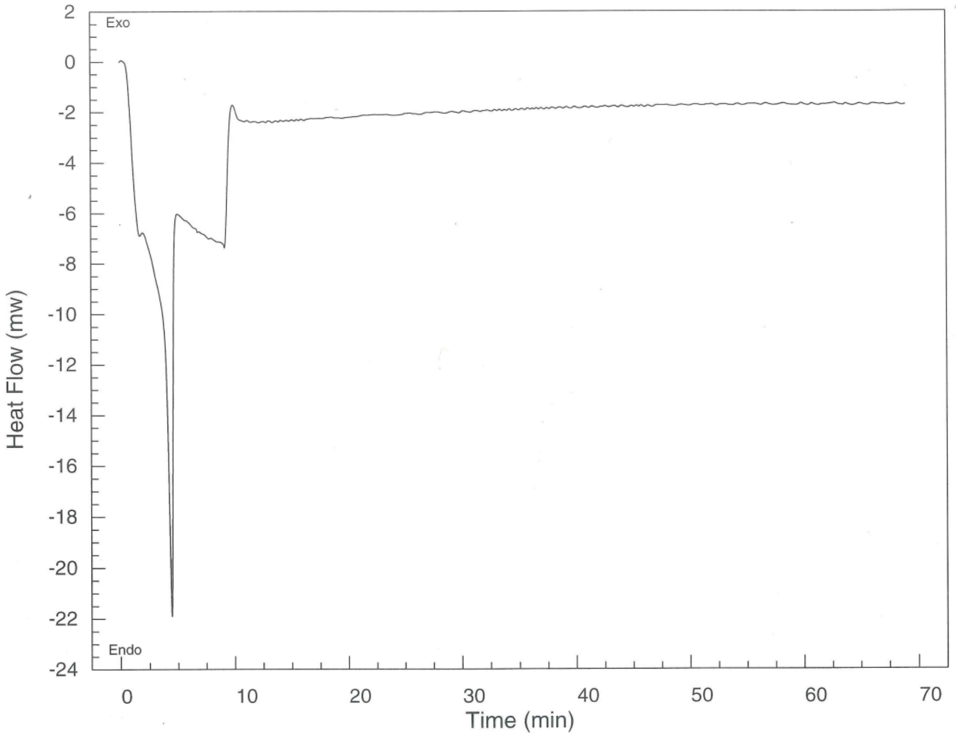


Figure D. 8 Isothermal Treatment of PA12 0.5% (w/w) at 200°C for 1 Hour

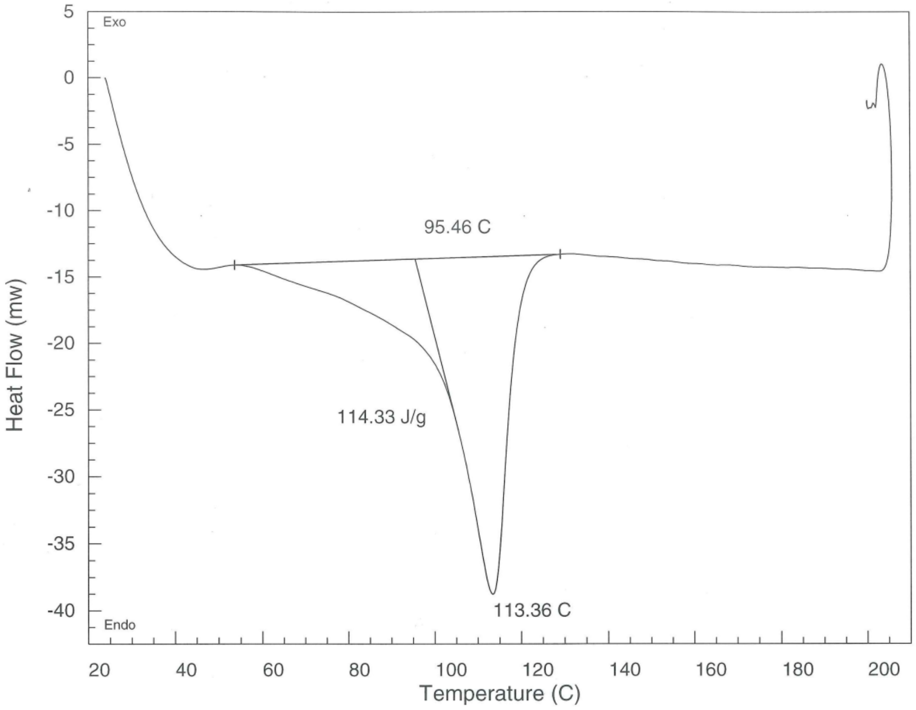


Figure D. 9 PA12 0.09% (w/w) Sample Thermogram

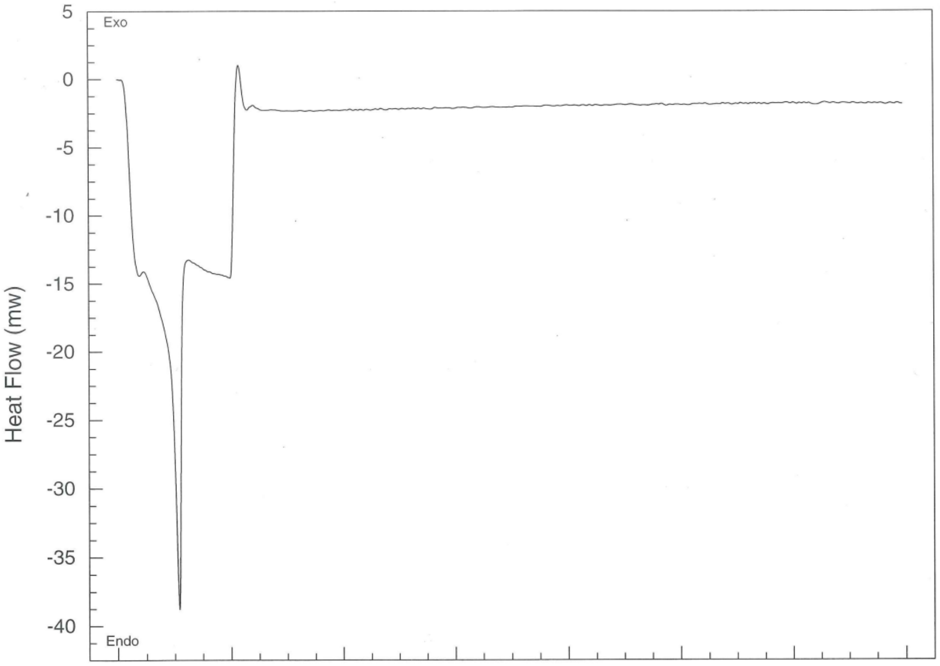


Figure D. 10 Isothermal Treatment of PA12 0.09% (w/w) at 200°C for 1 Hour

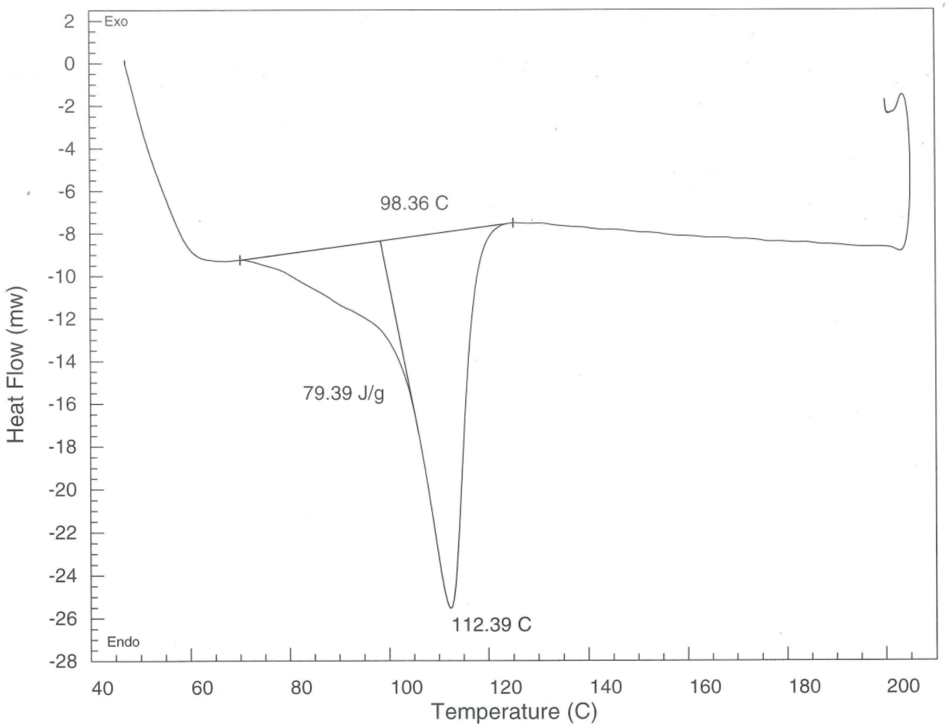


Figure D. 11 TPU 1% (w/w) Sample Thermogram

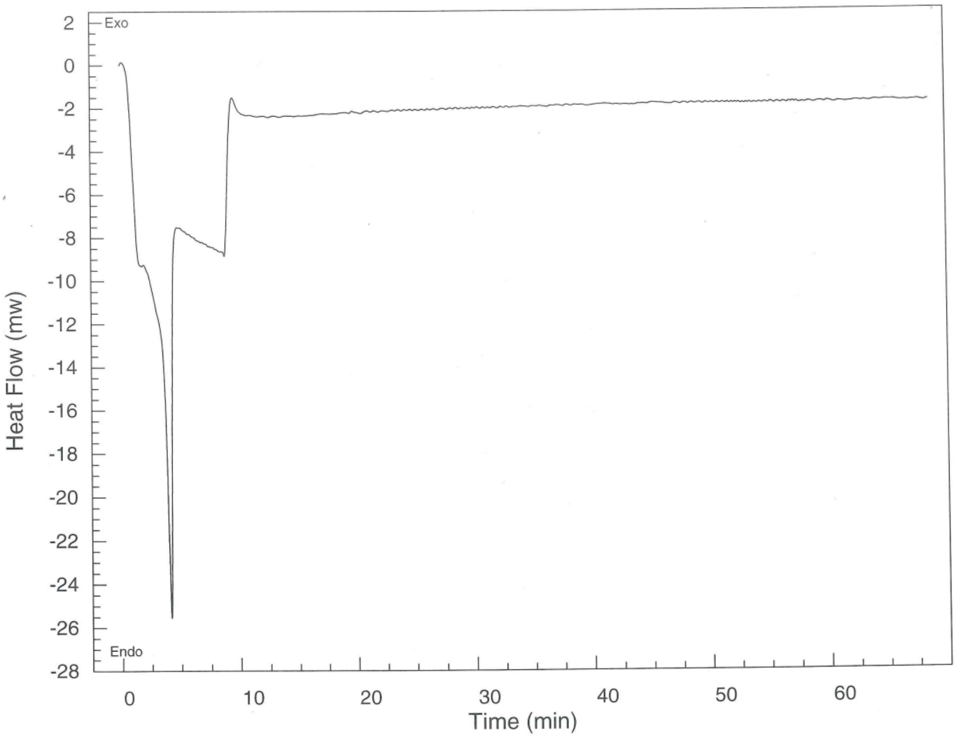


Figure D. 12 Isothermal Treatment of TPU 1% (w/w) at 200°C for 1 Hour

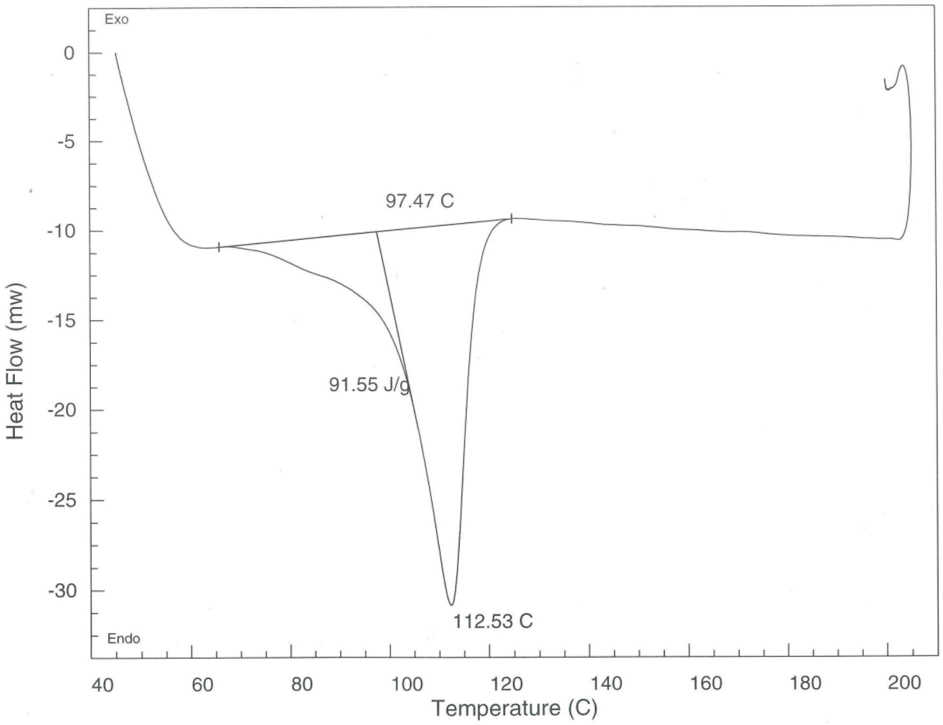


Figure D. 13 TPU 0.5% (w/w) Sample Thermogram

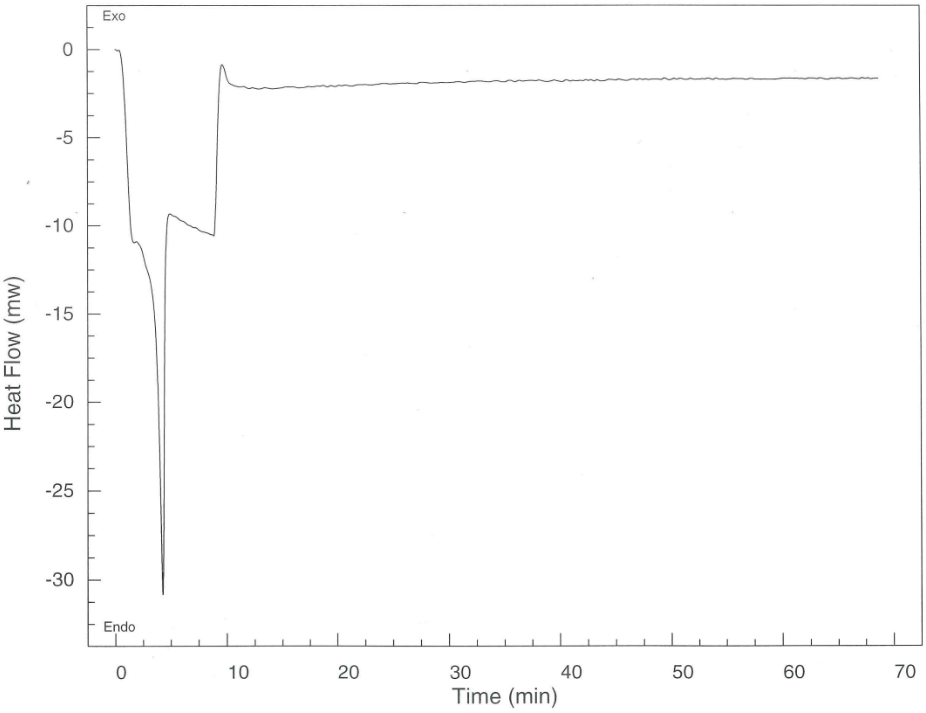


Figure D. 14 Isothermal Treatment of TPU 0.5% (w/w) at 200°C for 1 Hour

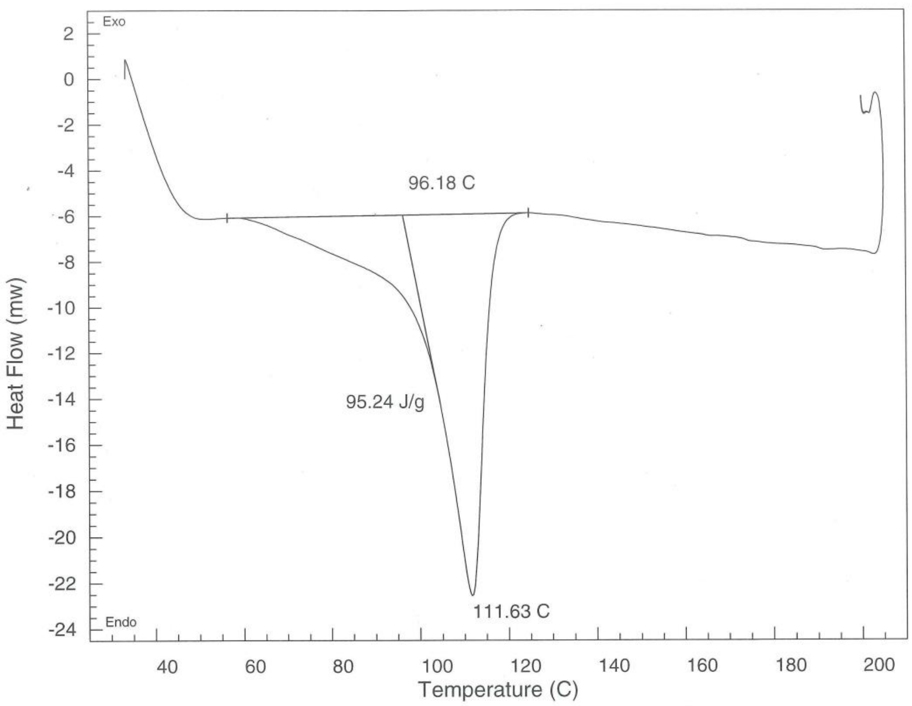


Figure D. 15 TPU 0.09% (w/w) Sample Thermogram

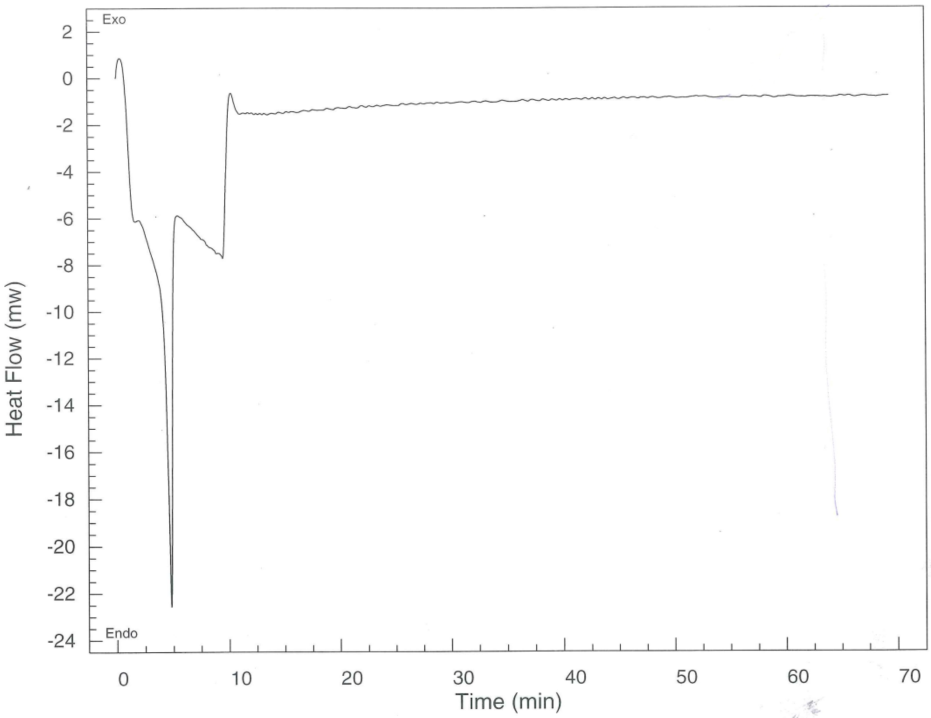


Figure D. 16 Isothermal Treatment of TPU 0.09% (w/w) at 200°C for 1 Hour