GRAFT COPOLYMERIZATION OF p-ACRYLOYLOXYBENZOIC ACID ONTO HIGH DENSITY POLYETHYLENE

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Approval of the Graduate School of Natural and Applied Sciences.

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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The monomer, p-acryloyloxybenzoic acid (ABA) was synthesized by condensation reaction of acryloyl chloride and p-hydroxybenzoic acid in alkaline medium. Polymerization of the monomer and grafting of the produced polymer (PABA) onto high density polyethylene (HDPE) were expected to be carried simultaneously in melt mixing at high temperature. The graft copolymerization was studied at varying concentrations of the monomer in the reaction mixture at constant temperature (200 ^{0}C).

Grafted HDPE samples were investigated by several techniques such as DSC, FTIR, MFI and mechanical testing.

The tensile tests of PABA-g-HDPE showed an improvement particularly in stress at yield and Young's modulus whereas the strain at break values showed a decrease for all compositions compared to neat HDPE.

Keywords: High Density Polyethylene, acryloyloxybenzoic acid, polyacryloyloxybenzoic acid, liquid crystalline polymers and graft copolymerization.

ÖZ

p-AKRİLOİLOKSİBENZOİK ASİTİN YÜKSEK YOĞUNLUKLU POLİETİLEN ÜZERİNE AŞI KOPOLİMERLEŞMESİ

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P-Akriloiloksibenzoik asit (ABA) monomeri, bazik ortamda, akriloil klorürün, p-hidroksibenzoik asit ile kondensasyon tepkimesiyle sentezlendi. Monomerin polimerleşmesi ve oluşan polimerin (PABA), HDPE üzerine aşı kopolimerleşmesinin, eriyik halde yapılan karıştırma işleminde, eş zamanlı olarak gerçekleşmesi beklendi. Monomerin aşı kopolimerleşmesi, monomerin, tepkime ortamındaki değişen derişimleri için ve sabit tepkime sıcaklığında (200 ^{0}C) çalışıldı.

Aşı kopolimerleşmesine uğramış HDPE örnekleri, DSC, FTIR, MFI ve mekanik testler ile karakterize edildi.

PABA-g-HDPE örnekleri için yapılan mekanik testlerde, özellikle akma noktasındaki gerilim direnci ve Young’s modulus değerlerinde, saf HDPE’ne oranla gelişme görüldü. Kopmada yüzde uzama değerlerinde, artan ABA miktarına bağlı, düşme gözlendi.

Anahtar Kelimeler: Yüksek yoğunluklu polietilen, akriloiloksibenzoik asit, poliakriloiloksibenzoik asit, sıvı kristal polimerler ve aşı kopolimerleşmesi.

To My Family

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ABBREVIATIONS

HDPE : High Density Polyethylene
TP : Thermoplastic
LCP : Liquid Crystalline Polymer
ABA : p-Acryloyloxybenzoic Acid
MBA : p-Methacryloyloxybenzoic Acid
PABA : Polyacryloyloxybenzoic Acid
PABA-g-HDPE : Polyacryloyloxybenzoic Acid-graft- High Density Polyethylene
DSC : Differential Scanning Calorimetry
FTIR : Fourier Transform Infrared Spectrometry
MFI : Melt Flow Index
SEM : Scanning Electron Microscopy
RP : Reprocessed

CHAPTER 1

INTRODUCTION

There has been a growing demand for modification of plastic materials in the hope of obtaining favourable properties. Due to limited number of monomers offered for polymerization, blending and alloying of polymers with other polymeric components had a significant development in recent years [1-4].

Polyethylene (PE) is one of the most widely used polymer due to its advantageous properties such as high chemical resistance, high impact strength and flexibility beside its low cost. However, the practical applications of PE materials are limited because of its chemically inert surface and low surface energy.

There are several methods for modifying polymers such as surface modification by physical or chemical methods, degradation or graft copolymerization. A remarkable progress has been noted in the modification of polymeric material by graft copolymerization for producing functional polyolefines. Depending on the purpose, different functional groups can be grafted onto polymer for the desired properties. Both surface and bulk properties of the polymers can be altered by grafting such as tensile strength, abrasion resistance, adhesion and also thermal and photochemical stability without changing the structure of polymer backbone [5].

1.1 General Review on HDPE, LCPs and Their Blends

1.1.1. High-Density Polyethylene (HDPE)

Polyethylene is the simplest polymeric hydrocarbon with just two carbons and four hydrogens in the repeating unit. Due to its low cost and ease of manufacture, it has a wide range of applications in the plastic industry.

Polyethylene is polymerized from ethylene gas which can easily be obtained from crude oil or natural gas. Among the three types of commercially made PE, high density (linear) polyethylene (HDPE) can be obtained by using several methods such as polymerization with organometallic compounds at moderate pressure. Under these conditions, the polymer chain length is very great, having molar masses about many hundred thousands. It is hard, tough and quickly spring back to its original shape. As known, free radicalic mechanism occurs at high temperature and pressure but low temperature and pressure have to be ensured in order to produce a linear polymer or by using Ziegler-Natta catalyst. [6].

Typical HDPE is 90% crystalline and due to its high degree of crystallinity, it has a higher crystalline melting point, greater tensile strength and hardness compared to low density (branched) polyethylene. Owing to its linear structure with little entanglements in the melt, HDPE molecules tend to be aligned in the direction of flow when processed in the melt.While cooling, rapid crystallization and high shrinkage occur because of this orientation. Faster cooling rate compared to LDPE, is a big advantage in very high-volume processes [6-7].

The addition of fillers and reinforcing agents is resulted with an increase for heat deflection temperature and decrease for the coefficient of linear expansion for HDPE. And it is also known that filled HDPE is harder and has better strength properties than unfilled HDPE [8-9].

1.1.2. Liquid Crystalline Polymers

The liquid crystalline state is intermediate between crystalline state and liquid state being neither crystalline nor liquid. Liquid crystalline polymers are extended, rod-like and rigid molecules. Because of their chemically complex and structurally distinct properties, they do not behave like any of conventional liquid, amorphous or crystalline classifications but may be evaluated as a different state of matter named liquid crystalline state.

LCP molecules can appear in highly ordered configurations in liquid conditions whereas other polymer molecules appear disordered structure and are referred to as lyotropic systems. As solids, this highly ordered configuration remains in a particular temperature range without need for the addition of solvent molecules and these systems are referred to as thermotropic systems. There are also many types of liquid crystal states, depending upon the amount of order in the material and mainly can be classified into three groups due to their arrangements as nematic, smectic and cholesteric.

Basic properties of LCPs are being affected by the orientability of the material in the fluid state. Flow field, especially uniaxial extensional flow field, is the dominating factor which the formation of oriented LCP fibrils is strongly influenced.

By the deformation of the LCP phase in polymer blends with the effect of extensional flow field, LCP fibrils formation occurs with high aspect ratios and this fibril formation is the basic reason for reinforcement effect of the matrix.

LCPs exhibit remarkable properties as high mechanical strength and chemical resistance, electrical insulation, stiffness, superior barrier properties and temperature resistance with a higher melting temperature than the other polymers at the same conditions owing to its organized structure.

1.1.3. Blends of Liquid Crystalline Polymers with Thermoplastics

There has been a considerable interest in polymeric material research for improvement of physical properties with composites produced by using blends of LCP with thermoplastics [10].

Several methods are being known for modification of commodity plastics as using proper fillers and reinforcement agents, copolymerization with polar monomers or grafting of functional compounds to the polymer backbone.

One relatively new type of reinforcement is to blend thermotropic liquid crystalline polymers and thermoplastics in the hope of obtaining development for the properties of blend . It has been reported earlier that neat LCPs have very high mechanical properties due to their stiff molecular backbones [11], their relative ease to orient and to retain this orientation for up to several minutes in the melt state [12-13].

Creation of LCP fibrils by use of appropriate processing conditions is the basic point for reinforcement of TP matrices with LCPs. These fibrils reinforce the matrix similar to the fiber-reinforced composites and due to this similarity, LCP-reinforced TPs are often termed *in situ* composites.

In addition, these *in situ* composites can easily be processed beside the TPs reinforced with the solid reinforcing agents. [13].

There are several factors that affect the ability of LCPs to reinforce commodity plastics as flow field, processing temperature, concentration and dispersion of LCP, missibility of the components and effect of compatibilizers [14].

The influence of flow field is very dominant on the formation of oriented LCP fibrils from drops. Ide and Ophir [15] reported that molecular orientation within neat LCPs is strongly affected by uniaxial extentional flow field.

The processing temperature also has to be adjusted sufficiently. Generally high temperatures are required for the formation of reinforcing fibrillar structure of LCP. While typically LCPs are processed temperatures above 300 ^{0}C , commodity resins can go through degradation at this temperatures. Despite this temperature difference, when the processing temperature of each material suitably adjusted, fibrillar structure with increased mechanical properties can be observed [14]. On the other hand, temperatures higher than the melting point of the LCP may cause a decrease for the mechanical properties of the blend. Nobile et al. [16] reported that while droplet morphology was observed at 260 ^{0}C for PET / PHB (polyhydroxybutyrate) blend, decreasing the process temperature to 220 ^{0}C resulted fibrillar morphology formation.

Correspondingly weaker mechanical properties were measured for the blend processed at higher temperature than for the blend processed at lower temperature.

This result can be explained depend on the two factors; the first factor is that higher hydrodynamic stresses at lower temperatures provide the conditions needed to deform smaller LCP droplets [16].

Besides the effects of flow field and processing temperature, concentration of LCP within a polymer matrix has to be considered as a critical factor in creation of a fibrous morphology [16-18]. Blizard and Baird [18] has reported this point with blends of a LCP based on poly(ethyleneterphtalate) / p-hydroxybenzoic acid (PET / PHB) with PC or nylon 6.6 matrices. For lower concentration of LCP were found to have a droplet morphology but fibrous structure was obtained at higher concentrations.

While the above factors significantly affect the ability of LCPs to reinforce TPs, the degree of missibility is one of the important factors for the final properties. While immisible systems displayed strengths that did not differ from the strength of the matrix; partially miscible systems were found to have the highest strengths [19]. Because of polymer pairs with enhanced mechanical properties are desired, the mechanical properties of two less suitable polymers might be enhanced by the addition of third interfacially active component. This process is termed as compatibilization [20-21]. Rubbery materials are generally used as compatibilizer in order to improve the toughness and impact strength of the polymer matrix.

1.2. Reinforcement of Polyolefines with LCPs

Thermoplastic composites, based on blends of liquid crystalline polymers with commodity resins form the dominating group among the polymer blends. As far as these type of blends are widely studied, unfortunately most of the thermoplastics are incompatible with the common LCPs.

Thus, limited processing conditions with insufficient adhesion and dispersion of LCP droplets without adequate elongation are the basic reasons of lower reinforcing effect of LCPs than expected [22-24].

Poor dispersion and adhesion problems can be solved by addition of the compatibilizing agents such as ethylene-acrylic acid copolymer and maleic anhydride grafted PE [26,28-29].

There are several studies about the addition of LCPs into flexible resins, such as polyamides, polyesters, polycarbonates, polysulfones etc [25]. On the contrary, blends of PE and LCPs were carried out in a few studies. Differences between melting/processing temperatures of the two polymers beside the incompatible nature prevents to obtain enhancement in mechanical and morphological properties. And it has been reported that PE has received very little consideration as a matrix for LCP blends [26-32].

The mechanical properties of neat PE, MA-g-high density PE and SBH (SBH; mole ratio sebacic acid (S): 4,4′-dihydroxybiphenyl (B): 4-hydroxybenzoic acid (H) = 1 : 1 : 2) -g-PE were investigated in the study of La Mantia et al [33]. Effect of the addition of 5 wt% compatibilizers on the mechanical properties of compression molded specimens of PE/LCP (LCP:SBH) blends were studied in their research.

In this study, it was reported that the mechanical properties PE were better than MA-grafted high density PE compatibilized PE/SBH blend, because of the higher degree of crystallinity of incompatibilized PE. It is observed that the addition of 20% SBH into PE caused a decrease for the elongation at break values compared to neat SBH. This fragility of blend was the result of lack of interphase adhesion. 5% MA-grafted high density PE addition to the PE/SBH blend did not alter the mechanical properties.

In particular, a decrease was reported for the elongation at break values altough the ductility of neat MA-grafted high density polyethylene is higher than PE. The result of this study was stated as the compatibilizing ability of MA-grafted PE was very poor [33].

La Mantia et. al. [32] have studied on the mechanical properties of blends of SBH with different types of PE samples . A reduction was observed for the tensile strength of all types of HDPE polymers with the increasing SBH content.

Elongation at break values also showed a reduction especially in the range of 5-15% LCP content. There are several studies for the blends of polypropylene with various LCPs [41-45].,

Pazzagli and Pracella [34] have reported that Polyethylene terephthalate (PET)/HDPE-g-Glycidyl methacrylate (GMA) blends displayed improved phase dispersion and interfacial adhesion as compared to unfunctionalized PET/HDPE blend. Moreover, it has also been reported that the compatibilization effectiveness of polyolefines grafted with GMA, in blends with polar polymers such as PET, is higher than that of the same polyolefines grafted with maleic anhydride (MAH) or acrylic acid (AA) [35-40].

Polypropylene is one of the most commonly used polyolefines among the plastic materials due to its easy processable nature and economy compared to the other engineering polymers.

There had been several investigations for modification of some properties of PP such as tensile properties and impact resistance. Although some moduli improvements are observed for PP/LCP blends, there were little or no improvement for the tensile properties.

Owing to non-polar structure of PP beside the more polar LCPs, functionalized PP was used as compatibilizer. Functionalization of PP is frequently done by maleic anhydride (MAH) which is a highly reactive monomer. Grafting MAH onto PP increases the polarity of PP and due to its ability to react with $–NH_2$, -OH and –COOH groups of other polymers, MAH molecules can form chemical links between components [10]. It is reported by Baird and his coworkers that compatibilized PP/LCP blends exhibit a more finely dispersed fibrillar structure than uncompatibilized blends and the tensile properties and modulus of the compatibilized blends are improved over those of uncompatibilized PP/LCP blends.

It also has been stated that compatibilizing agents reduce the interfacial tension which promotes interfacial adhesion and they also provide a finer and more uniform distribution of the dispersed phase.

1.3. Liquid Crystals, Poly(acryloyloxybenzoic acid)

1.3.1. PABA

Up to the present, there are a few publications about the studies on polyacryloyloxybenzoic acid (PABA) and polymethacryloyloxy (PMBA).

Menczel, Walsh and Wunderlich [46] attempted to study on the polymerization process of p-Acryloyloxybenzoic acid and they had reported that instead of a simple vinyl polymerization, ester interchange by acidolysis to poly(p-oxy-benzoate) (POB) is a competing reaction.

They also have analyzed the phase transitions of PABA as an example of transition behaviour of side chain mesomorphic polymers. Their attempts to produce amorphous PABA was not always succesful by using solution polymerization followed by precipitation.

In early studies of Blumstein et al. [47], it was reported that two crystal forms have been observed for PABA as one (1) was reported to have a monoclinic and the other (2) was identified as smectic. Beside the mentioned forms above, PABA may exhibit another highly mobile mesophase state which was produced by melting of crystal for 1 or 2 or out of the amorphous PABA above the glass transition.

Crystallinity and order in atactic PABA and Polymethacryloyloxybenzoic acid (PMBA) was studied by Blumstein et al. [47]. It was reported that the family of p-n-alkoxybenzoic acids display nematic and/or smectic liquid crystalline organization but neither MBA nor ABA display mesomorphic behaviour.

Both monomers gave a sharp transition from crystal to isotropic melt resulted with a rapid polymerization of the melt. They had also reported that the development of crystallinity in both PABA and PMBA depends on the polymerization conditions. In their study, it is stated that the crystallites of both polymers exhibit significant heat stability which the crystallinity in PABA started to decompose at 250 ^{0}C and displayed an endothermic peak at 252 ^{0}C probably due to the melting of crystallites.

Only one research on the blends of PABA and PMBA with a thermoplastic was reported in common literature. Sainath and coworkers [48] have studied on the thermal behaviour and morphology of PABA/nylon 6 (PA6) blends and they had stated that increasing PABA content caused a decrease both for melting point and crystallinity of PA6.

Çetin [5] studied the graft copolymerization of the monomers, ABA and p-methacryloyloxybenzoic acid (MBA), onto isotactic polypropylene, with bulk melt polymerization. The IPP used in the graft copolymerization was firstly subjected to γ-radiation to create active sites for grafting. The graft copolymerization of the monomers, ABA and MBA onto propylene were initiated by these active sites. He has reported that the amount of grafting increased with the increase of concentration of monomers in the reaction medium.

1.4. Graft Copolymerization

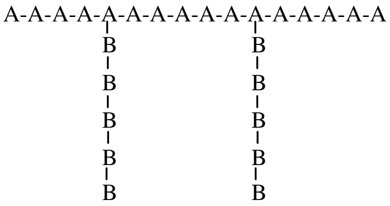
A polymer consisting of two or more chemically different monomer units is defined as copolymer. There are mainly three types of linear copolymers;

1)	A-A-B-A-B-A-B-B-B-A-B-A-A	Random Copolymer
2)	A-B-A-B-A-B-A-B-A-B-A-B-A	Alternating Copolymer
3)	A-A-A-A-B-B-B-B-B-A-A-A-A	Block Copolymer

However, a graft copolymer is composed of a polymer backbone with monomer units A and a polymer with monomer units B, branched on the backbone.

A graft copolymer exhibits the characteristics of the two basic homopolymers, while random copolymers possess the properties intermediate between its two basic homopolymers [49].

Schematically, the structure of a graft copolymer can be represented as below;



Graft copolymer

Grafting can be achieved by several methods such as chemical methods and radiation induction. Radiation induced graft copolymerization is the most widely used method because of several reasons like enabiling both bulk and surface copolymerization, applicability in wide range of temperature with varying sizes of grafting component and also easy controlling of polymerization rate by the irradiation dose rate and reaction time [5].

Grafting can be also achieved thermally if there exist available active sites, like vinyl groups under extensive shear process.

1.5. Aim of the Work

The objective of this study is to carry out graft copolymerization of p-acryloyloxybenzoic acid onto HDPE, and to obtain improvement in the mechanical properties, processability of the polymeric material and dispersion of the liquid crystalline polymer in the graft copolymers.

CHAPTER 2

EXPERIMENTAL

2.1. Chemicals and Materials Used

2.1.1. Solvents and Reagents

Xylene and methanol (Riedel-de Haen A.G.) and acetone (Merck A.G.) were used without any purification. Technical grade ethanol was also used without purification.

P-acryloyloxybenzoic acid was synthesized by using acryloyl chloride (Aldrich A.G.) and p-hydroxybenzoic acid (Aldrich A.G.).

High density polyethylene, coded as S 0464, was supplied by PETKIM, Turkish Petrochemical Industry.

2.2. Synthesis of the Monomer

2.2.1. Synthesis of p-Acryloyloxybenzoic Acid

p-Acryloyloxybenzoic acid, ABA, was synthesized by condensation of acryloyl chloride with p-hydroxybenzoic acid in alkaline medium (Figure 2.1) as described by Blumstein and Kitagawa [50].

13.8 g (0.1 mol) p-hydroxybenzoic acid was added to a solution of 11 g (0.2 mol) KOH in 100 mL of distilled water in a flask equipped with a magnetic stirrer. The solution was cooled to 0-5°C, and then 9.1 g (0.1 mol) acryloyl chloride was added dropwise by stirring about 20 min. The stirring was then continued at room temperature for another 30 min. A precipitate formed after 3M HCl addition. The precipitate was filtered and washed with water. Then, ABA was purified by repeated recrystallization from acetone. The purity was checked by NMR as described by Çetin [5].

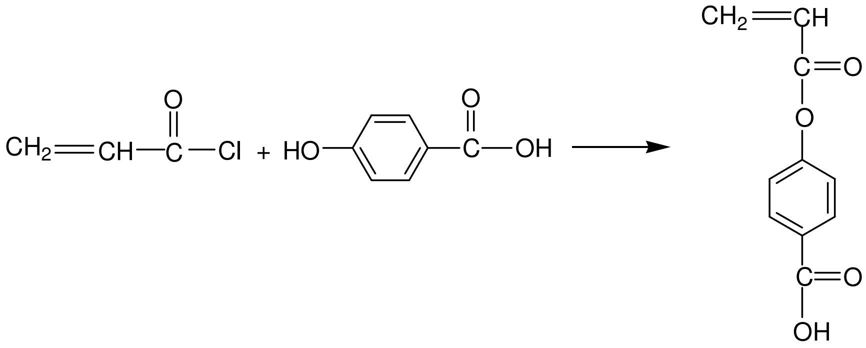


Figure 2.1. The simplified reaction between p-hydroxybenzoic acid and acryloyl chloride.

2.3. Polymerization of the Monomer, ABA

2.3.1. Sample Preparation and Grafting

The polymer HDPE and monomer (ABA) were mixed in mixing head of Brabender Plasticorder in desired proportions and the thermal graft copolymerization with simultaneous polymerization of the mixture was carried out at a pre-set temperature (200 ^{0}C) for a predetermined period of time (15 min.)

Three different compositions were prepared by mixing ABA with HDPE. ABA was dried under vacuum for 24 hours at 100 ^{0}C before processing in order to avoid hydrolytic chain scissions. Based on the percentages which are shown in Table 2.1, ABA was added to the polymer matrix.

Table 2.1 Compositions of PABA-g-HDPE samples

Composition	HDPE	ABA
Neat HDPE	46.00 g	-
5% PABA+HDPE	43.70 g	2.30 g
10% PABA+HDPE	41.40 g	4.60 g
15% PABA+HDPE	38.25 g	6.75 g

Melt mixing was carried out at 5 rpm of rotor for 5 minutes and was then increased gradually to the final value of 60 rpm. The operation was continued until constant torque was observed, i.e. about 10 minutes, and the mixing temperature in Brabender was well below the degradation temperature of PABA-g-HDPE.

This mixture was compression molded at 200 ^{0}C and approximately 2.0 mm thick sample plates were obtained. These 2 mm thick samples were used for subsequent mechanical and thermal tests. All compositions were reprocessed in order to ensure the effect of grafting on mechanical properties as described above. Possible grafting reaction between ABA and HDPE is shown in Figure 2.2. It is also possible that the vinyl group of ABA may start the reaction via abstraction of H from the main chain.

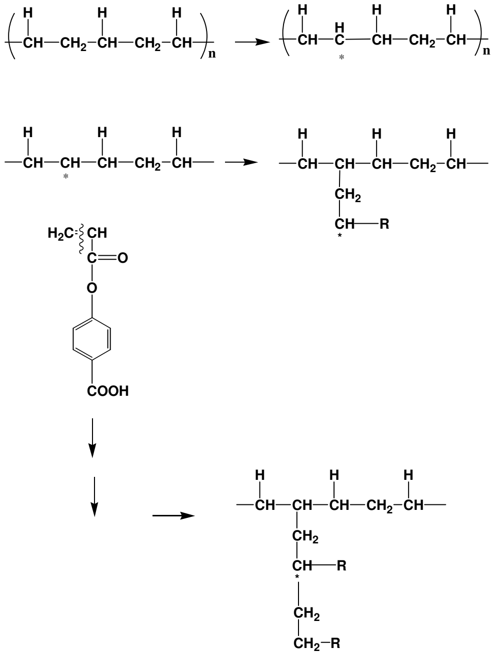


Figure 2.2. The grafting reaction between ABA and HDPE. (R stands for the substituent of vinyl group)

2.4. Characterization and Instruments

2.4.1. FT-IR Measurements

FT-IR characterization of HDPE, ABA and the blends of ABA/HDPE were done with a Nicolet DX 510 FTIR spectrometer. FT-IR spectra of monomer,ABA, was obtained from KBr pellets and spectra of HDPE and PABA/HDPE blends were obtained directly by using thin films.

2.4.2. Differential Scanning Calorimetry (DSC) Analysis

Thermal properties of the samples which sample sizes are varying between 10-15 mg were analyzed by using Dupont Thermal Analyst 2000 Differential Scanning Calorimeter 910 S, with a heating rate of 20 ^{0}C/min under nitrogen atmosphere. By interpreting the obtained thermograms, the glass transition temperature (T_g) and melting temperature (T_m) of the samples were determined.

2.4.3. Melt Flow Index

Melt flow properties were analyzed by using Coesfeld Material Test, Meltflixer LT at 190 ^{0}C. Samples were cut into small flakes by hand. The cylinder of the instrument was fed with flakes.Flakes were kept in the cylinder for 5 minutes in order to complete the melting of all samples. While applying 5.00 kg load, extruded samples were cut at 600-second time intervals. Weight of the cut samples were reported as g/10 min.

2.4.4 Determination of Degree of Grafting

The mixture of PABA-g-HDPE samples and DMSO were transferred to the reaction flask. The flask was then, heated up to the boiling temperature of DMSO, keeping the temperature constant for 3 hours to remove soluble products especially monomer and homopolymer (polyacryloyloxybenzoic acid). At the end of the reaction time, the flask was cooled to room temperature and opened. The grafted HDPE was rewashed extensively with methanol several times to ensure the removal of DMSO. The graft copolymerized HDPE samples, was then dried in vacuum at 75 ^{0}C for 4-5 hours. The amount of grafting was determined gravimetrically and expressed as a percentage of grafted polymer by weight in the products.

2.4.5. Mechanical Properties

Tensile properties of neat HDPE and PABA-g-HDPE samples were determined by Instron Tensile Testing Machine (Model TM 1102) at room temperature. The test samples from the sheets were cut in standart dumpbell shapes. Crosshead speed and gauge length in testing were 10 cm/min and 1 cm, respectively.The stress-strain values were computed from the load (F)-elongation values measured during the tests by the following relations:

$$\sigma = (F/A_o)$$

Where σ (Mpa) is the tensile stress, F is the load (tensile force) applied , and A_o is the original (undeformed) cross-sectional area of the gauge region of the specimen.

Strain, ε, is defined as

$$\varepsilon = (\Delta L/L_o)$$

where L_o is the initial gauge length, and ΔL is the change in the gauge length due to deformation.

The tensile modulus (Young's Modulus), E, which is the initial slope of the stress-strain curve, is also calculated as

$$E = \sigma/\varepsilon$$

2.4.6. Scanning Electron Microscope (SEM) Study

Morphological properties of tensile and impact fractured surfaces were studied by using scanning electron microscope, JEOL, JSM-6400.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Characterizations

3.1.1. FTIR Characterization of High Density Polyethylene

FT-IR spectrum of HDPE is given in Figure 3.1. The absorption bands of streching vibrations of CH_2 group were at 2915 and 2847 cm^{-1}. The absorption bands due to bending vibrations of CH_2 group was observed at 1462 cm^{-1}. The bending vibration of C-C group was observed at 728 and 718 cm^{-1}.

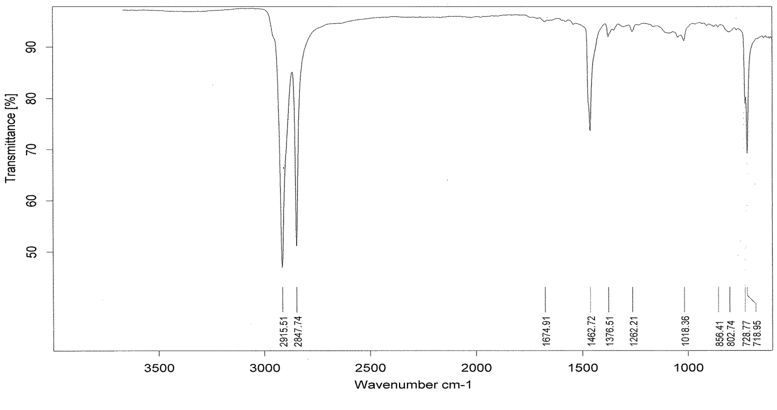


Figure 3.1 FTIR spectrum of neat HDPE

3.1.2. FTIR Characterization of p-Acryloyloxybenzoic Acid

The FTIR spectrum of monomer ABA is shown in Figure 3.2. Broad bands in between 3200-2500 cm^{-1} are due to the carboxylic acid –OH and C-H streching vibrations. C=O streching vibrations of ester groups can be observed as the bands at 1742 cm^{-1}. The strong band at 1688 cm^{-1} is due to C=O stretching vibrations of aryl carboxylic acids. The bands at 1600 and 1500 cm^{-1} are peculiar to aromatic compounds which includes C=C bonds in the structure. The sharp bands in between 800-1000 cm^{-1} represent the vinylic C-H out-of-plane bending vibrations.

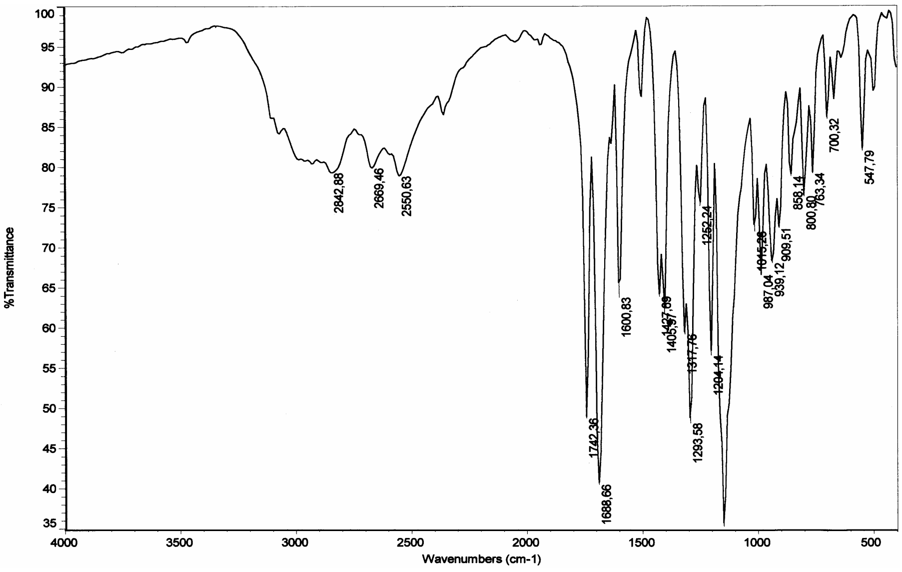


Figure 3.2. FTIR spectrum of acryloyloxybenzoic acid

3.1.3. FTIR Characterization of PABA-g-HDPE Samples

FTIR analysis of the products as shown in Figure 3.3. and Figure 3.4. confirmed the graft copolymerization of ABA onto HDPE. The characteristic absorption bands of PABA due to aromatic, carbonyl and carboxylic groups and of the aliphatic groups due to HDPE and main chain of PABA were also observed in FTIR spectra of the graft coproducts.

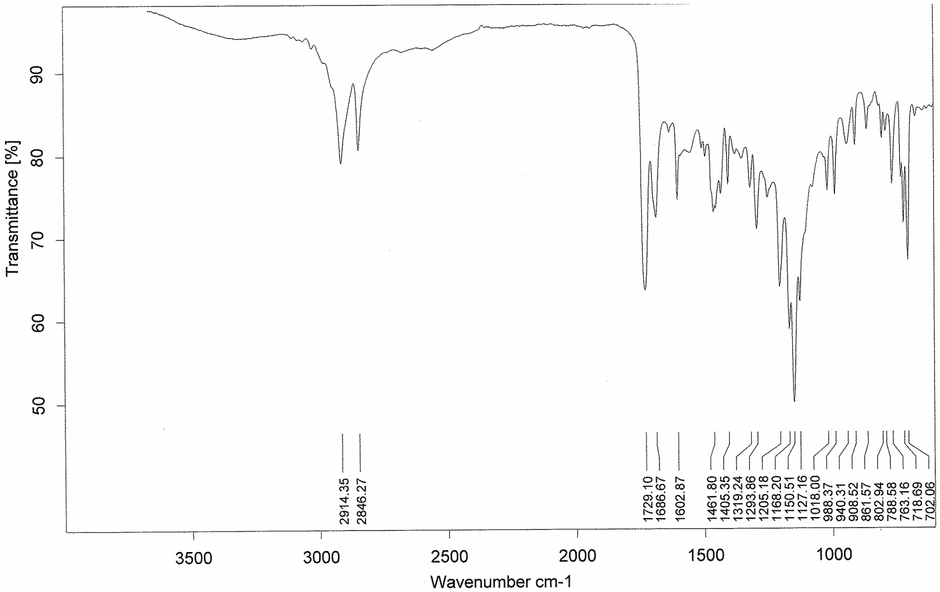


Figure 3.3 FTIR spectrum of 5% ABA containing HDPE graft

Strong band at 1729 cm^{-1} is a characteristic of C=O stretching vibrations of ester group, a strong band at 1687 is cm^{-1} due to C=O stretching vibrations of aryl carboxylic acids, a band at 1602 is cm^{-1} due to C=C stretching vibrations of aromatic compounds.

Four bands at 800, 909, 939 and 987 cm^{-1} that were seen in the spectrum of ABA due to vinylic C-H out-of-plane bending vibrations disappeared in the spectrum of both 5% ABA and 10%ABA containing coproducts.

Because of insolubility of the graft coproducts, PABA-g-HDPE in any solvent , NMR analysis could not be carried out.

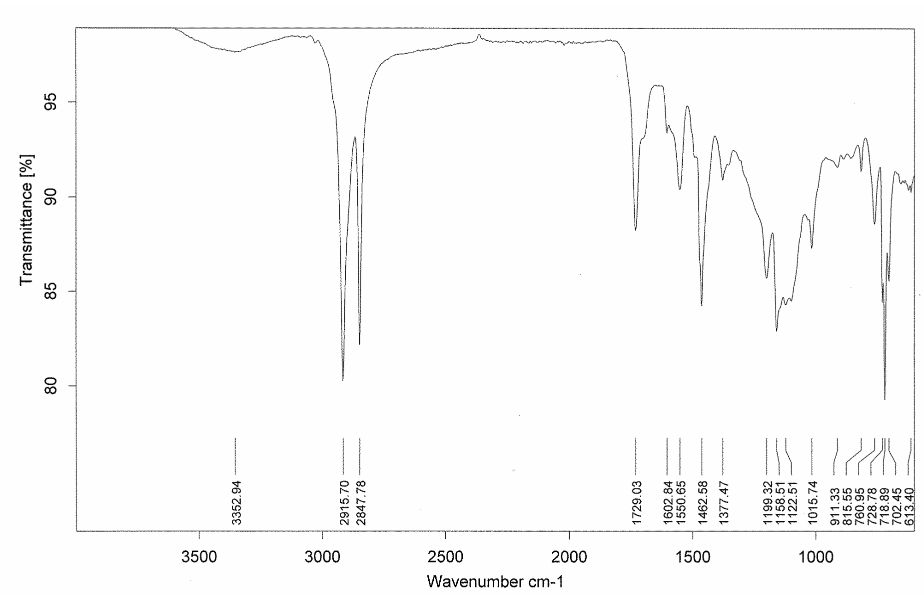


Figure 3.4 FTIR spectrum of 10% ABA containing HDPE graft

3.1.4. Thermal Characterization of ABA, Neat HDPE and Grafted HDPE

The thermal properties and crystallization behaviour of ABA, PABA-g-HDPE and neat HDPE were studied by DSC in order to find out the effects of LCP addition to polymer matrix.

The DSC measurements of ABA were carried out in N_2 atmosphere with heating rate of 20 ^{0}C/min from 25 ^{0}C to 300 ^{0}C. As shown in the Figure 3.5., DSC melting point of ABA was observed at 199-200 ^{0}C as reported in literature [52].

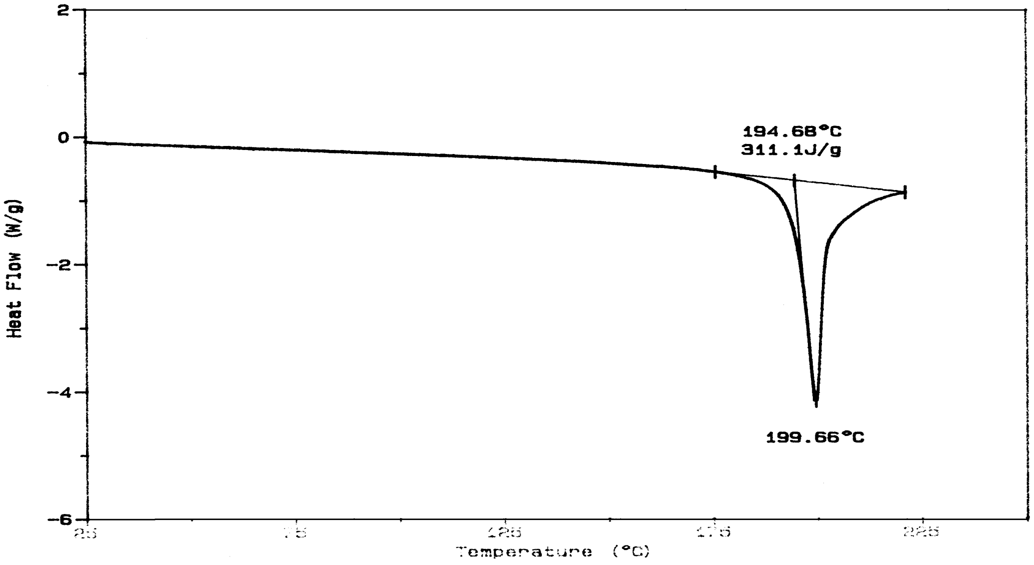


Figure 3.5. DSC thermogram of acryloyloxybenzoic acid

Melting point of HDPE was found as 136 ^{0}C in N_2 atmosphere in DSC test as shown in Figure 3.6. This agrees well with the literature.

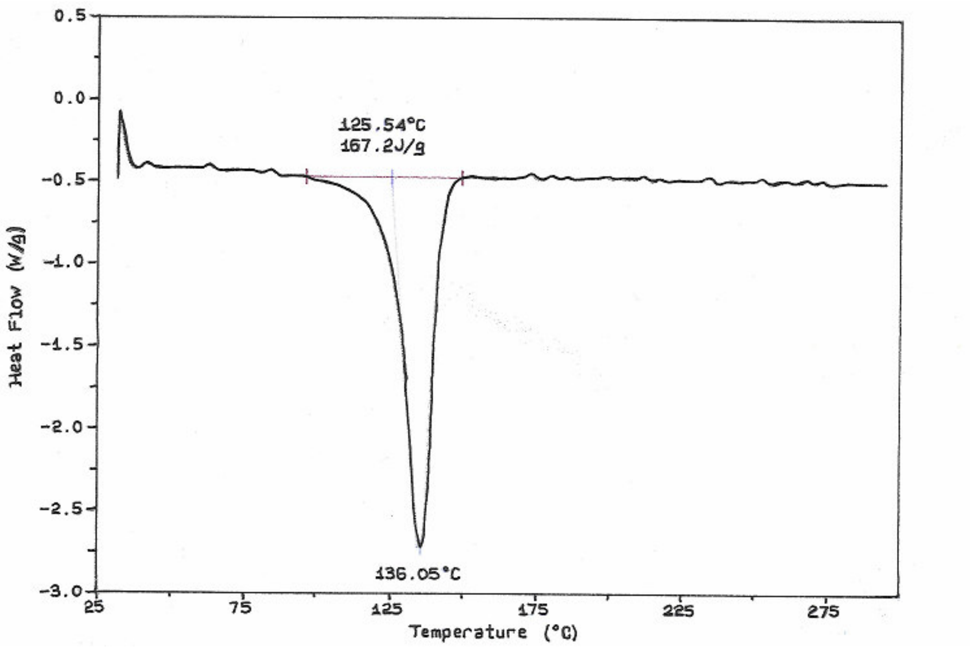


Figure 3.6. DSC thermogram of neat HDPE

The crystalline melting of grafted PABA was observed weakly at 292 ^{0}C in the thermogram of PABA-g-HDPE sample, Figure 3.7. Intensity of this peak is highest for 15% ABA containing coproduct compared to 5% and 10% ABA containing PABA-g-HDPE sample.

In grafted HDPE samples, melting point of HDPE was found to be around 135 ^{0}C , as shown in Figure 3.7. Therefore, the addition of ABA for all compositions does not cause any alteration in the crystallinity of the main matrix.

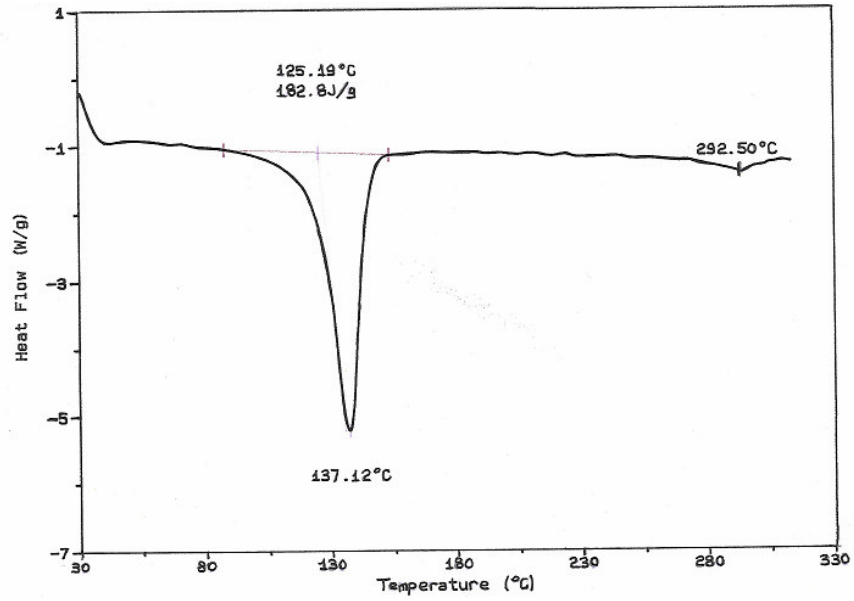


Figure 3.7 DSC thermogram of 15% ABA containing HDPE sample

3.2. Gravimetric Analysis for Grafting

The variation of grafting upon changing the mixing ratio of HDPE and monomer ABA was also studied as described in 2.4.4. It was observed that the amount of grafting increased with increasing concentration of ABA in reaction medium.

Reprocessed samples showed higher extent of grafting values compared to the processed samples. The extent of grafting was calculated by using the following equation;

$$\%\text{Grafting} = (W_{\text{initial}} - W_{\text{final}}) \times 100 / W_{\text{initial}}$$

Table 3.1 The dependence of content of PABA grafted onto HDPE on concentration of ABA in reaction mixture

%ABA in reaction mixture	5	10	15
%PABA grafted	3.80	9.09	14.00

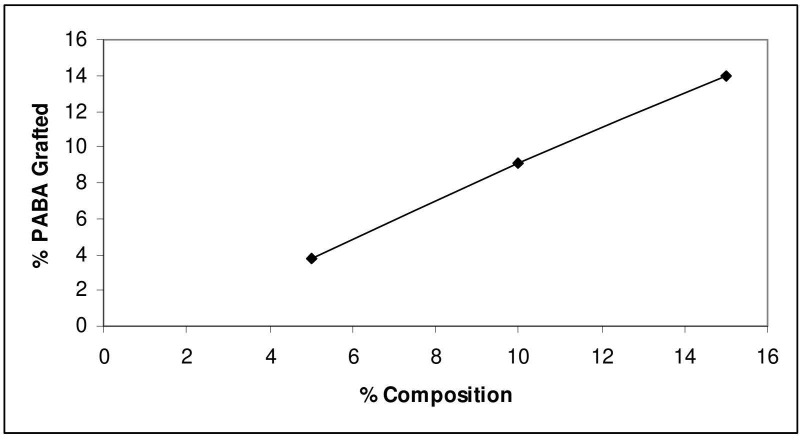


Figure 3.8 The dependence of PABA content grafted onto HDPE on concentration of ABA in reaction mixture

3.3. Melt Flow Properties

The rate of extrusion of molten material was characterized by the melt flow index test. The melt index is a measure of flow inversely related to melt viscosity and is of cited in particular terms such as the weight of a material to pass through a standard orifice in 10 minutes at a specified temperature.

Compression molded samples were cut into small flakes by hand grinding and filled through a die of defined length and diameter under pre-determined temperature and load. Physical properties and morphology of the polymer and testing parameters such as temperature and load are the effective factors on the rheological characteristics of polymer melts.

Melt flow index of pure HDPE and ABA containing HDPE samples were characterized according to ASTM D 1238-90b.as described in experimental section. Ten measurements were carried out for each compositions and based on the average MFI values. Figure 3.9 was obtained by plotting the MFI values versus percent composition. The numerical value of MFI values are given in Table 3.2.

Table 3.2. MFI (g/10 min) vs. percent ABA

Composition	Average MFI (g/10 min)
HDPE	0.58
5% PABA+HDPE	0.053
10% PABA+HDPE	0.046

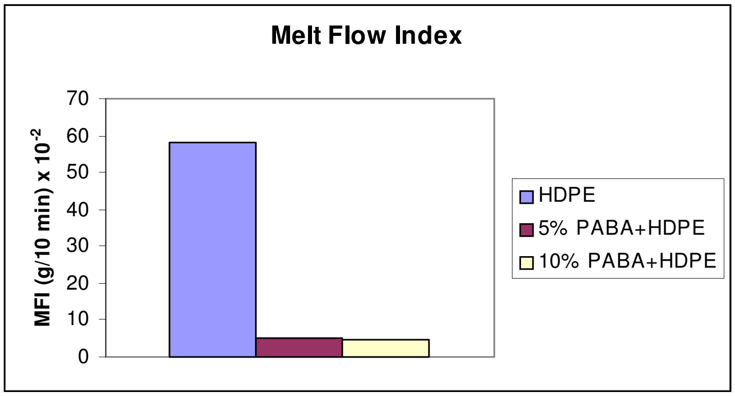


Figure 3.9 MFI (g/10 min) vs. percent ABA

The flow properties of matrix polymer were affected by the presence of PABA. According to volumetric flow rate values which are given as MFI values, an increase was observed for the viscosity with increasing content of monomer in the coproduct. MFI values were so low for 15% ABA containing coproduct, such they cannot be measured properly. In other words, as the ABA content increased in HDPE matrix, MFI values decreased. The possible reason of decrease in MFI is light crosslinking caused by ABA during processing.

3.4. Mechanical Properties of the Polymers

The tensile properties of the pure HDPE and graft copolymers were characterized in order to interpret the effect of grafted monomer to HDPE and its dependence on the varying amounts of monomer. Monomer (ABA) and polymer (HDPE) mixture which was mixed in Brabender Plasti-Corder was molded at 200 ^{0}C at compression molding.

The processing temperature did not exceed 200 ^{0}C because the PABA units of the graft coproducts start to degrade above 200 ^{0}C by the mechanism shown in Figure 3.10 [5].

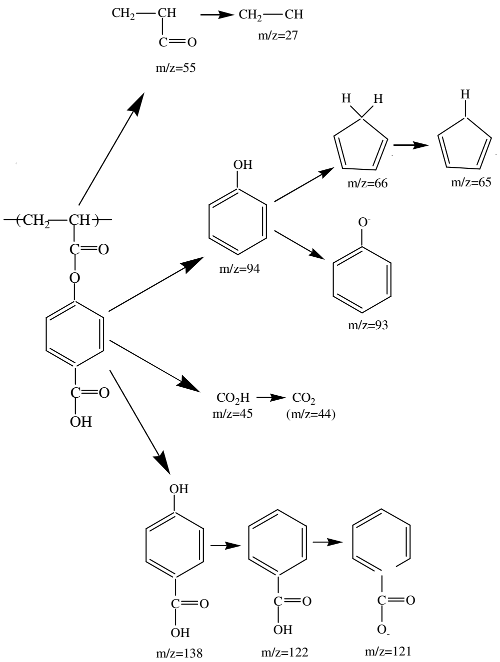


Figure 3.10 Degradation mechanism of PABA [5].

PABA units of the graft coproducts were considered to be in solid state at this processing temperature but this temperature was above the glass transition temperature (Tg) of PABA, therefore PABA units in grafted HDPE samples were presumed to be oriented in molten polymer matrix.

It was also observed that processing at 200 ^{0}C became more difficult with increasing content of ABA, although the samples containing low percantages of ABA (5% and 10%) could be processed at this temperature. In samples containing 15% ABA, we had difficulties of obtaining succesfully molded test samples. Also some yellowing was observed because of the degradation of grafted polymers just above this processing temperature.

Experimental results showed that neat HDPE has appreciably good tensile strength, percentage strain at break and stress at break values.In PABA-g-HDPE samples, there had been also significant improvements in the mechanical properties even in this processing conditions such as tensile strength at yield and Young's modulus.

Stress-Strain curve of neat HDPE and PABA-g-HDPE are given in Figure 3.11. Neat HDPE showed a great extent of cold drawing or orientation, also there existed yield stress in grafted HDPE coproducts and a decrease was observed for the percentage strain values of PABA-g-HDPE with the increasing content of ABA. Note that % elongation axis did not go further to break because of figure limitations.

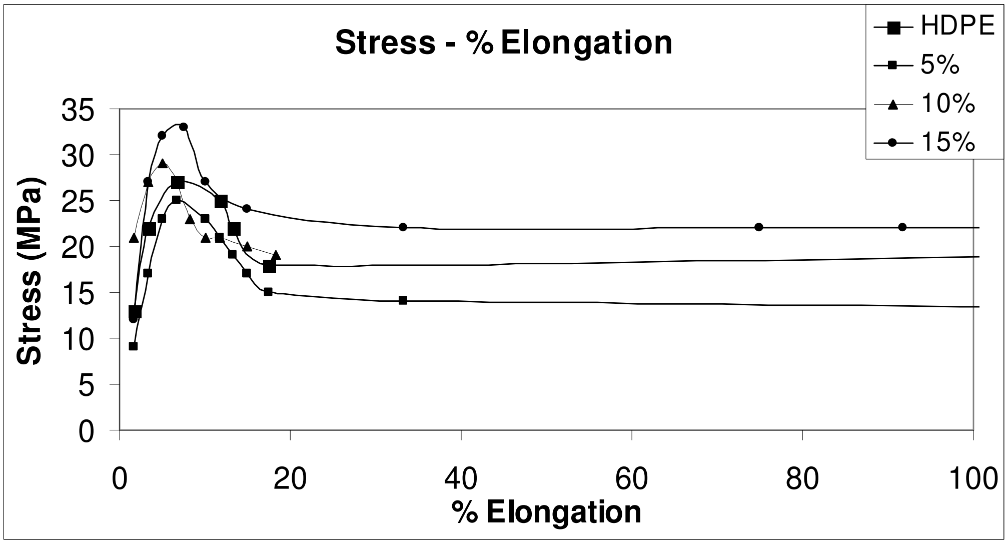


Figure 3.11. Stress-strain curves of neat HDPE and PABA-g-HDPE samples

The variation of stress at break of PABA-g-HDPE on content of ABA is shown in Figure 3.12. The strength of PABA-g-HDPE samples decreased with increasing percantage of ABA in the graft coproducts. The maximum, 31.22 MPa was obtained for neat HDPE, which is very high compared to the stress at break of 5% and 10% ABA containing coproducts, 22.33 and 19.00 MPa, respectively, followed by an increase for 15% ABA containing sample, as shown in Table 3.3. and Figure 3.12.

In neat HDPE sample and 5% ABA containing coproduct, we observed an indication of fibrillar fracture because of cold drawing orientation, but the others failed in ductile nature.

Table 3.3. Stress at break of PABA-g-HDPE with % ABA in samples

% ABA	0	5.0	10.0	15.0
Stress at break (MPa)	31.22± 2.86	22.33± 2.80	19.00± 1.00	22.00± 0.82

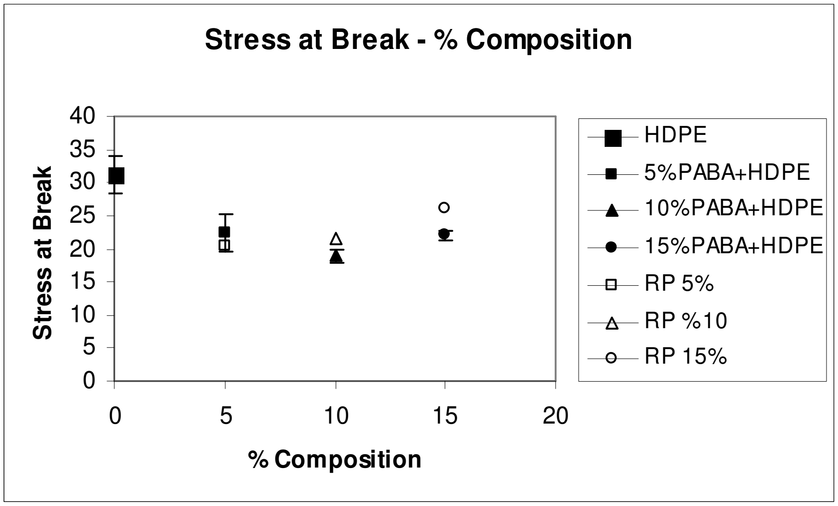


Figure 3.12. The dependence of ultimate strength of PABA-g-HDPE with %ABA in sample

The results of stress at yield value of PABA-g-HDPE are given in Table 3.4 and Figure 3.13. The variation of yield stress observed in PABA-g-HDPE samples showed increasing trend but never reached the neat HDPE yield stress. The maximum yield stress was observed in the sample contained 15% ABA, with 30.00 MPa which is lower compared to the yield stress value of neat HDPE.

Table 3.4. Yield Stress of PABA-g-HDPE with % ABA in samples

% ABA	0	5.0	10.0	15.0
Stress at Yield (MPa)	31.56± 2.83	26.67± 2.73	28.29 ± 0.95	30.00 ± 2.16

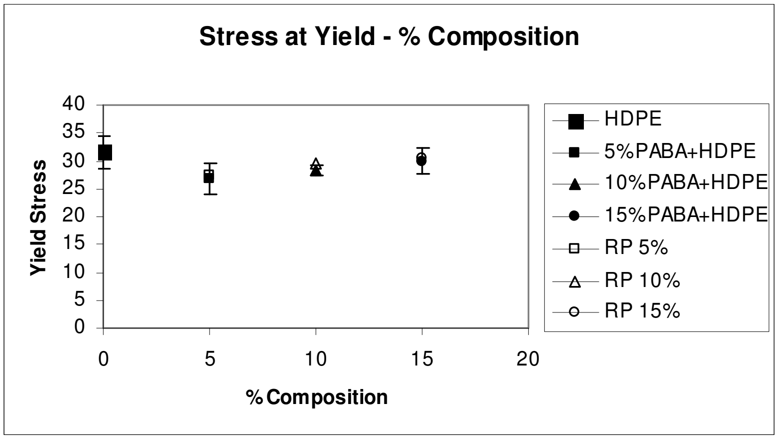


Figure 3.13 The dependence of yield stress of PABA-g-HDPE with %ABA in sample

Young's modulus can be used as an indication of stiffness. Improved modulus was observed in the specimens containing 5% and 10% ABA containing coproducts compared to neat HDPE, Table 3.5 and Figure 3.14. A slight decrease was observed for the sample containing 15% ABA. The maximum, 1294 MPa was reached at 10% ABA containing PABA-g-HDPE.

Table 3.5. Young's modulus of PABA-g-HDPE with %ABA in sample

% ABA	0	5.0	10.0	15.0
Modulus (MPa)	647	1137	1294	1250

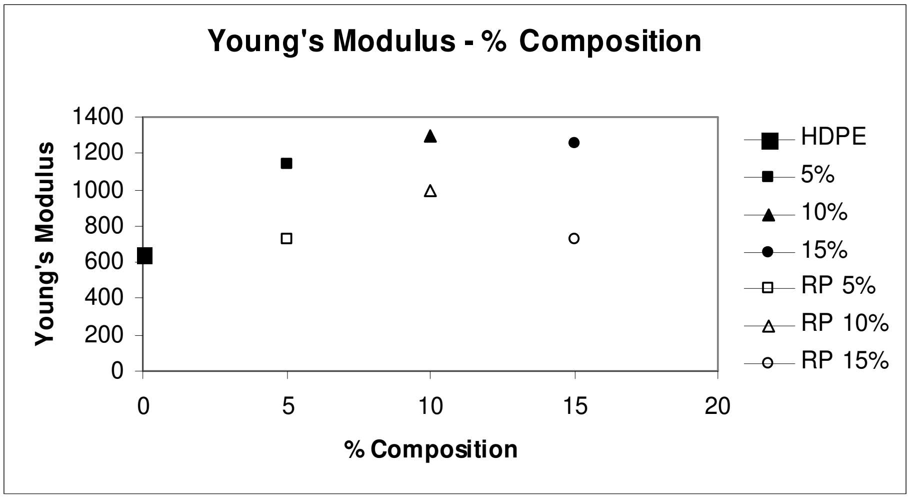


Figure 3.14. The dependence of Young's modulus of PABA-g-HDPE with %ABA in sample

Having relatively high modulus, 5% and 10% ABA containing samples showed lower strain at yield compared to neat HDPE . Percentage strain at break was increased for 15%ABA containing PABA-g-HDPE compared to 10% ABA containing coproduct.

The low percentage of elongation at break observed in 10% ABA graft may due to its highest modulus among other samples, i.e. increased rigidity. Consequently, this sample failed in brittle manner rather than ductile and showed less cold drawing behaviour. As a result of having high modulus, its fracture was almost in brittle nature.

The dependence of percentage strain at break of PABA-g-HDPE with % ABA in sample is given in Table 3.6. and Figure 3.15. Neat HDPE has a very high percentage strain at break value, typical of a polymer, however grafted HDPE samples have very low values showing lower plastic deformation. Therefore, this result was consistant with our expectations.

Table 3.6. Percentage Strain at Break of PABA-g-HDPE with %ABA in sample

% ABA	0	5.0	10.0	15.0
Strain at Break	529.62± 19.60	523.62± 28.11	120± 25.17	190.03± 40.81

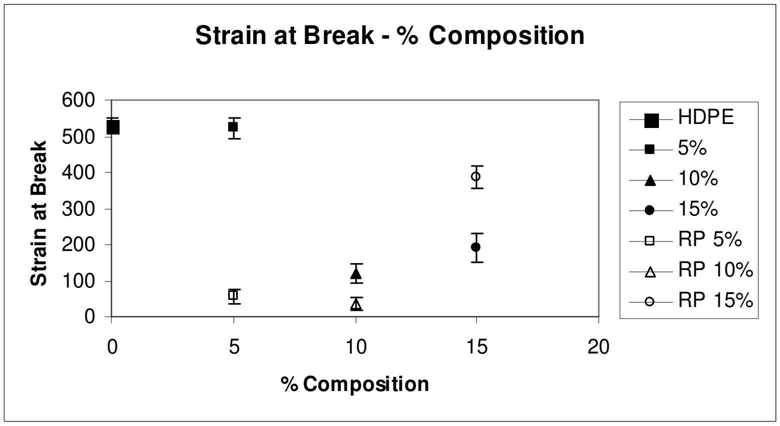


Figure 3.15. The dependence of Percentage Strain at Break of PABA-g-HDPE with % ABA in sample

Having relatively high modulus, 10% ABA containing coproduct showed low strain at yield values as seen in Figure 3.16. In the same way, 15% ABA containing PABA-g-HDPE sample possessing lower Young's modulus compared to 10% containing coproduct showed higher percentage strain at yield value.

Table 3.7. Percentage Strain at Yield of PABA-g-HDPE with %ABA in sample

% ABA	0	5.0	10.0	15.0
Strain at Yield	7.22± 1.16	6.97± 0.65	5.00± 0.00	7.28± 1.05

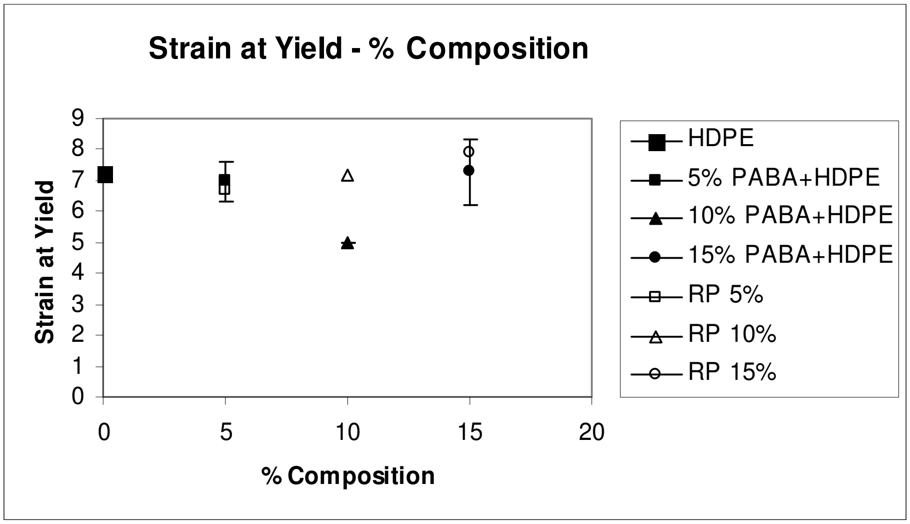


Figure 3.16. The dependence of Percentage Strain at Yield of PABA-g-HDPE with % ABA in sample

All compositions were reprocessed in order to ensure the effect of grafting on mechanical properties. But it was seen that the tensile properties of reprocessed samples which are nomenclatured as ‘RP’ slightly changed as shown in Figure 3.17.

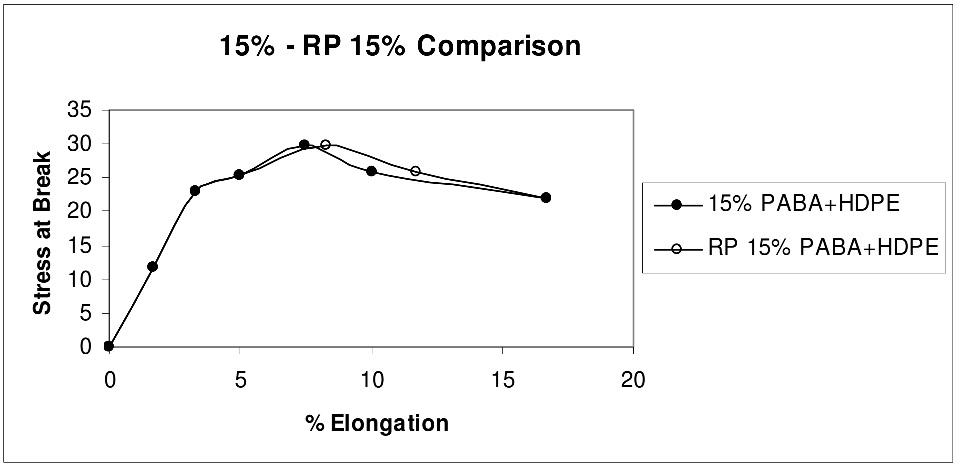


Figure 3.17. The comparison of Tensile Strength of PABA-g-HDPE with 15% ABA in sample and reprocessed PABA-g-HDPE with 15% ABA

3.6. SEM Analysis

The tensile fractured surfaces of composites were studied with scanning electron microscopy and SEM photographs of compression molded grafted HDPE samples are given in Figure 3.18-3.20.

As the content of ABA increases, the morphology of fracture did not significantly alter and they were basically in fibrillar nature. SEM photographs of neat HDPE which is not given also showed that fracture was slightly different with longer fibrils compared to ABA containing samples.

As a result of orientation of macromolecules, no brittle fracture was observed and all samples were broken with yield upon drawing.

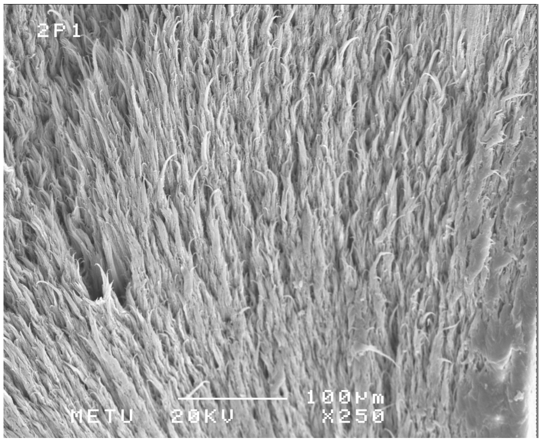


Figure 3.18. SEM Photograph of the fractured surface of 10% ABA containing PABA-g-HDPE sample,

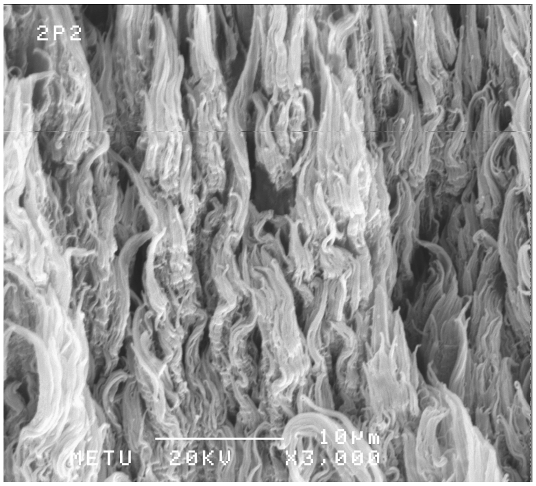


Figure 3.19. SEM Photograph of the fractured surface of 10% ABA containing PABA-g-HDPE sample (at higher magnification of Figure 3.18)

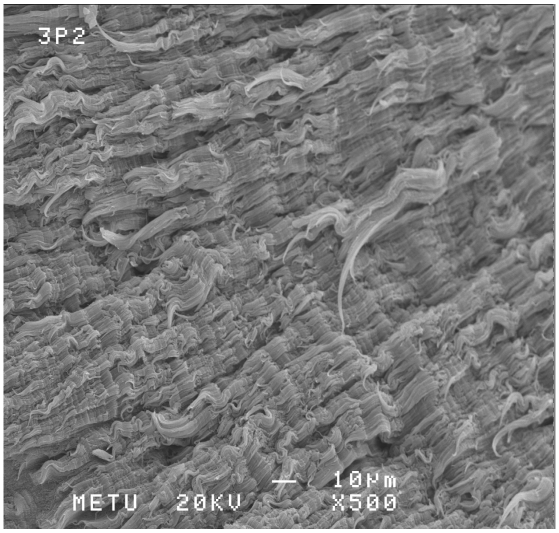


Figure 3.20. SEM Photograph of the fractured surface of 15% ABA containing PABA-g-HDPE sample

CHAPTER 4

CONCLUSIONS

Graft copolymerization with simultaneous polymerization of monomer (ABA) onto HDPE, at constant concentration of the monomer (5-10-15%) in the reaction mixture was carried out at a pre-set mixing temperature. The extent of grafting was studied by using extraction methods and maximum extent of grafting value was achieved for initial 15% ABA containing mixture. The result of this study showed that the grafting extent increased with increasing content of monomer.

FTIR analysis of the products confirmed the graft copolymerization of ABA onto HDPE. The characteristic absorption bands of PABA were observed in FTIR spectra of the coproducts whereas the characteristic absorption bands of ABA, especially vinyl absorption peak, disappeared.

In DSC tests of grafted HDPE samples, the crystalline melting of PABA was observed at 292 ^{0}C in thermograms of PABA-g-HDPE samples. Also, it is observed that the addition of ABA for all compositions does not cause any alteration in the crystallinity of the main polymer matrix.

The flow properties of matrix polymer were strongly affected by the presence of PABA. Increasing the content of ABA caused a decrease for MFI values of grafted HDPE samples, possibly due to slight extent of crosslinking.

All the graft coproducts showed fibrillar structure upon drawing of grafted HDPE samples and increasing content of ABA did not significantly alter the morphology of fracture

The improvement in the mechanical properties was obtained particularly in stress at yield and modulus, whereas the strain at break values showed a decrease for all compositions of coproducts compared to neat HDPE. The tensile properties of reprocessed samples was shown to be slightly changed for all compositions of PABA-g-HDPE samples.

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