GRAFT COPOLYMERIZATION OF p-ACRYLOYLOXYBENZOIC ACID ONTO POLYPROPYLENE

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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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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Acryloyloxybenzoic acid (ABA) was prepared by the condensation reaction of acryloyl chloride with p-hydroxybenzoic acid in alkaline medium. The polymerization and grafting of ABA onto Polypropylene were anticipated to occur simultaneously in melt mixing at high temperature. The monomer showed liquid crystalline property. For a better dispersion of ABA in PP before graft copolymerization, a masterbatch of 50-50 (by weight) low density polyethylene + ABA was prepared, which was then used for 5, 10, 15 % ABA + PP mixtures in the Brabender Plasti Corder. Furthermore, these compositions were reprocessed at the same temperature in the molten state.

Compression molding was used to prepare films for characterization experiments at 200 ºC under 15000 psi for approximately 3-5 minutes. The graft copolymers were characterized by several techniques; DSC, FTIR, MFI, SEM and mechanical testing.

In DSC thermograms the crystallization of PP was seen at approximately 160ºC. An endothermic peak was also assigned to grafted PABA at 280ºC .

The incorporation of ABA onto the PP backbone as a graft copolymer (PABA-g-PP) at low percentages results in a possible rearrangement, where tensile strength values increased, while strain decreased. The grafting goes through thermal radicalic mechanism.

MFI values were found to increase from 8.7 to 16.35 g/10 min at 10 wt % ABA, then decreased to 10.57 g/10 min at 15 wt % ABA. It is most likely that the presence of PABA produced easy orientational flow up to 10 % of ABA, but at 15 % ABA addition caused a slight decrease in MFI.

The tensile test specimens were analyzed by Scanning Electron Microscope. None of the three samples exhibited phase separation. This observation confirms that the graft copolymerization occurs in a homogenous manner onto PP. The brittle nature of material is observed at all three compositions.

Keywords: Polypropylene, acryloyloxybenzoic acid, poly(acryloyloxybenzoic acid), liquid crystalline polymers, graft copolymerization

ÖZ

p-AKRİLOİLOKSİBENZOİK ASİTİN POLİPROPİLEN ÜZERİNE AŞI KOPOLİMERLEŞMESİ

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Akriloiloksibenzoik asit (ABA) monomeri bazik ortamda akrilol klorürün p-hidroksibenzoik asit ile kondensasyon tepkimesiyle sentezlendi. ABA'nın polimerizasyonunun ve PP üzerine aşı kopolimerizasyonunun, yüksek sıcaklıkta, eriyik halde yapılan karıştırma işleminde, eş zamanlı gerçekleşmesi beklendi. Monomer sıvı kristalik özellik göstermektedir. ABA monomerinin PP içerisinde, aşı kopolimerizasyonu ile bağlanması öncesi dağılımını artırmak için kütlece % 50-50 Alçak yoğunluklu PE ve ABA anakarışımı kullanıldı. Bu ana karışımdan % 5, 10, 15'lik ABA + PP karışımları Brabender Plasti-Corder içerisinde hazırlandı. Ayrıca % 5, 10, 15'lik olarak hazırlanan bu karışımlar aynı sıcaklıkta eriyik halde tekrar işleme tabi tutuldular.

Karakterizasyon testlerinde kullanılan filmler 200ºC ve 15000 psi basınçta basılarak hazırlandı.Aşı kopolimerleri DSC, FTIR, MFI, SEM ve mekanik testler ile karakterize edildi.

DSC thermogramlarında PP’nin kristalizasyonu yaklaşık 160ºC’de görülmektedir. Ayrıca 280 ºC’de PABA’ya ait endotermik pik göze çarpmaktadır.

ABA’nın düşük konsantrasyonlarda PP üzerine aşı kopolimerizasyonu ile bağlanması sonucunda, kopma dayanım özelliklerinde artışa sebep olurken % uzama miktarlarında düşüş gözlenmiştir. Aşı kopolimerizayonu ısı etkisi ile radikalik polimerizasyon mekanizması ile gerçekleşmektedir.

MFI değerleri, kütlece % 10 ABA’da 8.7 ’den 16.35 g/10 dak’ya yükseldi ve daha sonra % 15 için 10.57 g/10dak’ya düştü. Karışımda % 10 oranında PABA bulunması durumunda PABA’nın varlığının yönlenme ile akış kolaylığı sağladığı, fakat % 15’lere çıkıldığında artışın MFI değerlerinde hafif düşüşe neden olduğu gözlemlenmiştir.

Test numuneleri, Elektron mikroskobu ile analiz edildi. % 5, 10 ve 15’lik karışımların hiçbirinde faz ayrımına rastlanmadı. Bu da monomerimizin aşı kopolimerizayonu ile PP ile bağlanmasının homojen bir şekilde gerçekleştiğini doğrulamaktadır. Ayrıca test numunelerinde, mekanik testler sırasında görülen kırılgan yapı, % 5, 10 ve 15’lik karışımlar için SEM analizlerinde de görülmüştür.

Anahtar Kelimeler:Poliropilen, akrilloiloksibenzoik asit, poliakriloiksibenzoik asit,sıvı kristalik polimerler, aşı kopolimerleşmesi

To My Family

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ABREVIATION

ABA	p-Acryloyloxybenzoic Acid
PP	Polypropylene
LCP	Liquid Crystalline Polymers
LC	Liquid Crystal
PABA	Poly(Acryloyloxybenzoic Acid)
DSC	Differantial Scanning Calorimetry
FTIR	Fourier Transform Infrared Spectroscopy
MFI	Melt Flow Index
MAH	Maleic Anhydride
MAP	Maleic Anhydride Grafted Polypropylene
DMSO	Dimethyl sulfoxide
TP	Thermoplastic
SEM	Scanning Electron Microscope
IPP	Isotactic Polypropylene

CHAPTER 1

INTRODUCTION

The modification of polyolefins by functionalizing to obtain engineering materials with superior properties has been an area of interest. Especially, polypropylene (PP) is one of the most commonly used plastics because of its good properties, wide applicability, and low cost. However, it is limited in its application in several technologically important fields due to its low surface energy, lack of reactive sites, difficulty to dye, extremely poor hygroscpicity, low melting and sticking temperatures, low impact strength, sensitivity to photo or thermal oxidation, and poor compatibility with synthetic polar polymers. Effective surface modification techniques must be found to overcome these shortcomings.

Graft copolymerization onto PP with a variety of monomers offers an effective approach to introduce some desirable properties into the polymer without adversely affecting the architecture of the PP backbone.

1.1 Polypropylene, PP

Polypropylene is a crystalline thermoplastic polyolefin resin. It assumes a special position because of its stereoregular structure, being the first member of the growing family of synthetic stereoregular polymers to achieve industrial importance.

Polypropylene chains are made of carbon- carbon or propylene repeating units. The individual chains are entangled in stable form in the solid state. Carbon bond is very strong in nature, however this strength is not realized in the polymer because of the random entanglement of the coils. During crystallization polymers can organize into regular structures reducing the degree of molecular randomization, and thus the strength and modulus of polymers can be improved. When the crystal segments are lengthened this results in a stronger and stiffer fibres. The molecules in the extended chain conformation are locked, and a fully aligned polymer has a very high strength and modulus.

Isotactic polypropylene crystallizes in at least three different crystalline modifications, α (or monoclinic), β (or hexagonal) and γ (triclinic), all containing 3_1 helices with the same value of the chain axis but different modes of the packing of the chains[1-4].The α form is the most important and conventional one. It is produced by industry in large amounts and the most extensively studied primary crystalline phase. It is the most stable form and can be easily obtained by crystallization from the melt or from solution. β form is occasionally found in commercial PP, usually at low levels [4].It can be only partially formed in samples mixed with other crystal forms. The crystals formed rich or pure in β form were reported to be prepared through rapid quenching [4] zone solidification [5,6], crystallization in a temperature gradient [7,8,9] or use of selective nucleating agent [10].γ form can be observed in low molecular weight isotactic polypropylene [11] or in the crystals obtained at higher pressure than 200 MPa [12-15]. On the other hand, one may find coexistence of the α and γ forms in the crystals [16].

1.2 Liquid Crystalline Polymers

Liquid crystalline polymers (LCPs) belong to a class of materials that exhibit an intermediate state between a solid crystal and an isotropic liquid where oriented self-assembly of the molecular structures can be achieved. In the crystal state, there is long range order in position and orientation,while in the liquid state there are no long range ordering in either of them. Figure 1.1 is the comparison of the crystal (a), liquid crystal (b) and the liquid state (c)

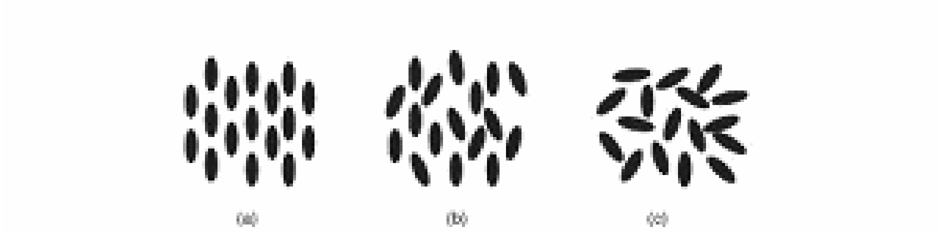


Fig. 1.1 The schematics of (a) crystal, (b) liquid crystal and (c)liquid state

The structure of the LCPs composed of long chain rod-like molecules which are found to be associated in an ordered fashion and form elongated domains [17] Within the domain these stiff molecules are found to be parallel with each other. This organized structure constitute anisotropy both in the fluid and solid states. Along with an external forces applied , the order is increased, and since longer relaxation times are associated within the orientation decay of LCPs, the order is preserved upon coagulation or solidification of the lyotropic or thermotropic LCPs respectively [18,19].

LCPs are divided into two broad categories according to the principal means of achieving fluidity. *Lyotropic liquid crystals* are molecules that show liquid crystalline behavior in solutions. This behavior is concentration dependent. That is why, a given mesogen will not show liquid crystalline behavior in solution at all concentrations.

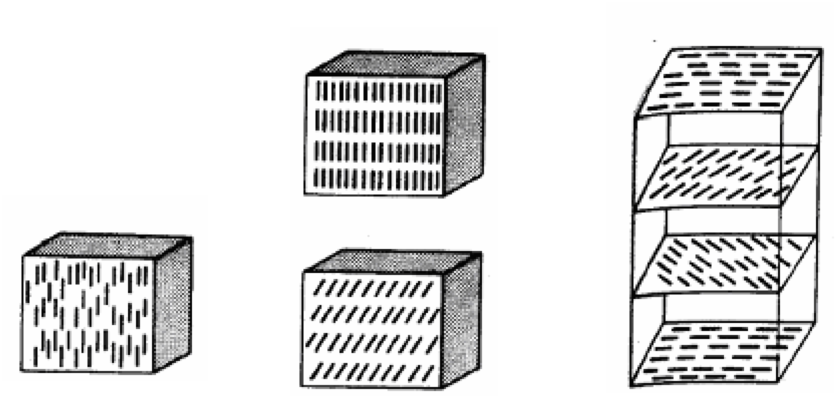
Thermotropic liquid crystals are molecules, that show liquid crystalline behavior above their solid crystalline melting point. They may be single or multicomponent melts. Thermotropic behavior is also temperature dependent; that is the liquid crystalline behavior is only seen over a limited temperature range. [20].

Within each category, three distinctive supramolecular organizational or structural classes of LCs have been identified: the nematic, smectic and twisted nematic (Fig.1.2).

The ***nematic phase*** is mesogens which are oriented in the same direction at least locally where the direction of orientation is termed as "director". However, with respect to each other there is no order. That is, they are randomly distributed, but they are all pointing in the same direction.

In ***smectic phase***, the mesogens are all aligned towards same director, but in addition, the individual rods possess a layered structure, which is due to the ends of the rods arranging themselves into common phases. The two most common types of smectic phases are smectic A and smectic C; the former occurring when the director is perpendicular to the ordering of the layers and the latter when the director is skewed from this layering.

The ***cholesteric phase (twisted nematic)*** is similar to a nematic phase, but the mesogens have been twisted about an axis perpendicular to the director in a periodic manner. This occurs spontaneously due to the chiral nature of the mesogens associated with this phase. For this reason this mesophase is also referred to as chiral cholesteric [21].



(a)Nematic Phase (b) Smectic Phase (c) Cholesteric Phase

Fig. 1.2 Physical Structure of LC Polymers

The rod-like molecular conformation and chain stiffness give LCPs many attractive properties such as low viscosity, shear sensitiveness, low mould shrinkage and long relaxation time [22]. By achieving a high state of orientation and extension in these extended rigid-chain molecules during processing, highly crystalline products with high modulus and high strength are obtained. The moduli and strengths of these chain-extended liquid crystalline polymers are considerably higher than those of the chain-folded semicrystalline commodity polymers. The organized structure of liquid crystalline polymers also gives rise to have significantly increased crystalline melting temperatures with respect to the other polymers at the same conditions.The orientability of a LCP in the fluid state is the basic factor that affects its properties and distribution in the solid state.

1.2.1 Poly(Acryloyloxybenzoic Acid), PABA

The crystallinity and order in atactic PABA was studied by Blumstein et al. [23]. It was reported that the family of p-n-alkoxybenzoic acids displays nematic and/or smectic liquid crystalline organization, beginning with the n-propoxy homologue. On the other hand, ABA gives a sharp transition from crystal to isotropic that we can not draw a conclusion about the mesomorphic behaviour of ABA. PABA was obtained by heating the corresponding monomers at or above the melting point and by solution polymerization in dimethylformamide.

Two crystal forms have been reported for PABA [23]; One of these (form I) with a higher degree of crystallinity which may reach 40% and a higher crystallite perception has a monoclinic structure, and the other (form II), obtained on rapid polymerization of the monomer at or above its melting point, was identified as smectic E_t. Form I can be obtained either on casting of a film of form II from DMF or on slower polymerization in thin layer of the molten monomer. It was reported that bulk polymerization by heating on a hot stage leads to an isotropic p-acryloyloxybenzoic acid (PABA) melt which forms a mobile, nematic Schlieren texture out of which spherulites grow as the polymerization to PABA progresses. The development of spherulitic structures is more pronounced for poly(acryloyloxybenzoic acid) than for the poly(methacryloyloxybenzoic acid).

The development of crystallinity depends strongly on the experimental conditions [23]. The developed crystallinity and the organization of side groups proceeded beyond the formation of a long range lamellar (smectic) order in these atactic polymers were endowed with the hydrogen bonded benzoic acid moieties.

The phase transitions of PABA were studied by Menczel and Wunderlich [24] and it was reported that PABA may exhibit, beside the reported smectic E_t form [23], another highly mobile mesophase state which is probably nematic. It is produced by melting of crystal forms I and II, by Blumstein et al. [23], or out of amorphous PABA above the glass transition. Amorphous PABA was prepared by quick thermal polymerization. Sometimes partially crystalline polymers were obtained even by this method. It has been assumed that the partially crystalline samples arose probably whenever the monomer was not sufficiently dried before polymerization. In this case a small amount of oligomer of poly(p-oxybenzoate) is formed, which is liquid crystalline or crystalline depending on its molecular weight. As the acryl-polymerization proceeds, poly(p-oxybenzoate) crystals may act as seeds for crystallization of PABA. On the other hand amorphous PABA showed a strong heating rate dependent heat capacity incresase [24].The glass transition is followed at higher temperature by an exotherm. Optical microscopy showed that the sample in this temperature region is becoming birefringent, but no endotherm was observed in the melting of PABA. It was then concluded that the observed exotherm corresponded to the amophous to mesophase transition, and a strong heating rate dependence of the glass transition, however, that amorphous PABA has a normal hysterisis behaviour [24].

Blumstein et al. [23], reported the melting point of PABA as 252°C. Menczel and Wunderlich [24] used optical microscopy and DSC measurements combined with thermogravimetric analysis in order to investigate the melting point. Optical microscopy showed that the polymer melts approximately at 252°C. This is not, however, a crystal to isotropic transition; but a mobile, liquid crystal phase which is observed beyond melting. From the texture under the microscope it was classified as a *nematic* phase. Certain amount of decomposition also occurs during the melting [23].

Thermogravimetry showed 19% and 7% weight loss at the temperature at about the end of the melting endotherm for modifications I and II, respectively. Furthermore, the polymerization of p-acryloyloxybenzoic acid was investigated to resolve the questions such as the nucleation of the mesophase and transformation of the mesophase into solid by parallel use of optical microscopy and quantitative thermal analysis by Menczel et al. [25].The search led to, however, the discovery of a much more complicated reaction instead of simple vinyl polymerization. It was assumed that the observed mesophase is not connected with p-acryloyloxybenzoic acid or poly(acryloyloxybenzoic acid). The polymer is not involved in mesophase formation, but seems to cause solidification of the spherulites, *schlieren* texture, and isomorphous material.

After melting of ABA, which leads to an isotropic phase, acidolysis produces acrylic acid and oligomers of poly(p-oxybenzoate), POB, and the oligomers of POB are the root of the mesophase formation. Polymerization of ABA without oligoester formation gives no intermediate mesophase.

1.3 Reinforcement of PP with LCP’s

Blends of PP with several LCPs have been studied by several workers [26,27] These blends show some improvements in modulus, the similar or even lower tensile strength has been obtained in the absence of appropriate compatibilizers due to nonpolar nature of PP and more polar LCPs.

For this reason, in recent years the studies have been directed towards the preparation and characterization of PP/LCP blends containing different compatibilizers. The effect of maleic anhydride grafted PP (MAP) on the mechanical properties and morphology of the PP/LCP blends were reported in several articles [28,29,30]. It was found that the addition of MAP to the PP phase leads to significant increase in the mechanical properties of PP/LCP blends. The reinforcing LCP fibrils were found to be much more finely dispersed in the matrix, and the reduced interfacial tension and increased adhesion indicated that MAP compatibilized the PP/LCP blends. The interactions such as hydrogen bonding was believed to be responsible for the compatibilizing effect of MAP, instead of reaction with LCP.

Maleic anhydride (MAH) is a highly reactive monomer used frequently for radically initiated functionalization of PP. MAH molecules grafted onto PP not only increase the polarity, but also react with groups, such as $–NH_2$, -OH, and –COOH, of other polymers thus forming chemical links between components [31].On the other hand, a compatibilizer creates a droplet morphology resulting in lower tensile properties. In the reinforcement of TP with LCP the compatibilizer must not cause the loss of fibrous morphology, and it must improve the adhesion between phases.

Miller and coworkers [32-34] have used an acrylic acid-fuctionalized PP (PPAA) and a PPAA-based graft copolymer for the compatibilization of PP/LCP blends and the improvements in interfacial adhesion and thus in fibre properties, thermal stability and crystallinity of the blend products have been obtained. The improvements have been attributed to the promotion of specific interactions between the blend components.

Miettinen et al. [35] have used a reactive terpolymer containing an epoxy end-group as a compatibilizer for PP/LCP blends. It was proposed that the carboxyl end groups of the polyesters react with the epoxy group of the compatibilizer. The addition of a compatibilizer leads to a smaller size of the dispersed domains, thereby causing them to adhere better in the matrix. In another study, Chiou et al. [36] used a reactive compatibilizer based on the ethylene- glycidyl methacrylate copolymer (EGMA) for the PP/LCP blends.

The compatibilized PP/LCP blends showed finer dispersed LCP domains but lower PP crystallinity. It was suggested that the epoxy functional groups of the EGMA copolymer can react with the carboxylic acid and/or the hydroxyl end groups of the liquid crystalline copolyester.

1.3.1 Blends and Combining Thermoplastics with LCP’s

Thermotropic main-chain liquid crystalline polymers are melt blended with thermoplastics in order to achieve a so called *in situ* composite structure within oriented LCP fibrils in the thermoplastic matrix. Generally adding LCP increases the mechanical strength and the stiffness of the thermoplastic matrix polymer. Moreover, even relatively a small amounts of LCP may cause a reduction in the melt viscosity, and thus improve the processability. [37-38]. LCPs thus offer an interesting means to enhance the properties of thermoplastis.

LCPs and thermoplastics are generally immiscible and form a two-phase structure. Often a so called skin/core morphology is found with thin fibrillar LCP phases in the skin region and spherical or elipsoidal LCP domains in the core. The size and the shape of the LCP domains depend on LCP content, viscosity ratio of the two polymers, and processing conditions (e.g., temperature and shear forces). Orientation of the LCP phases during the processing and the formation of fine fibrils can be significantly increased by elongational drawing, which leads to improved physical properties in the fiber direction [38] .

Compatibilization is a process by which an incompatible blend is conditioned less incompatible, so that the resulting material is useful for engineering purposes. This kind of compatibility does not imply thermodynamical compatibility, in which the polymers exist in a single molecularly blended homogenus phase [39].

Compatibilization can be either physical or chemical in nature involving partial miscibility, entanglements of polymer chains, physical interactions, or chemical reactions. The usual effects are a reduction in the interfacial energy, a stabilized morphology with perhaps fiber dispersion, and an increase in the interfacial adhesion [39].

The compatibility of a binary blend depends upon the interaction between the two types of polymers. Careful selection of the components is of the great importance. In particular, the ratio of the melt viscosities and the chemical nature of the components affect the blend compatibility. The dispersed LCP phase should have slightly lower viscosity than the matrix polymer at the processing conditions in order to obtain good dispersion and the desired fibrous morphology. Chemical similarity may lead to partial miscibility, and the presence of functional groups to a reaction, and both of these may increase compatibility. One route to a compatibilized blend is thus to functionalize either or both of the blend components.

A different type of compatibilization involves the addition of a compatibilization agent, or compatibilizer, to act as a bridge between the binary blend components at their interfaces. The action of such compatibilizer as block and graft copolymers is based on the reactivity or miscibility of their segments with at least one of the blend components. They are in fact interfacial agents, since they tend to enrich and act at the interfaces as emulsifiers enhancing the interaction between the blend components through covalent or ionic bonding. Besides block and graft copolymers, a variety of lower molecular weight reactive chemicals promote copolymer formation or cross-linking reactions and thereby improve compatibility.

The main requirements for a compatible blend of an LCP and a thermoplastic is the formation of fine oriented LCP fibres firmly attached in the thermoplastic matrix. Thus, improving the compatibility in most cases means increasing the interfacial adhesion, which may further increase the impact strength.

1.4 Modification Techniques for Polyolefins

The surface chemistry and physics of polymers can be altered by several surface modifying techniques such as surface coating, degradation, hydrolysis, and radiation induced, photochemistry-induced, or catalytic-initiated graft copolymerization. [40].

1.4.1 Graft Copolymerization

The graft copolymerization may introduce some desirable properties into the polymer without a change in the architecture of the polymer backbone and thus gives rise to commercial importance for polymer applications.The modified properties of polymers by grafting results in increased intermolecular interactions and possible crosslinking of the macromolecules. By these interactions, grafting improves adhesion, tensile strength, abrasion resistance and enhances thermal and photochemical stability, and it improves compatibility for required engineered polyolefin composites [40].

There are several methods for preparing graft copolymers, and the common feature of the methods is that an active site is created in a pre-existing macromolecule. This active site may be a radical or a chemical group, which is involved in the polymerization process. A graft copolymer is then obtained by reaction of this activated polymer with monomer or other macromolecule.

Three graft-copolymerization methods are conventionally used for grafting of various monomer on polyolefins: the radiation method, solution recation method, and melt-mixing method.

Among those, the melt-mixing method is considered the most simple, economical, efficient and appropriate for industrial purposes.

Radiation induced graft copolymerization can be achieved by ionizing radiation or ultra-violet light. Radiation can initiate the reaction by the production of radicals, which then start a conventional polymerization sequence comparable with what obtained with a chemical catalyst acting as initiator. Among the methods radiation grafting is one of the most promising methods because of several advantages; A variety of the radiation doses produces different initiation rates, hence diffent products. The effect of temperature, which is relatively unimportant for radiation initiation, can be beter assessed, controlled and utilized on propagation rate. The lack of any chemical initiator results in the product not contaminated by any side products brought about by the initiators. High penetration of energetic radiation into the polymer matrix, rapid and also uniformly distributed active sites for initiating grafting thoughout the matrix are some of the major advantages in radiation.

There are three posibilities for graft copolymerization mechanism of monomer. In possibility 1 (Fig.1.3), PP initiated by the effect of shear force and temperature without initiator. Then maleic anhydride attract to this active side.

The bond of Maleic anhydride (MAH) open, then proton (H^+) of carboxylic group attract to O^-. And a new bond form between the C and the remaining part of monomer. Thus one of the branches, consist of carboxylic and the other one anhydride group.

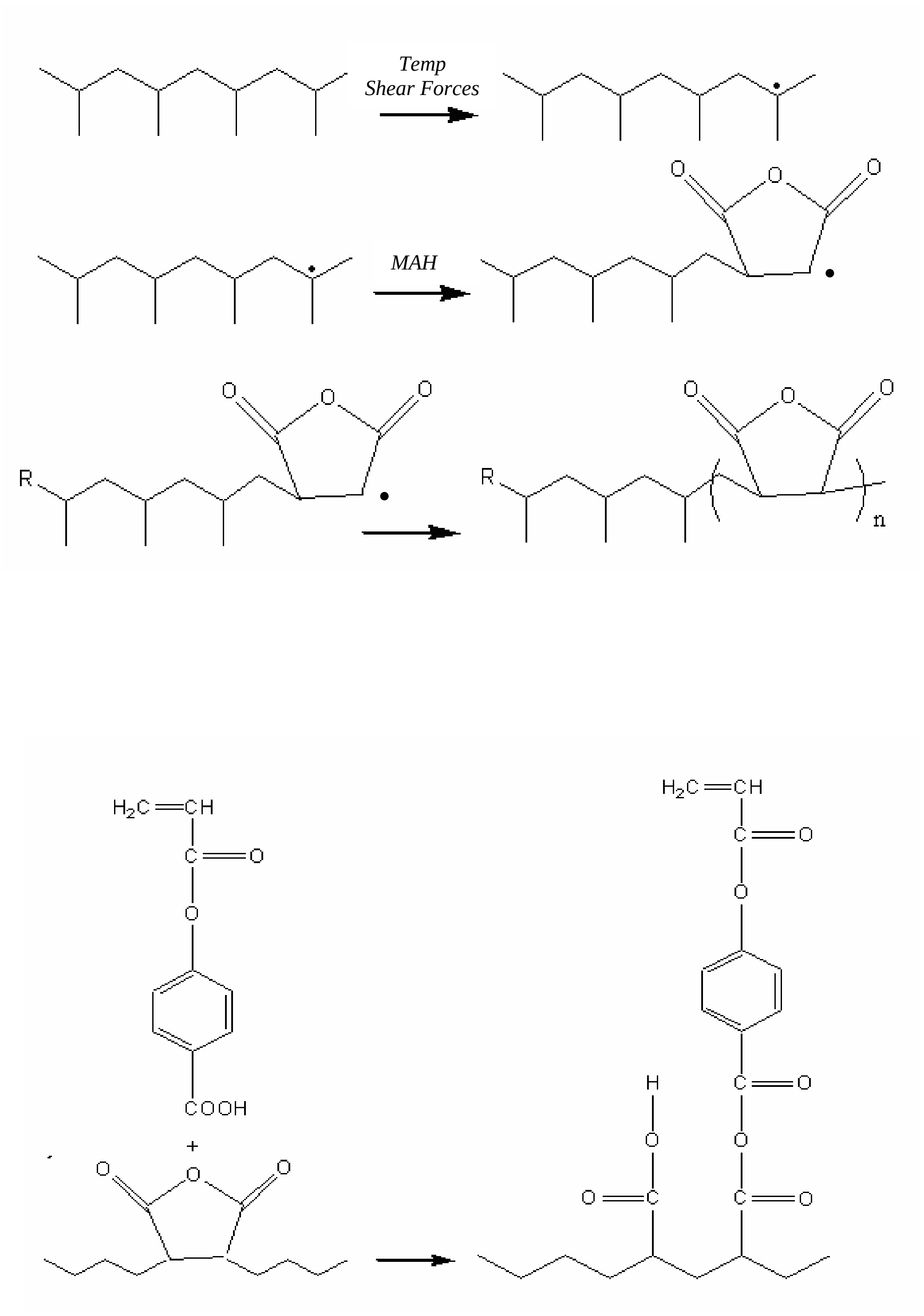


Fig. 1.3 Possible Grafting Reaction 1

MAH is a highly reactive monomer used frequently for initiation of PP. The MAH molecules grafted onto PP not only increase the polarity , but also react with groups, such as $-NH_2$, -OH, and –COOH, of other polymers thus forming chemical links between components. In the second possibility (Fig. 1.4), the grafting reactions between MAH- functionalized PP and monomer ABA starts with double bond breakage. Both the branches consist of ABA and polymerization goes through the activated –CH groups.

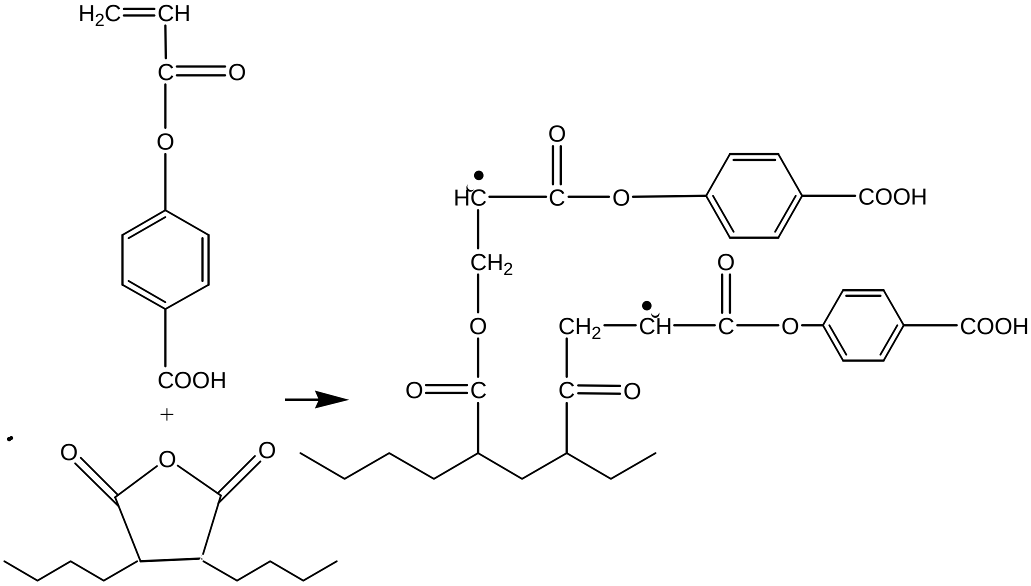
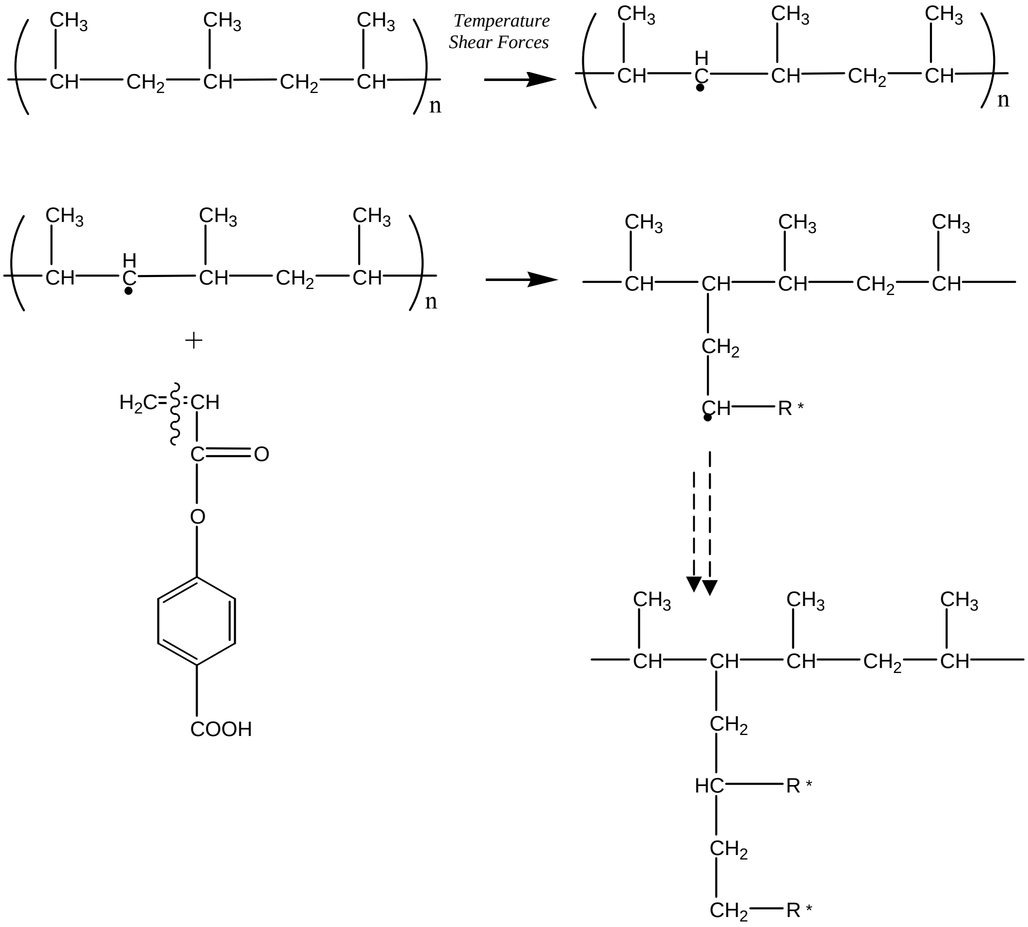


Fig. 1.4 Possible Grafting Reaction 2

In the third possibility (Fig.1.5) the effect of MAH is neglected, and initiated PP directly react with monomer without initiator.



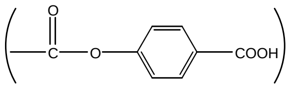
Note R* represents 

Fig. 1.5 Possible Grafting Reaction 3

1.5. Aim of the Study

The objective of the this study is to investigate the polymerization of p-acryloyloxybenzoic acid and to carry out graft copolymerization of this monomer onto polypropylene in melt. It was planned to get an improvement in processability and dispersion of the reinforcing liquid crystalline polymer phase in the graft copolymers.

CHAPTER 2

EXPERIMENTAL

2.1. Chemicals and Materials Used

2.1.1. Solvents and Reagents

Acryloyl chloride (Aldrich A.G.), p-hydroxybenzoic acid (Aldrich A.G.) were the main chemicals for the preparation of p-acryloyloxybenzoic acid monomer.

Acetone (Merck A.G.) was used without any purification. The granular PP (Petoplen MH-418, melt flow index(g/10 min) =5.0, density (g/cm3) =0.905) was supplied by the Turkish Petrochemical Industry (PETKIM, Izmir, Turkey).

Maleic Anhydride used in this study was supplied by Poliya A.Ş (Mw:98.06 g/mol)

2.2. Synthesis of the Monomers

2.2.1. Synthesis of p-Acryloyloxybenzoic Acid

p-Acryloyloxybenzoic (ABA) was prepared by the reaction of p-hydroxybenzoic acid with acryloyl chloride in alkaline medium [41].

13.8 g (0.1 mol) p-hydroxybenzoic acid was added to a solution of 11g (0.2 mol) KOH in 100 mL of distilled water in a flask equipped with a magnetic stirrer. The solution was cooled to 0-5ºC and then 9.1 g (0.1 mol) of acryloyl chloride was added dropwise with stirring for 1 h and stirring was continued at room temperature for 30 min. After acidification with cooled dilute HCl, the precipiate of ; ABA (mp 170ºC) as colourless needles was collected by filtration and purified by repeated recrystallization from acetone. Purity of monomer was also checked by NMR

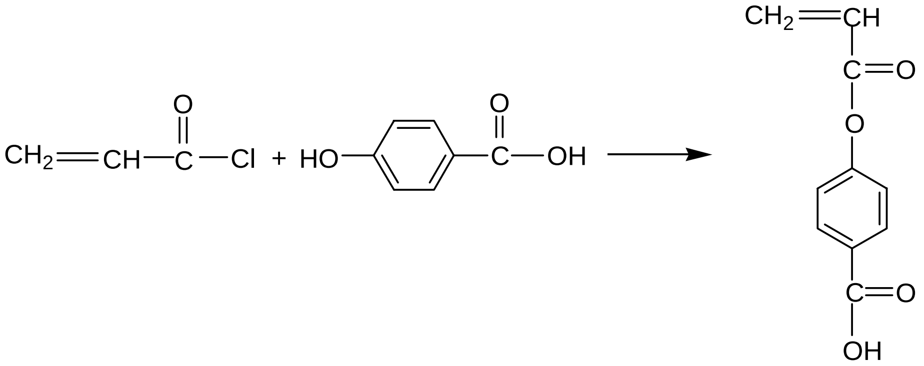


Figure 2.1. The simplified reaction between p-hydroxybenzoic acid and acryloyl chloride.

2.2.2. Masterbatch Preparation

Polyethylene, Petkim I-20, was mixed with ABA at 170ºC in the Brabender for 2-3 minutes. ABA was distrubuted as small flakes in PE matrix. The masterbatch composition was 50-50 % by weight. Then, this masterbatch was compression molded in the hot press at 170ºC and cut into granules for further work.

2.2.3 Polymerization in Molten State

Polymerization of ABA was carried out in the presence of molten PP at the Brabender Plasti-Corder. Three different composition was prepared by mixing PP with masterbatch to obtain 5, 10 and 15% ABA in IPP matrix. The amounts of ABA-PE masterbatch and PP are given in Table 2.1.

Table 2.1 Melt Compositions

Composition	**IPP (g)**	**Masterbatch (g)**	**Maleic Anhydride (g)**	**End ABA Content (%)**
Pure PP	46	-	-	0
5 % ABA + IPP	41.4	4.6	0.46	5
10 %ABA + IPP	36.8	9.2	0.46	10
15% ABA + IPP	32.2	13.8	0.46	15

After heating to the required temperature (200ºC), the rotor was started and defined amount of polypropylene was added to the preheated chamber. The sample was processed until a steady state torque was obtained in order to make fully melted polypropylene. After that 0.46 g (1% of total batch size) maleic anhydride used as a compatibilizer. It was added into to the chamber and mixed for 5 minutes so that homogenous melt obtained.

After decreasing the temperature to 180-200ºC of the molten PP in the brabender mixing head, the above mentioned amounts of masterbatches were added to obtain 5,10 and 15 % PABA, and mixed for 5 minutes.

A hot press was used to prepare films and sheets for testing experiments. Films were produced by placing mixture between a sandwich consisting of two metal shims, two polyester films known as photocopying acetate, and a picture frame type of mold. The time, temperature, and pressure of molding varied depending on the experiment (usually 3-5 min. at 200-250ºC, under 15000 psi). Films were removed from the press and quenched into tap water.

2.2.4 Reprocess of PABA-g-PP films

PABA-g-PP thin films which have 5, 10, 15 % wt PABA were reprocessed in the Brabender under the same conditions above mentioned. Reprocessing was carried to look for any property changes in terms of mechanical properties upon grafting.

2.3.Characterizations and Instruments

2.3.1 Differential Scanning Calorimetry (DSC)

Dupont Thermal Analyst 2000 Differential Scanning Calorimeter 910 S was used to characterize the thermal properties of the samples. A typical experiment used a nitrogen purge, a heating rate of 20 ^{0}C/min, and a sample size of 10-15 mg of the previously prepared compression molded films.

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR measurements were conducted on a Nicole DX 510 spectrometer to characterize polypropylene, ABA, and PABA-g PP .FTIR spectra of monomer was obatained from KBr pellets and spectra of polypropylene , and PABA-g-PP were directly using thin films of that two samples.

2.3.3 Mechanical Testing

Tensile tests were performed according to ASTM D638M (Standart Test Method for Tensile Properties of Plastics) by Instron Tensile Testing Machine (Model TM 1102) at room temperature. The shape and the dimensions of the specimens are given in Figure 2.2 and Table 2.2. The crosshead speed of the machine was set at 50 mm/min.

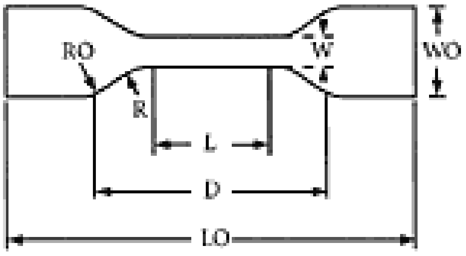


Figure 2.2 Tensile Test Specimen

Table 2.2 Tensile test specimen dimensions

D – Distance between grips	3 cm
T – Thickness	1.3 mm
W –Width of narrow section	7 mm

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

$$E = \sigma/\varepsilon$$

The impact strength of the test samples were determined by Coesfeld Material Test Pendulum Impact Tester at room temperature. The samples were prepared as they were prepared for tensile tests.

2.3.4 Melt Flow Index

Melt flow index test was performed by using a Coesfeld Material Test Meltfixer LT at 230ºC. Samples were cut into small flakes and these flakes were fed into the cylinder of the instrument. 5 kg load was applied and extruded samples were cut at 30 s and 60s intervals. Weight of the cut samples were reported as g/10 min.

2.3.5 Gravimetric Analysis

After copolymerization, the grafted films were put into a flask filled with approximately 200 ml dimethyl sulfoxide, DMSO. The flask was then heated up to boiling temperature of DMSO and kept the temperature constant for 3 hours.

The polyacryloyloxybenzoic acid homopolymer was removed by DMSO washing.

At the end of 3 hours, the flask was cooled to room temperature. Then, the samples were washed with methanol to remove DMSO. The process was repeated several times because DMSO was very difficult to remove. The graft copolymerized PP was dried in the oven at 90 ºC for twelve hours. The amount of grafting was determined gravimetrically and expressed as a percentage of grafted polymer by weight in products.

2.3.6 Scanning Electron Microscopy (SEM)

SEM micrographs were obtained using JEOL, JSM-6400 with an accelerating voltage of 20 kV. Samples were coated with a layer of gold. Micrographs of fracture surfaces were obtained from the Instron tested specimens at room temperature.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Morphological Analysis

3.1.1. FTIR Characterization of Polypropylene, PP

FTIR spectrum of PP is given in Figure 3.1. The absorption bands of stretching vibrations of CH_3 group were at 2961 and 2875 cm^{-1}, and CH_2 group at 2921 and 2838 cm^{-1}. The absorption bands due to bending vibrations of CH_3 and CH_2 groups were observed at 1378 and 1460 cm^{-1}, respectively. The bending vibrations of C-C and C-H groups were observed between 1166 and 841 cm^{-1}.

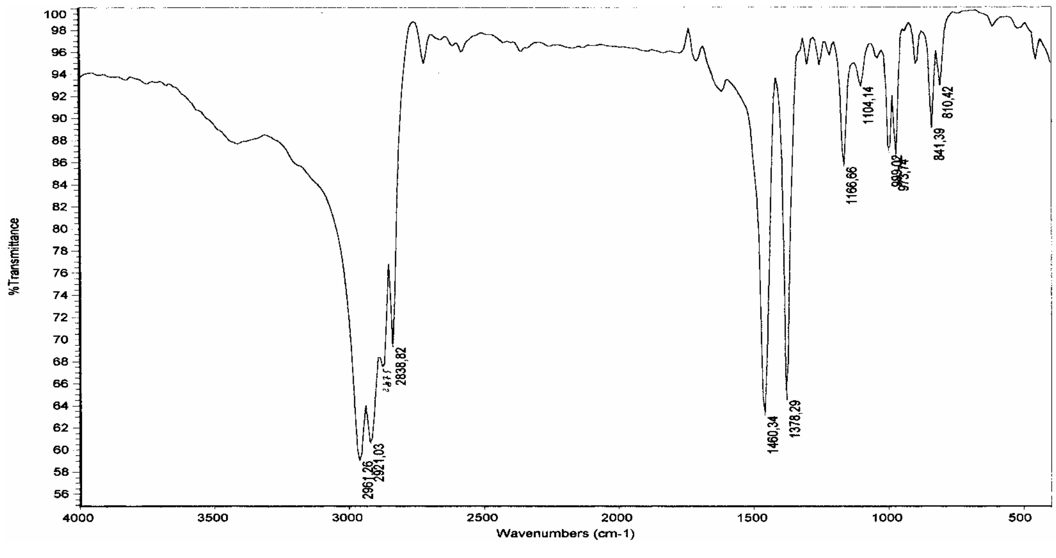


Figure 3.1. FTIR spectrum of PP

3.1.2. FTIR Characterization of Acryloyloxybenzoic Acid

In Figure 3.2 ,the FTIR spectrum of ABA, at 3200-2500 cm^{-1} broad bands can be seen due to the carboxylic acid O-H and C-H stretching vibrations. The strong bands at 1742 cm^{-1} and 1688 cm^{-1} are characteristic of C=O stretching vibrations of ester groups and aryl carboxylic acids respectively. The bands at 1600 and 1500 cm^{-1} are assigned to C=C stretching vibrations of aromatic compounds. The four bands at 800, 909, 939 and 987 cm^{-1} are due to vinylic C-H out-of-plane bending vibrations.

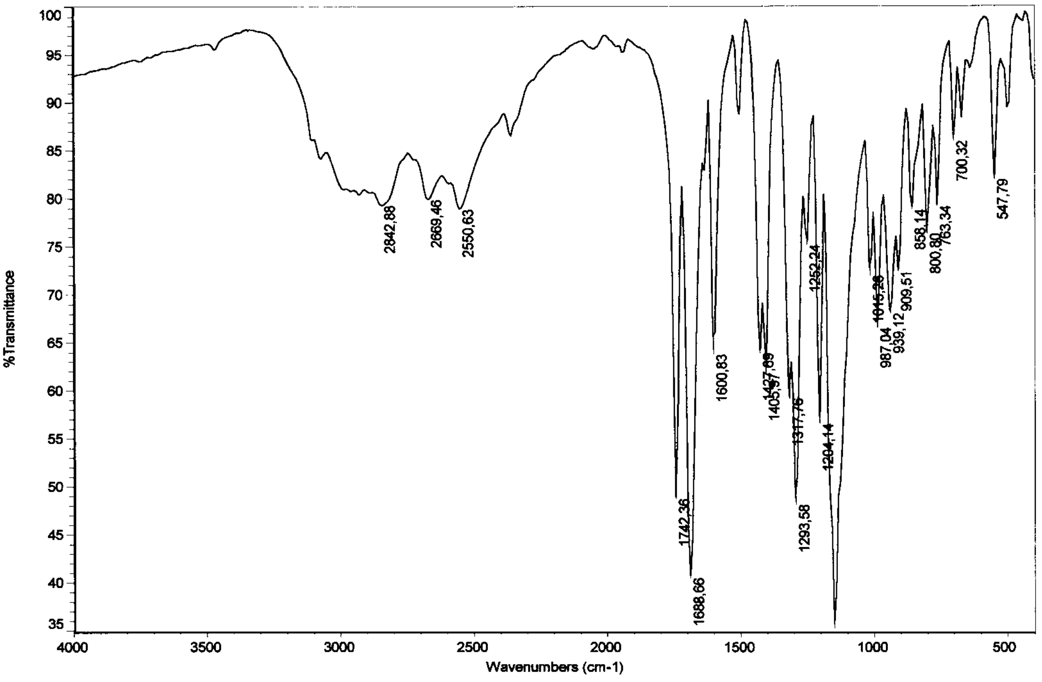


Figure 3.2. FTIR spectrum of Acryloyloxybenzoic acid

3.1.3. FTIR Characterization of PABA-g-PP

The absorbtion bands of PABA due to aromatic, carbonyl and carboxylic groups and the aliphatic groups due to PP and main chain of PABA were observed. No absorption bands between 800-900 cm^{-1} are seen in the spectra; which monomer ABA has in this range.

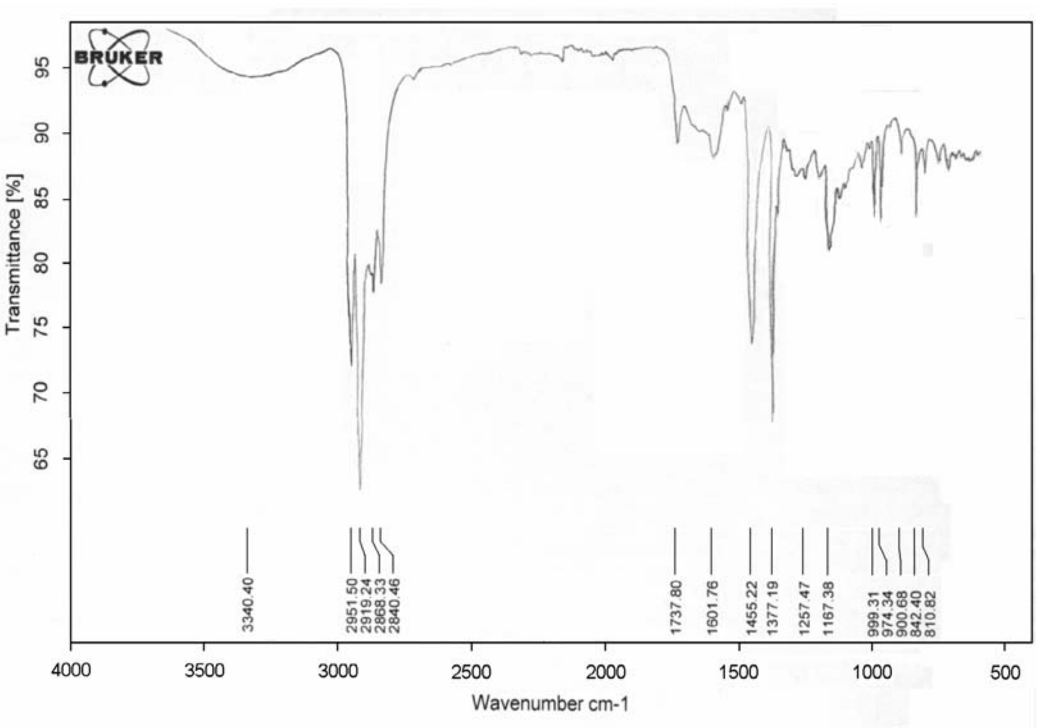


Figure 3.3. FTIR spectrum of 10 % PABA-g-PP

3.2. Thermal Analysis

3.2.1 Thermal Characterization of PP

The thermal characterizations of PP and ABA were given in Figures 3.4 and 3.5. The crystalline melting point of PP and monomer ABA were found to be 161 ºC and 199 ºC, respectively. Both agrees well with the literature [23]

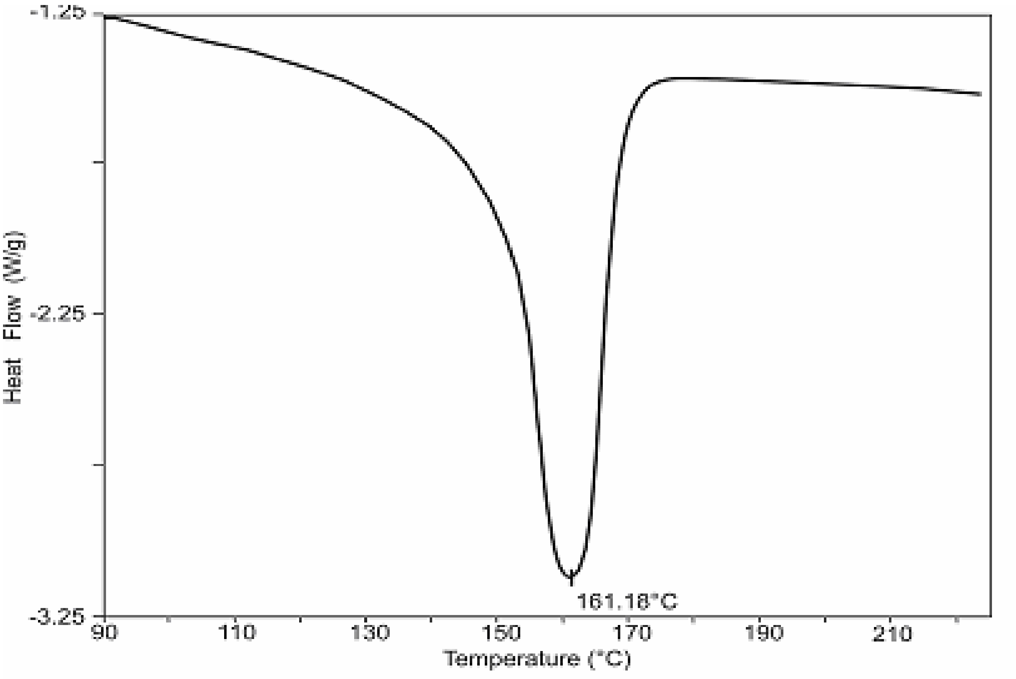


Figure 3.4 DSC thermogram of PP

3.2.2 Thermal Characterization of ABA

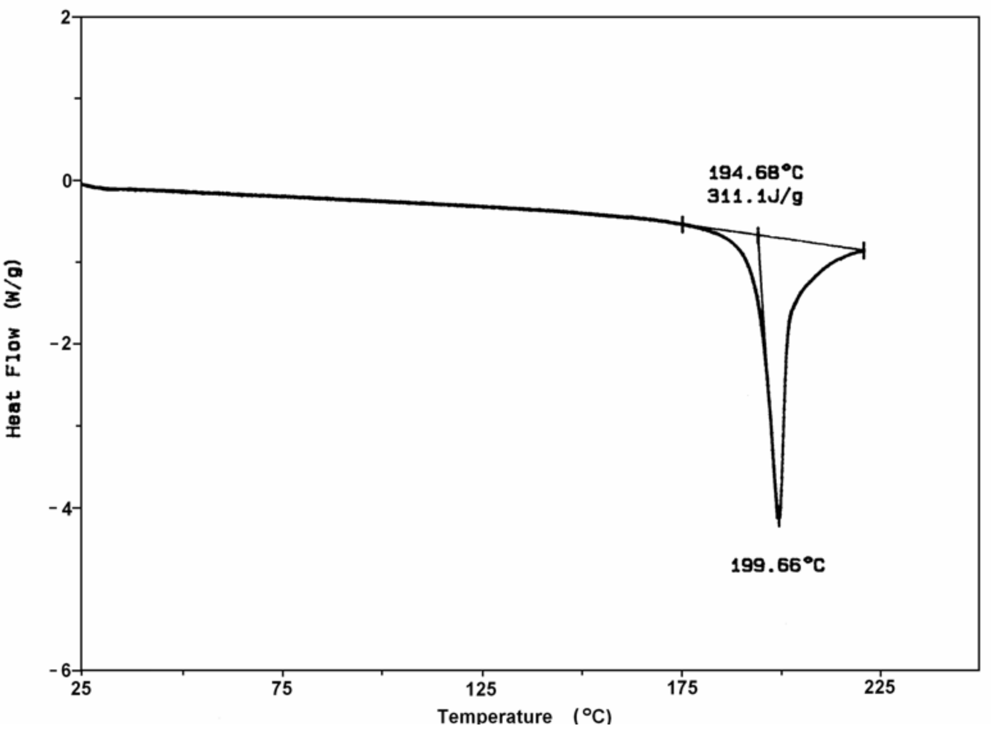


Figure 3.5 DSC thermogram of ABA

3.2.3 Thermal Characterization of PABA-g-PP

The degree of crystallinity of the PP in the graft copolymers was calculated from the DSC thermogram using the heat of fusion 209J/g for 100 % crystalline form of PP [42].The results are given in Table 3.1, also the DSC thermogram, heating and cooling of 15 % PABA-g-PP was given in Figure 3.6

The melting peak of PP was seen at approximately 160ºC, in DSC thermograms, also, an endothermic peak is assigned to grafted PABA at 280ºC. Percent crystallinity decreased with the increase of PABA content in mixture.

The upper curve in Fig.3.6 is the cooling of the same sample and no crystallization peak of PABA was seen.

Table 3.1 DSC Data of the Mixtures

Sample	**Heat of Fusion, J/g** **(Calculated as reference 209 J/g for PP)**	**% Crystallinity**
5 % PABA +PP	90.71	43.4
10 %PABA + PP	71.38	34.2
15 % PABA +PP	67.60	32.3

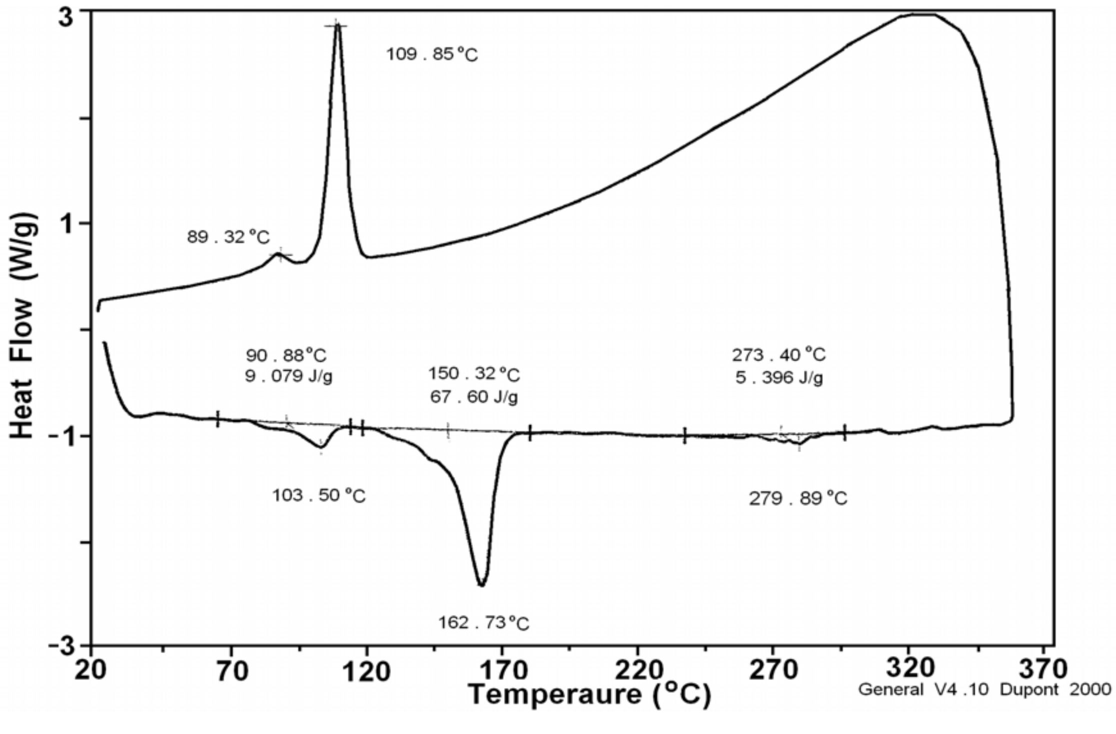


Figure 3.6 DSC thermogram of 15 % PABA-g-PP

3.3 Melt Flow Analysis

The effect of different ABA concentration on PP are examined by using MFI values plotted on Fig.3.7, also Table 3.2.

Table 3.2 Avarage MFI Values

Sample	Avarage MFI (g/10 min) (Process Samples)	Avarage MFI (g/10 min) (Reprocessed Samples)
PP	8.70	-
5 % PABA + PP	9.83	35.07
10 % PABA +PP	16.35	24.15
15 % PABA +PP	10.57	29.2

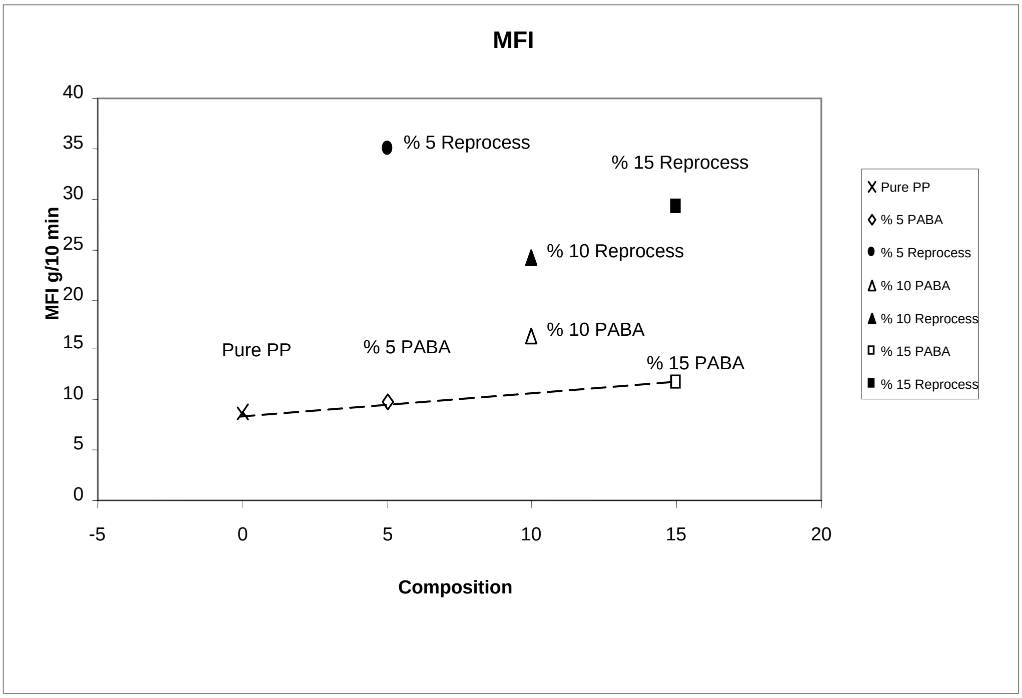


Figure 3.7 MFI Values for 5, 10,15 % PABA +PP

MFI values increased from 8.70 g/10 min to 16.35 g/10 min at 10 wt % ABA, then decreased to 10.57 g/10 min at 15 wt % ABA. It is most likely that the presence of PABA produced easy orientational flow up to 10 % ABA, but at the 15 % ABA addition caused a slight decrease in MFI. Furthermore, it is known that the addition of MAH results in chain scission, therefore the increase in MFI value is also due to this effect.

MFI measurement of reprocessed samples possibly caused extensive degradation in PP, indeed, these samples showed yellowing, therefore we observed high MFI compared to initial values.

3.4 Mechanical Analysis

The polymerization and grafting of ABA onto Polypropylene were anticipated to occur simultaneously in melt mixing at high temperature. For better dipersion of ABA in PP before graft copolymerization, 50-50 % PE-ABA masterbatch was used as mentioned in experimental part. Then, this masterbatch was mixed with molten PP according to given portions in Table 2.1.Maleic Anhydride used in the molten PP, before the addition of ABA was assumed to enhance the graft copolymerization by opening the double bond. Then grafting go through thermal radicalic polymerization as mentioned in Çetin’s thesis [43] Furthermore, these compositions were reprocessed at the same temperature in the molten state.

The ultimate tensile strength variations are given in Table 3.3 for processed and reprocessed samples.

Table 3.3 Ultimate Tensile Strength of Samples

	Ultimate Strength (MPa)
PP	21.00±1.64
PP (Yield stress)	32.00±1.20
% 5 PABA +PP	37.00±2.00
% 5 PABA+PP (reprocess)	35.00±4.03
%10 PABA+PP	33.00±1.25
% 10 PABA+PP (reprocess)	30.50±2.60
%15 PABA +PP	27.00±3.98
%15 PABA+PP (reprocess)	28.00±3.31

Particularly, improvement in ultimate tensile strength and modulus were observed, but with loss of yield stress and loss in percent elongation, therefore the samples were mostly broken in brittle manner.

When we examine Fig. 3.8 the strength of PABA-g-PP samples increased with the increase of PABA up to 5 %. The maximum strength was 37 MPa for normal process of 5 % PABA-g-PP. Both for 5 and 10 % PABA content the ultimate strength values are higher than yield stress of pure PP. Increase of PABA on the mixture caused more rigidity so that early fracture occurred.

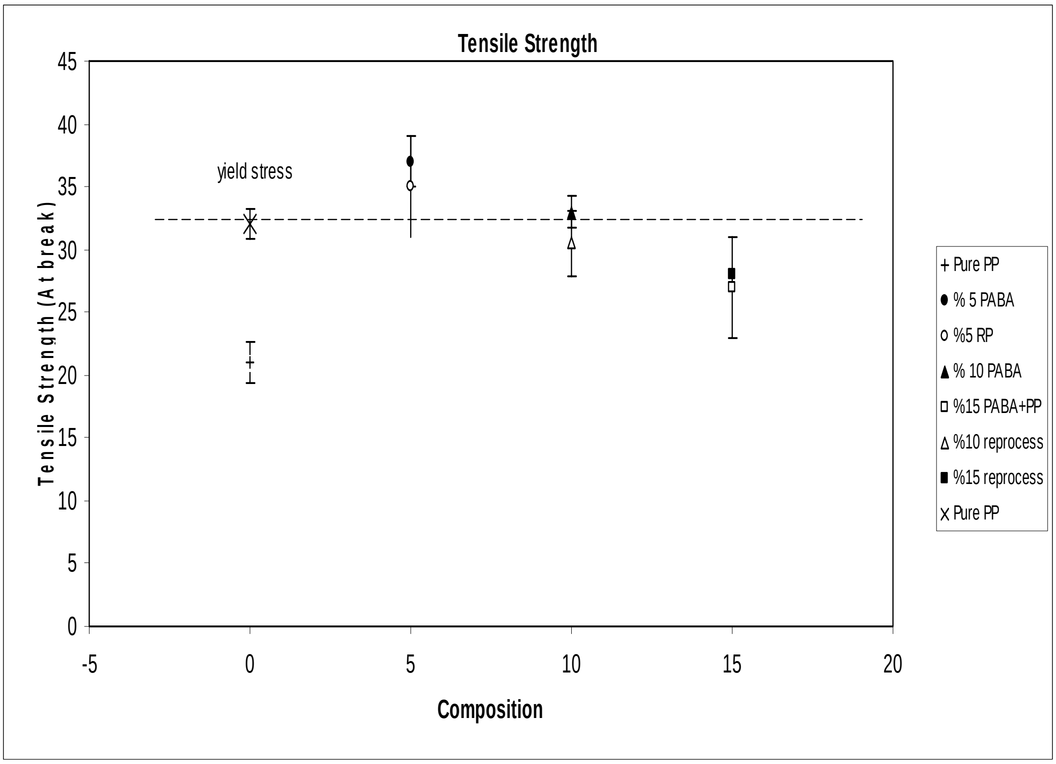


Figure 3.8 The dependence of ultimate strength of PABA-g-PP on content of PABA

Although PP shows a great extent of cold drawing or orientational flow, grafted products showed no elongation and broken in a brittle nature. % elongation was decreased with the increase of PABA content that could be seen in Table 3.4 and Fig. 3.9. Note the scale change in % elongation in Fig.3.9.

Table. 3.4 % Elongation of Samples

	% Elongation
PP	286.70±0.24
% 5 PABA +PP	8.30±0.81
% 5 PABA+PP (reprocess)	8.33±1.13
%10 PABA+PP	6.70±0.66
% 10 PABA+PP (reprocess)	5.80±0.62
%15 PABA +PP	4.80±0.78
%15 PABA+PP (reprocess)	4.17±0.46

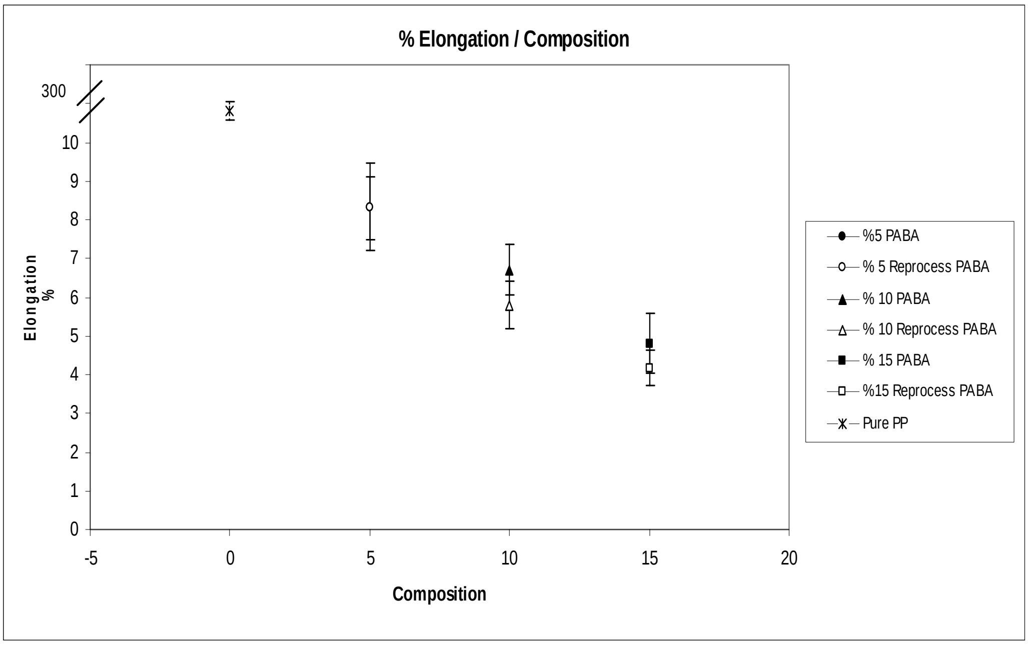


Figure 3.9 The dependence of % elongation of PABA-g-PP on content of PABA

Stress- strain curve of PABA-g-PP is given in Fig. 3.10. No yield stress in any of the grafted polymers observed. As the PABA content increases in grafting rigidity also increases so that early fracture occurred. Also note that there is a scale change in strain values in Fig.3.10.

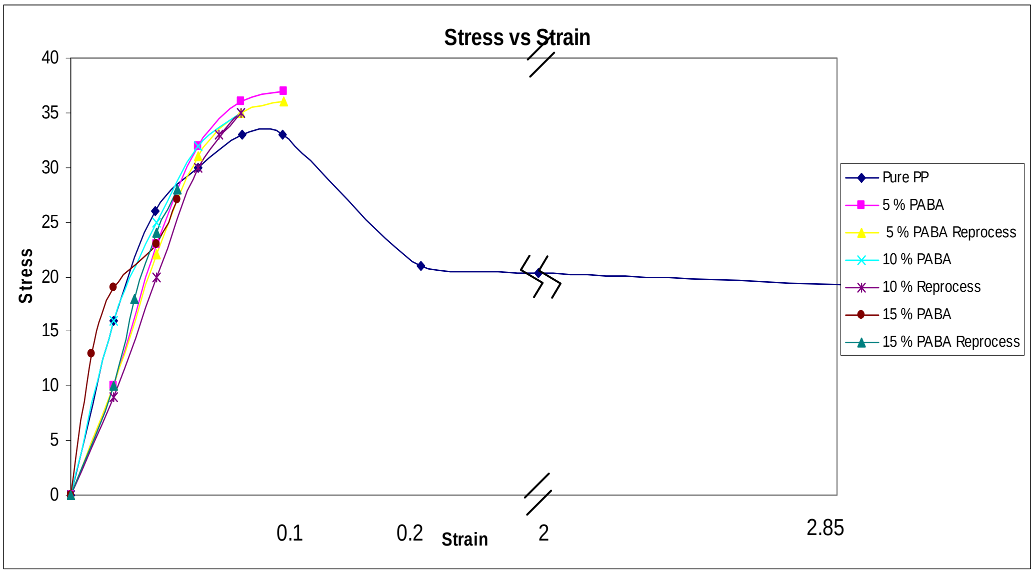


Fig.3.10 Stress- Strain curves of PP, processed and reprocessed PABA-g-PP

Increase in Young's Modulus values was observed with PABA content in the products that can be seen on Fig.3.11. The maximum value; 840 MPa which was reached at 15 % was very high compared with pure PP.

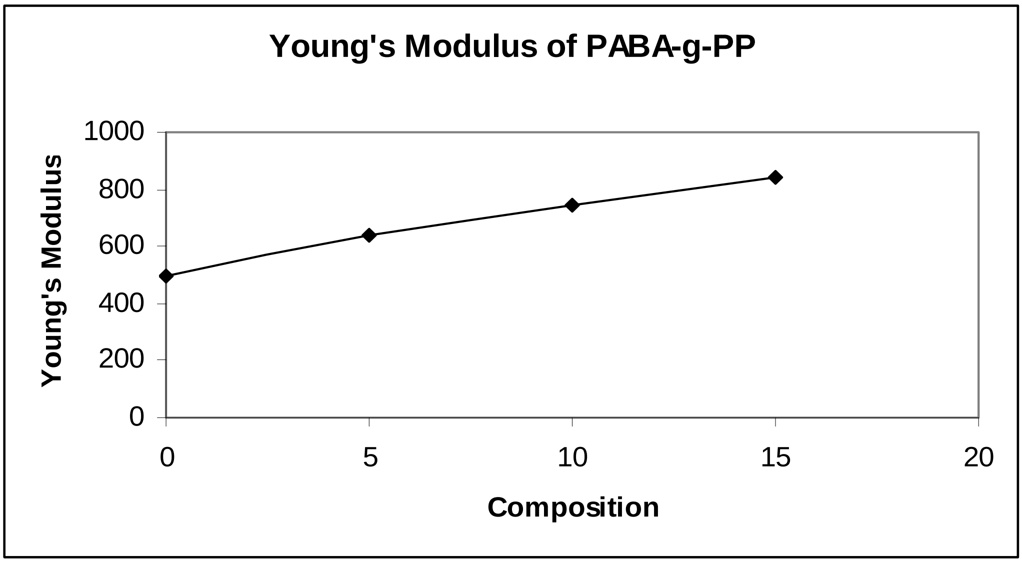


Figure 3.11 The dependence of Young's Modulus of PABA-g-PP on content of PABA

3.5 Gravimetric Analysis for Grafting

For the determination of grafting yield, gravimetric analysis was used. It was seen that by increasing the amount of ABA in mixture, the amount of grafting increased. The extensive extraction showed that enough grafting was achieved.

Table 3.5 The dependence of PABA grafted onto PP on concentration of ABA

% ABA in rxn mixture	**5**	**10**	**15**
% PABA grafted (Normal Process)	3.70	7.87	12.44

3.6 SEM Analysis of the Graft Copolymers

The tensile test specimens were analyzed by Scanning Electron Microscope. For 5, 10, 15 % PABA-g-PP micrographs are given in Fig 3.12,13,14 respectively. None of three samples exhibited phase separation. This was confirmed that the graft copolymerization occurred in a homogenous manner onto PP.

By increasing the amount of PABA in the mixture we already observed a loss of yield stress and loss in percent elongation, which further caused a brittle fracture. This was also confirmed by Scanning micrographs.

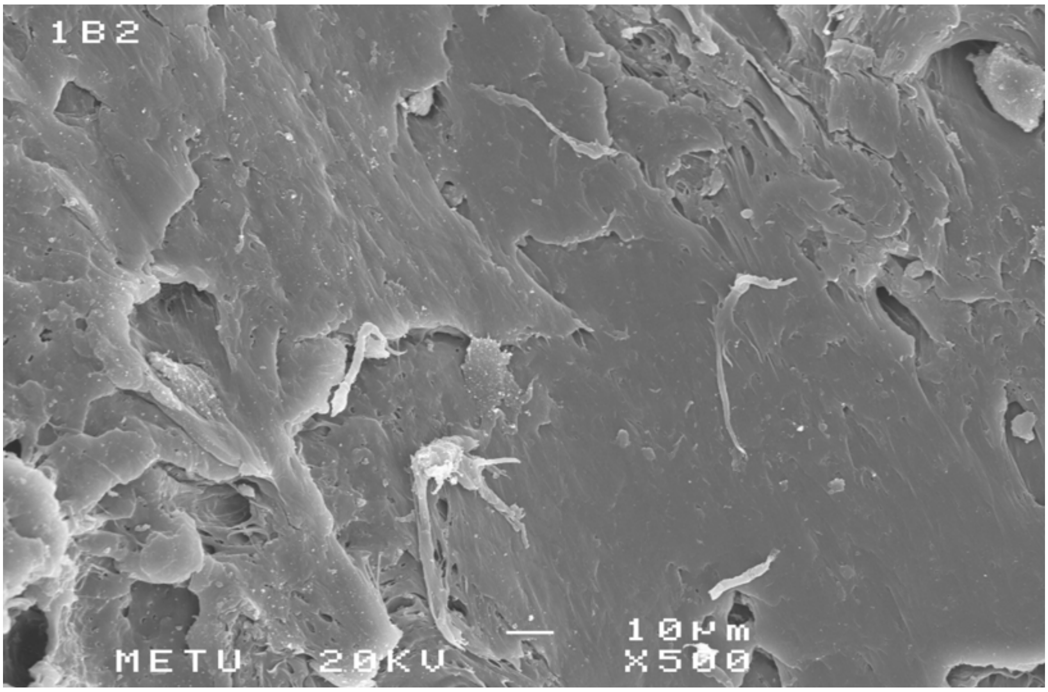


Fig.3.12 SEM photograph of 5 % PABA-g-PP

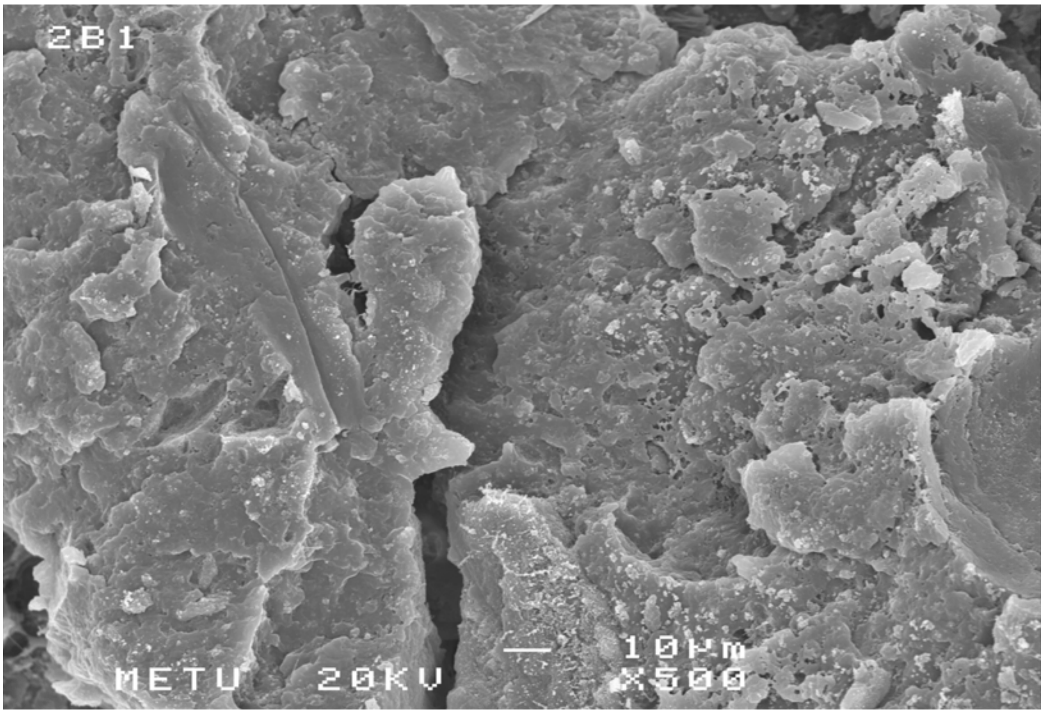


Fig.3.13 SEM photograph of 10 % PABA-g-PP

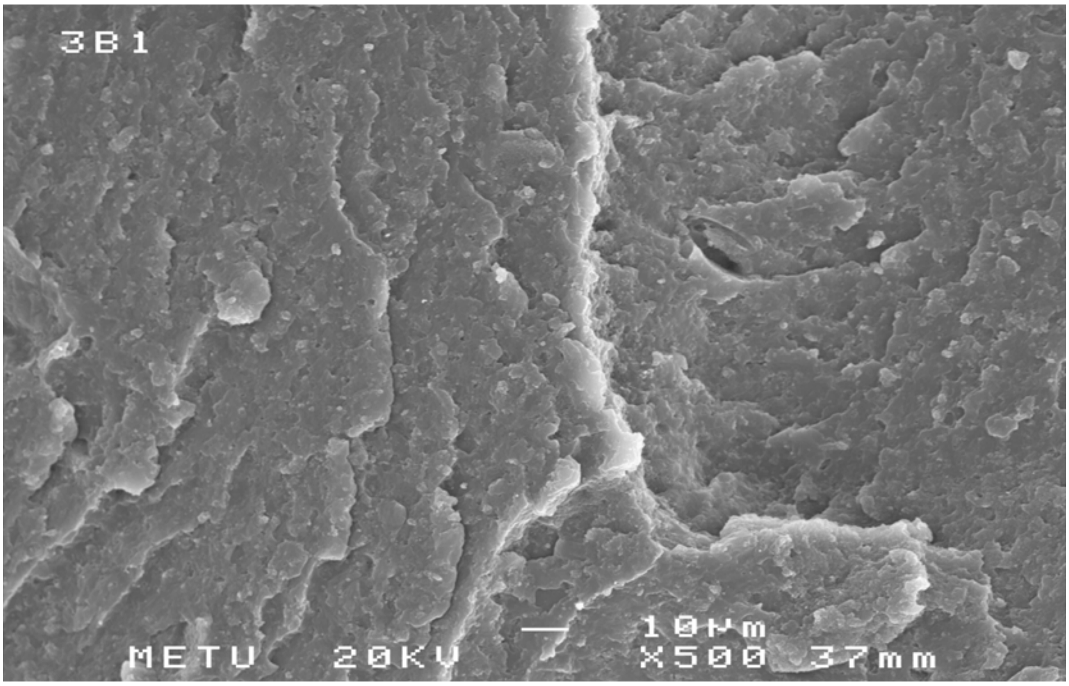


Fig.3.14 SEM photograph of 15 % PABA-g-PP

CHAPTER 4

CONCLUSIONS

The polymerization and grafting of ABA onto Polypropylene occured in the Brabender Plasti-Corder simultaneously by melt mixing at high temperature. For dispersion of monomer with PP, a masterbatch of 50-50 (by weight) low density polyethylene + ABA was used. Then, this masterbatch was mixed with melted PP, into this, maleic anhydride was added to obtain 5, 10, 15 % ABA + PP mixtures, in the Brabender Plasti Corder, at 200°. Furthermore, these compositions were reprocessed at the same temperature in the molten state.

Thermal and mechanical tests were done to examine the behaviour of the mixture. Particularly, improvement in ultimate tensile strength and modulus were observed, but with loss of yield stress and loss in percent elongation, therefore the samples were mostly broken in brittle manner.

The strength of PABA-g-PP samples increased with the increase of PABA up to 5 %. However it is observed that both for 5 and 10 % PABA content, the ultimate strength values are higher than the yield stress of pure PP. The decrease detected in tensile property is probably due to the problem of processing at the temperature. Also, increase of PABA content in grafting caused more rigidity so that early fracture occurred.

Although PP shows a great extent of cold drawing or orientational flow, grafted products showed no elongation and were broken in a brittle nature. No yield stress in any of the grafted polymers observed.

MFI values increased at 10 wt % ABA, then decreased. It is most likely that the presence of PABA produced easy orientational flow up to 10 % ABA, but at the 15 % ABA addition caused a slight decrease in MFI. Higher MFI values that observed for the reprocessed samples were due to the degradation of PP.

Grafting yield was determined by gravimetric analysis. By increasing the amount of ABA in mixture, the amount of grafting increased. The extensive extraction showed that enough grafting was achieved.

Scanning Electron Microscopy had given some insight about the morphology. When the photographs are examined, no phase separation is observed. Thus it is concluded that homogeneous grafting of PABA onto PP occurred. Also, the brittle nature of material could be seen at all three compositions.

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