MODIFICATION OF POLYPROPYLENE FILMS FOR ANTISTATIC AND ANTI-SCRATCH PROPERTIES

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ABSTRACT

MODIFICATION OF POLYPROPYLENE FILMS FOR ANTISTATIC AND ANTI-SCRATCH PROPERTIES

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Polypropylene films are widely used in industry, especially for packaging purposes. However, these films become statically charged when they are subject to friction. The accumulation of charges in some applications can be harmful, especially for the electronic devices and can cause undesirable appearance due to the attraction of dusts. Furthermore, minimum susceptibility to mechanically induced surface damage is a desired property since scratches reduce the mechanical strength and the bright texture of the film in packaging of commercial items and limit the applications of the material.

This study aims to provide antistatic character to polypropylene films by the utilization of conductive fillers which function independent of humidity and enhance their scratch resistance by means of aromatic based additives.

Polypyrrole-polypropylene composites including 2%, 5%, 7% and 9% pyrrole were synthesized by chemical modification. 2% of pyrrole was adequate to provide antistatic character to the films. Moreover, they attained conductive property when the pyrrole content exceeds 7%.

Polypropylene based materials containing four different compositions of 1,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, p-phenylene diamine and hydroquinone were prepared by mechanical mixing. Scratch resistance of polypropylene films increased significantly with the insertion of additives. The material containing 2% 1,7-dihydroxynaphthalene introduced the highest enhancement by more than 60%. Moreover, mechanical analysis results showed that insertion of the additives except hydroquinone increased Young's modulus of the polypropylene films. In addition, tensile strength and elongation at break of polypropylene films were enhanced significantly with insertion of the additives regardless of the additive type.

Keywords: polypropylene, antistatic, pyrrole, anti-scratch, aromatic based additives

ÖZ

POLİPROPİLEN FİLMLERE ANTİSTATİK VE ÇİZİLMEZLİK ÖZELLİKLERİ KAZANDIRILMASINA YÖNELİK MODİFİKASYON

Kürkçü, Pınar
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Polipropilen filmler sanayide özellikle paketleme amacıyla yaygın olarak kullanılmaktadır. Ancak, bu filmler sürtünmeye maruz kaldıklarında statik olarak yüklenmektedir. Yük birikimi, bir takım uygulamalarda, özellikle elektronik cihazlarda zararlı olabilmekte ve toz toplanması yoluyla istenmeyen durumlara neden olabilmektedir. Ayrıca, mekanik etkiyle oluşan yüzey hasarlarına karşı asgari duyarlılık; çiziklerin mekanik dayanımı azaltması, ticari paketlemelerde film yüzeyini parlatması ve malzemenin uygulama alanını kısıtlaması nedeniyle istenen bir özelliktir.

Bu çalışma, polipropilen filmlere nemden bağımsız olarak çalışan iletken dolgular kullanarak antistatik özellik kazandırmayı ve aromatik esaslı katkılarla çizilmeye karşı direnç artırmayı amaçlamaktadır.

%2, %5, %7 ve %9 oranında pirol içeren polipirol-polipropilen kompozitleri kimyasal modifikasyon yoluyla sentezlenmiştir. %2 oranında pirol, filmlere antistatik karakter kazandırılması için yeterli olmuştur. Ayrıca, polipropilen filmler %7’nin üzerindeki pirol oranlarında iletken özellik göstermiştir.

Dört farklı 1,7-dihidroksinaftalin, 2,3-dihidroksinaftalin, 2,7-dihidroksinaftalin, p-fenilen diamin ve hidrokinon bileşiminden oluşan polipropilen esaslı malzemeler mekanik karıştırma ile hazırlanmıştır. Katkı maddeleri polipropilen filmlerin çizik sertliğini önemli ölçüde artırmıştır. %2 oranında 1,7-dihidroksinaftalin içeren kompozit %60’tan fazla bir artışla çizilme direncinde en yüksek iyileştirmeyi göstermiştir. Ayrıca, mekanik dayanım testleri, hidrokinon dışındaki katkıların polipropilen filmlerin Young modülünü artırdığını göstermiştir. Ek olarak, polipropilen filmlerin gerilme dayanımı ve kopmada uzaması, katkı eklenmesiyle katkının türüne bakılmaksızın geliştirilmiştir.

Anahtar kelimeler: polipropilen, antistatik, pirol, çizilmezlik, aromatik bazlı katkı malzemeleri

to My Father

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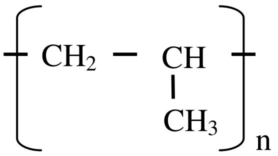
CHAPTER 1

INTRODUCTION

1.1 POLYPROPYLENE

Polypropylene (PP) is a crystalline thermoplastic polyolefin resin. It has been the first synthetic stereoregular polymer that achieved industrial importance [1]. Today it is the third-largest volume polyolefin and one of the major plastics worldwide [2]. The structure of polypropylene is given in Figure 1.1.



$$\left[CH_2 - \underset{CH_3}{\underset{|}{CH}} \right]_n$$

Figure 1.1 Structure of polypropylene

1.1.1 Historical Development

Shortly after the discovery of high density polyethylene, Giulio Natta found that propylene can also be polymerized by using coordination catalysts. Polymerization resulted in two different forms of PP: an amorphous, rubbery and soluble form and a highly crystalline, hard and insoluble form. The former one, a by-product of the stereospecific polymerization process, can be classified as atactic PP whereas the latter one can be classified as isotactic PP [1].

It had not been possible to perform any steric control on polymerization processes until the discovery of stereospecific polymerization of PP. Therefore, polymerization of vinyl polymers had always led to atactic amorphous products. Polymerization of stereoregular isotactic PP by coordination catalysts was the first practical performance of steric control on the growth of a polymer chain. Besides being the starting point of PP industry, this was the first event in a long series of successful applications of coordination catalysts to other monomers, leading to stereoregular polymers of higher α-olefins, styrene and diolefins [1].

The properties of isotactic polypropylene enabled it to be utilized as a raw material for film and fiber industry as well as being a thermoplastic resin. Industrial production of PP was started in 1957 by Montecatini with the collaboration of Natta. Moreover, Montecatini introduced PP fiber on a small scale as early as 1957 and commercial production of PP film was also started [1].

Polymerization of syndiotactic PP was also performed by using coordination catalysts; however, this product has not achieved any commercial importance and has been only of scientific interest [1].

1.1.2 Raw Material

The main steps of propylene production process consist of recovery of olefins from petroleum refinery off-gases and thermal cracking of selected hydrocarbon feedstocks. The cracking operation is usually performed in tubular furnaces at temperatures between 700 and 900ºC based on the nature of the feed. Several variables such as temperature, pressure, residence time, etc. affect the yield of the olefin [1]. Physical properties of propylene are given in Table 1.1.

Table 1.1 Physical properties of propylene [1]

Boiling point, ºC	-47.70
Triple point, ºC	-185.25
Critical temperature, ºC	91.9
Critical density, g/ml	0.233

1.1.3 Polymerization

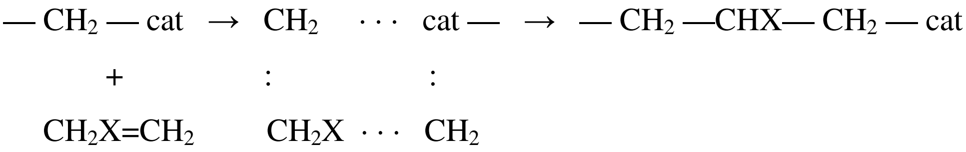
1.1.3.1 Catalysts

The effective catalyst systems in stereospecific polymerizations consist of a reducible compound of transition elements of group IV to VII and a reducing organometallic compound of metals of group I to III. Polymerization of isotactic PP is usually performed by catalyst systems consisting of crystalline $TiCl_3$ and alkylaluminum compounds. On the other hand, syndiotactic PP can be prepared by catalyst systems including vanadium triacetylacetonate and $Al(C_2H_5)_2Cl$. Coordination catalyst systems are called Ziegler-Natta catalysts [1].

1.1.3.2 Polymerization Mechanism

The most commonly utilized Ziegler-Natta catalyst systems for the stereoregular polymerization of propylene are prepared by suspending one or another violet form of powdered $TiCl_3$ in a hydrocarbon medium and adding certain amounts of alkylaluminum compounds. Although little chemical change occurs, adsorption and/or complex formation of the soluble alkyl on the surface of the insoluble halide takes place during this process [1].

When the adsorption or complex formation is taking place, the monomer is introduced between catalyst and growing chain by a cyclic transition state. Consequently, the polymer chain is growing like a hair from the root. A cis-opening of the double bond is required for this sort of insertion and subsequent reaction [1]. Cis-opening of propylene is given in Figure 1.2.



$$\begin{array}{ccccccc} \text{—}CH_2\text{—}cat & \rightarrow & CH_2 & \cdots & cat\text{—} & \rightarrow & \text{—}CH_2\text{—}CHX\text{—}CH_2\text{—}cat \\ + & & : & & : & & \\ CH_2X{=}CH_2 & & CH_2X & \cdots & CH_2 & & \end{array}$$

Figure 1.2 Cis-opening of propylene

There are two distinct opinions about the active sites on the catalyst surface and on the propagation mechanism. The first one assumes that the chain growth occurs at the titanium site with chlorine vacancies which become alkylated by the alkylaluminum compound. The second one assumes that polymerization occurs where monomer is inserted into alkyl bridges linking titanium and aluminum atoms in a bimetallic electron deficient complex [1].

1.1.3.3 Polymerization Process

Initially, alkylaluminum, an active form of $TiCl_3$ and a highly purified diluent are mixed in propeller-agitated vessels in order to produce a catalyst slurry. The prepared catalyst slurry, propylene and hydrocarbon diluent are fed into the polymerization vessel. Operating temperature and pressure commonly range between 50-80ºC and 4-6 atm, respectively. The residence time is of the order of several hours, based on the design of the reactor and on operating conditions [1].

The second step of PP polymerization process is the control of the molecular weight, which can either be performed by increasing the polymerization temperature or by chain transfer. Since the former one also affects the stereospecificity of the catalyst, chain transfer is considered as a more suitable method [1].

The final step of PP polymerization process is the polymer purification and finishing. In polymer purification, the reactor slurry is fed to a flash tank where unreacted propylene is vaporized. Propylene is recycled into the reactor after compression and purification. Then, the polymer slurry leaving the flash tank is centrifuged in order to remove diluent-containing catalyst residues and atactic PP. After centrifuge, polymer may be washed with water or methanol so as to remove catalyst residues more effectively. Then, polymer is dried, required additives are added and finally polymer is extruded and pelletized [1].

1.1.4 Properties of Polypropylene

The mechanical and thermal properties of polypropylene can vary based on the isotacticity, the molecular weight and its distribution and % crystallinity. Since PP is a viscoelastic material like other thermoplastics, its mechanical properties are strongly dependent on time, temperature and stress [3].

1.1.4.1 Density

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

1.1.4.2 Thermal Properties

Polypropylene has a glass transition temperature and a crystalline melting point of -10ºC and 160-170ºC, respectively. Moreover, it has a maximum continuous use temperature of 100ºC, which is significantly higher than those of the other commodity plastics and some other engineering plastics [3].

1.1.4.3 Mechanical Properties

The mechanical properties of isotactic PP depend on its % crystallinity. Due to its relatively high melting temperature, the crystalline phase maintains mechanical strength up to rather high temperatures [1]. It has high tensile strength, stiffness and hardness due to its crystallinity [2]. However, an increase in molecular weight leads to a reduction in tensile strength, stiffness, hardness but an increase in impact strength of polypropylene [3].

1.1.4.4 Electrical Properties

Polypropylene has an excellent electrical insulating property. It has outstandingly high resistivity, low dielectric constant and negligible power factor [3].

1.1.4.5 Solubility

Polypropylene is soluble only at elevated temperatures due to its crystalline character. Isotactic PP is soluble in “good” solvents such as xylene, tetralin, chlorinated aromatic and aliphatic hydrocarbons, etc. above 80ºC [1].

1.1.5 Applications

Applications of polypropylene range from injection-molded and blow-molded products and fibers and filaments to films and extrusion coatings. About half of the PP produced is utilized as injection-molded parts in automotive and appliance sectors. PP can be designed with an integral hinge fabricated into products ranging from pillboxes to cabinet doors. Extruded polypropylene fibers are utilized in products such as yarn for carpets, woven and knitted fabrics and upholstery fabrics. Nonwoven polypropylene fabrics are used in applications carpet backing, liners for disposable diapers, disposable hospital fabrics, reusable towels and furniture dust covers. PP filaments are used in rope and cordage applications. Nonwoven polypropylene soft film is used as overwrap of products such as shirts and hose whereas oriented polypropylene film is used as overwrap of items such as cigarettes, snacks and phonograph records [2].

1.2 COMPOSITES

The conventional metal alloys, ceramics and polymeric materials cannot meet the unusual combinations of properties that are desired in most of the modern technologies, especially in aerospace, underwater and transportation industries. The need for materials with such property combinations led to the development of composite materials [4].

A composite is considered to be a combined material made up of two or more components so as to obtain specific properties that are related to desired characteristics. The components of a composite do not dissolve or merge completely into each other; however, they act together. Both the components and the interface between them can usually be physically identified, and generally the behavior and properties of the interface control the properties of the composite. Although it consists of several similar or dissimilar materials, the composite itself behaves as a single product and any of the components acting alone cannot achieve the properties of the composite [5].

Many composite materials consist of two phases: matrix, the continuous phase, and the dispersed phase. The properties of the composites depend on properties of the constituent phases, their relative amounts and the geometry of the dispersed phase, i.e. shape of the particles, particle size, distribution and orientation [4].

Generally, the dispersed phase can consist of either a fibrous, powdered, spherical, crystalline or a whiskered and either an organic, inorganic, metallic or a ceramic material. Typical matrices include polyester, phenolic, epoxy, silicone, alkyd, melamine, polyimide, fluorocarbon, polycarbonate, acrylic, acetal, polypropylene, acrylonitrile-butadiene-styrene copolymer, polyethylene and polystyrene [5].

1.3 ANTISTATIC BEHAVIOR

Polymers are widely used as insulating materials for power electric machines and electrical devices since their dielectrics are chemically stable and easily manufactured [6].

Friction, especially at high speeds, results in static electricity buildup and the dissipation of electric charges on polymer surfaces is prevented due to their low volume and surface conductivity [7]. Static-induced accumulation of dust decreases the attractiveness and therefore saleability of products displayed on store shelves. The attraction of a formed part to the charged surfaces of a processing mold prevents proper ejection of the formed part and thus slows down production. Moreover, electrostatic charges can cause problems when textile, films or powders join up in automatic machinery. Sparks, explosions or fires can occur when static electricity is induced from plastics on nearby conductor. Also, sensitive semiconductors and similar complex microelectronic devices can be damaged from either the direct discharge from the conductive skin of personnel or by exposure of such devices to the close approach of a static-charged polymer material [2].

One of the techniques to remove the accumulated charges on polymer surfaces is the utilization of air-ionizing bars and blowers, which provide an atmosphere of ionized air capable of neutralizing the charged objects or surfaces. However, this does not provide permanent protection because it does not prevent another charge from forming once the object is removed from the ionized air atmosphere. The nonconductor must be made sufficiently conductive in order to ensure an extended removal of static charges from the surface. A layer of water can do this satisfactorily. Antistatic agents or antistats are hygroscopic chemicals that can generate this layer of water by attracting moisture from the atmosphere [2].

Main types of organic antistatic agents consist of quaternary ammonium compounds, amines and their derivatives, phosphate esters, fatty acid polyglycol esters and polyhydric alcohol derivates like glycerine and sorbitol. Selection of appropriate antistatic agent depends on its compatibility with the polymer, the end use of the part and the desired level of antistatic activity. The effect of antistatic agent on color, transparency and finish of the polymer part, its possible toxicity, stability during processing, degree of interference with physical properties and cost effectiveness also need to be considered [2].

The classical antistats are soap like molecules with a hydrophobic and a hydrophilic part. They migrate to the surface and increase the surface conductivity by attracting a layer of water. These antistats can easily be utilized; however, they have several disadvantages. They do not have volume conduction beneath the surface and they are generally easily removed and washed out. As a consequence, they are not effective for a long time [8]. Moreover, the efficacy of the antistats drops with decreasing relative humidity [7].

1.4 SCRATCH RESISTANCE

Polymers and polymer matrix composites are preferred for microelectronic packaging, coatings, aerospace, automotive, food packaging and biomedical applications due to their adequate strength, lightness, versatility, ease of processing and low cost [9]. It is important that the products are manufactured with durable, low-gloss first surfaces and aesthetically appealing. In order to maintain a good appearance, it is required that materials exhibit minimal susceptibility to mechanically induced surface damage and stress whitening does not occur [10]. However, polymers are more susceptible to scratches and abrasion when compared to other materials because they are relatively soft [9].

A scratch on the surface of a polymeric material is a large size flaw that can potentially be a stress raiser restricting the applicability during tensile, impact or fatigue loading [11]. Moreover, surface damage induced by scratch or any mechanical deformation process detracts the user from the subjective perception of quality of the product and limits the applicability of polymeric materials. Scratches can also decrease the mechanical strength of polymeric materials [10].

In general, the scratch performance of polymeric materials depends on the scratch stress field associated with the indenter geometry and properties of the polymeric materials. Other factors such as lubricant, filler and additives also affect the scratch performance of thermoplastic olefins. Scratches promote crazing, wedging, ironing and debonding that drastically increases the ability of the surface to scatter light, consequently increase in scratch visibility [10].

Polymeric materials should be characterized by high modulus and elastic recovery in order to enhance scratch resistance. Surface texture, crystalline orientation and impact strength are the other aspects of consideration. Even small decreases in percentage crystallinity enhance stress whitening. High modulus and yield stress characteristics of highly crystalline polymers lead to their lower susceptibility to stress whitening [11].

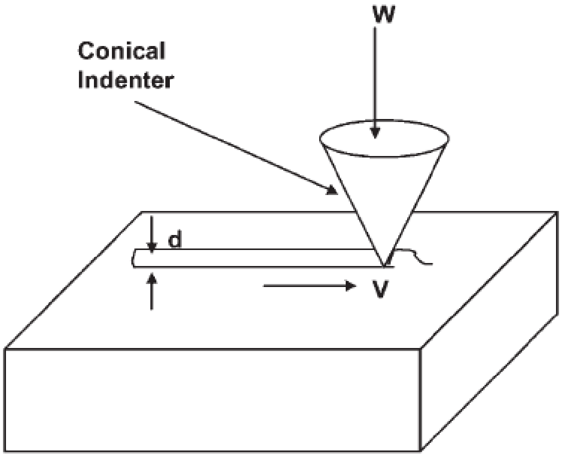


Figure 1.3 Schematic representation of the scratch test. W, V and d are normal applied load, scratching velocity and scratch width, respectively [10].

Scratch test has been developed so as to evaluate the scratch behavior of polymers. In a scratch test, an indenter with a constant penetration rate is used [10]. The geometry of the indenter can be conical tips with different included angles, spherical tips of different radii or Berkovich tip. Furthermore, the indenter can be made of various materials such as diamond, sapphire, steel, silicone nitrite, etc [9]. The scratch is done with a constant loading rate and constant scratch rate. A scratch tester is shown in Figure 1.3. The severity of the scratch damage is evaluated by using various techniques such as atomic force microscopy, optical microscope, scanning electron microscope, laser confocal microscope, Raman spectroscope, white-light interferometer, cross profilometer, tribometer, elipsometer, etc. [9]

1.5 POLYMER PROCESSING

1.5.1 Mixing

Besides achieving the desired shape, a suitable degree of homogeneity in composition and properties is required in the manufacture of products from polymeric materials. Thus, the aim of mixing is to attain an acceptable degree of homogeneity or uniformity of composition and to some extent of morphological structure [12].

1.5.1.1 Types of Mixing

The main types of mixing are dispersive mixing and distributive mixing. Dispersive mixing, which is also referred to as intensive mixing, involves the reduction in size of a cohesive component. Mixing of a pigment into a polymer in which the agglomerate size of the pigment has to be reduced below a certain minimum size to obtain good surface quality of the final product is an example of dispersive mixing. Dispersive mixing is illustrated in Figure 1.4 [13].

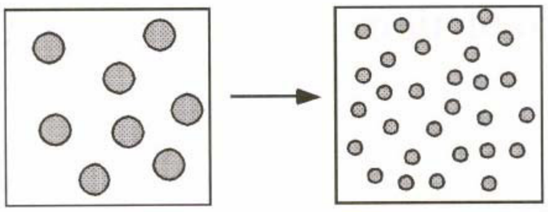


Figure 1.4 Schematic representation of dispersive mixing [13]

On the other hand, distributive mixing, which is also referred to as extensive or nondispersive mixing, is mixing in the absence of a cohesive resistance. Mixing of two miscible polymer melts such as polystyrene and polyphenylene oxide is an example of distributive mixing. Distributive mixing is illustrated in Figure 1.5 [13].

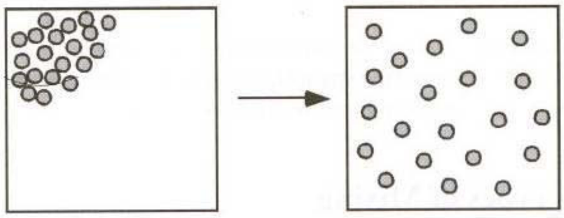


Figure 1.5 Schematic representation of distributive mixing [13]

1.5.1.2 Internal Mixers

The first internal mixer, which consists of a single rotor to mix the material, was introduced by Thomas Hancock around 1830. Around 1880, twin rotor mixers were developed by Werner and Pfleiderer. About forty years later, Banbury introduced an internal mixer, which includes a ram to force the material into the mixing chamber and to provide sealing. Banbury mixer's rotors were nonintermeshing and counter-rotating. Intermeshing counter-rotating internal mixers were developed by Cooke and Lasch. Also co-rotating internal mixer was introduced but could not achieve commercial interest [13].

A batch internal mixer mainly consists of the rotors, the mixer housing, the ram, the ram air cylinder, the feed hopper and the door for discharge, as illustrated in Figure 1.6 [13].

The internal mixers are widely employed in polymer industry, especially in the rubber industry. Batch internal mixers have several advantages. They accept feed stock in various forms. They have intensive mixing action and a well-defined residence time. Furthermore, quick material changes and a wide range of mixing procedures are possible [13].

Internal mixers can also handle sticky and blocky materials without much trouble. The mixing action of the internal mixer occurs in the narrow gaps between the rotor and the housing. High rates of shear and elongation occur in these regions, leading to intensive mixing action. Since the mixer has high horse power drives, it can handle high viscosity materials quite well [13].

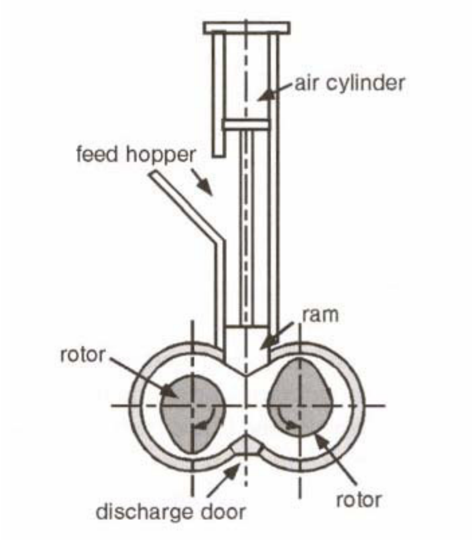


Figure 1.6 Schematic representation of a batch internal mixer [13]

However, internal mixers have also some disadvantages. For instance, they are not self-wiping mixing devices. Batch-to-batch variations can affect product quality. Moreover, it is difficult to achieve fine process control and handle high-temperature engineering plastics [13].

The order of the addition of the constituents is very important for good mixing in internal mixers. The sequence should be arranged to maintain adequate stiffness in the mixture until the most difficult step in the dispersion is achieved. In general, polymer and half of the filler are fed and mixed until the material softens. Then, the remaining filler is added and mixed until fully incorporated. Lastly, plasticizers or softeners are added and the mixing is completed. However, if the material softens quickly before a good dispersion is obtained, all ingredients can be added at once [13].

The main process variables in the batch mixing process are batch weight (fill factor), material feed temperature, mixer temperature, rotor speed, ram pressure and order and timing of the feeding of the ingredients [13].

1.5.2 Compression Molding

1.5.2.1 Principle

Compression molding basically includes the squeezing of the polymer between the two halves of a heated mold and its transformation into a solid product under the effect of the elevated mold temperature. Mold temperature, mold pressure and process time vary considerably depending upon the thermal and rheological properties of the polymer. However, mold temperatures and pressures are usually in the range 140-200ºC and 500-10,000 psi, respectively. Process time can be about 1 minute for relatively thin phenolic parts whereas over 1 hour for very thick rubber components [7].

In the compression molding process, first the polymer is placed in the bottom half of an open, heated mold. Then, the top half of the mold is placed over the bottom half and pressure is applied in order to cause the molten polymer to fill the mold cavity completely [14]. Usually a slight excess of polymer is placed in the mold to ensure its being completely filled. The rest of the polymer is forced out of the mold in a thin, easily removed film known as flash. [15]

1.5.2.2 Equipment

Compression molding presses can be either downstroking or upstroking types. They are generally slow-acting and hydraulically operated by a clamping ram or cylinder. Large presses use a frame whereas smaller ones often use a combination of tie bars and bolster plate. Daylight, which is the maximum platen separation, is another important characteristic of the press. It is associated with the stroke and the platen size [7]. An illustration of a compression molding equipment is shown in Figure 1.7.

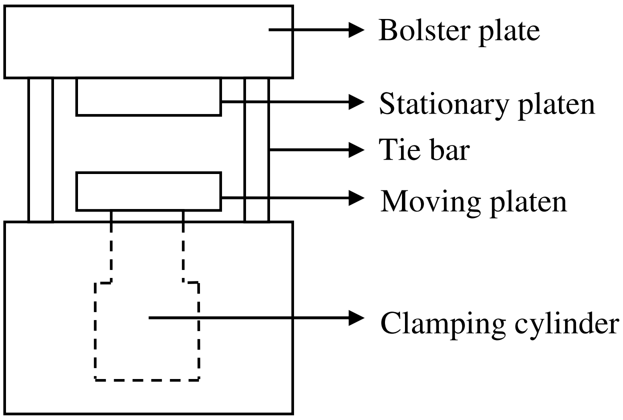


Figure 1.7 Schematic representation of an upstroking type compression molding press [7]

1.6 CHARACTERIZATION

1.6.1 Mechanical Properties

1.6.1.1 Tensile Test

Tensile modulus and tensile elongation are among the most important properties that indicate the strength of a material. Tensile test measures the ability of a material to withstand forces which tend to pull it apart and to determine to what extent the material stretches before breaking. Tensile modulus, which illustrates the relative stiffness of a material, can be determined from a stress-strain curve [16].

1.6.1.1.1 Equipment

The test is performed with the tensile testing machine of a constant-rate-of-crosshead movement. It consists of a fixed or essentially stationary member carrying one grip and a movable member carrying a second grip. A controlled-velocity drive mechanism is utilized. It has a load-indicating mechanism which is capable of indicating total tensile load with an accuracy of 1 percent of the indicated value or better. Recently, digital-type load indicators are commonly used since they are easier to read than the analog-type indicators. An extension indicator, which is called extensometer, is utilized so as to determine the distance between two designated points located within the gauge length of the test specimen as the specimen is stretched [16].

1.6.1.1.2 Test Specimens and Conditioning

The specimens for tensile tests can be prepared by injection molding, compression molding or machining operations from materials in sheet, plate, slab or similar form. Test specimen dimensions vary considerably due to the requirements. ASTM D638 Type I tensile test specimen is shown in Figure 1.8 [16].

Because the tensile properties of some plastics change rapidly with small changes in temperature, it is recommended that tests be performed in the standard laboratory atmosphere of 23±2°C and 50±5 percent relative humidity [16].

1.6.1.1.3 Test Procedure

The speed of testing, which can be defined as the relative rate of motion of the grips or test fixtures during the test, is chosen based on the specification of the material being tested. The most frequently used speed of testing is 0.2 in/min [16].

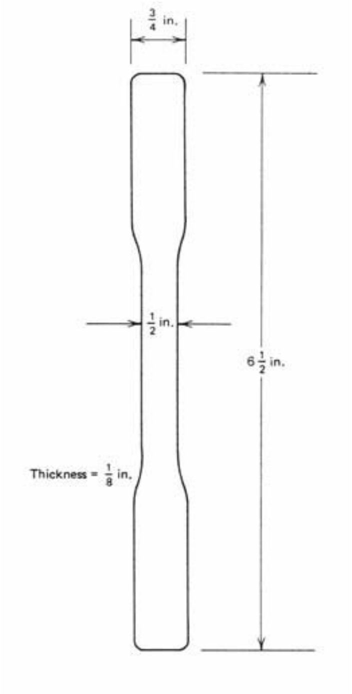


Figure 1.8 ASTM D638 Type I tensile test specimen [16]

Initially, the test specimen is positioned vertically in the grips of the testing machine. The grips are tightened evenly and firmly to prevent any slippage. After the speed of testing is set at the proper rate, the machine is started. As the specimen elongates, its resistance increases and is detected by a load cell. This load value (force) is recorded by the instrument. Moreover, some machines record the maximum (peak) load obtained by the specimen, which can be recalled after the test is completed. The elongation of the specimen is continued until a rupture of the specimen is observed. In addition, load value at break is recorded [16].

1.6.1.1.4 Calculations

A. Tensile Strength

The tensile strength can be calculated by dividing the maximum load by the original minimum cross-sectional area of the specimen. This result can be reported as either tensile strength at yield or tensile strength at break. However; these two terms can be calculated separately when a nominal yield or break load less than the maximum is present [17].

B. Percent Elongation

Percent elongation can be calculated by dividing the change in gauge length by the original gauge length and multiplying by 100. If the specimen gives a yield load that is larger than the load at break, percent elongation at yield is calculated. Otherwise, percent elongation at break is calculated [17].

C. Modulus of Elasticity

Modulus of elasticity can be calculated by extending the initial linear portion of the load-extension curve and dividing the difference in stress corresponding to any segment of section on this straight line by the corresponding difference in strain [17]. Representative stress-strain curves for different polymers are illustrated in Figure 1.9.

1.6.1.1.5 Factors Affecting the Test Results

There are several factors that affect the tensile test results.

A. Specimen Preparation and Specimen Size

Tensile strength values are affected by molecular orientation significantly. A load applied parallel to the direction of molecular orientation may result in higher values than the load applied perpendicular to the orientation. The opposite behavior is observed for elongation. In addition, the processed used to prepare the specimen has a significant effect. For instance, injection molded specimens generally yield higher tensile strength values than compression molded specimens. Machining usually lowers the tensile and elongation values due to small irregularities introduced into the machined specimen. Another important factor affecting the test results is specimen size. Tensile properties should only be compared for equivalent sample sizes and geometry [16].

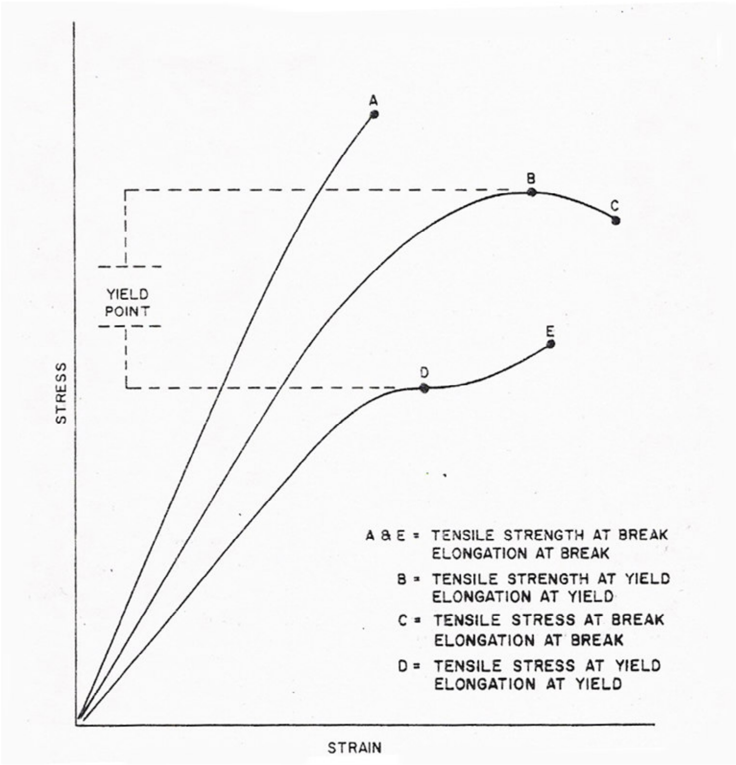


Figure 1.9 Representative stress-strain curves for different polymers [17]

B. Rate of Straining

The tensile strength and modulus increases with increasing strain rate. However, the elongation is inversely proportional to the strain rate [16].

C. Temperature

As it was mentioned previously, the tensile properties of some plastics vary rapidly as the temperature changes. Tensile strength and modulus decrease whereas elongation increases with increasing temperature [16].

1.6.2 Thermal Analysis

1.6.2.1 Differential Scanning Calorimetry

Differential scanning calorimetry, which is the most widely used thermal analysis technique, is generally employed in order to determine a polymer's glass transition temperature, melting temperature, degree of crystallinity, heat of fusion or degree of cure. It is an excellent technique to examine the failure of polymers owing to the small sample size required, its ability to denote the polymer's thermal history and its ability to determine the glass transition temperature of the polymer [18]. Figure 1.10 illustrates the basic thermal properties that can be obtained by differential scanning calorimetry and their practical applicability to polymers.

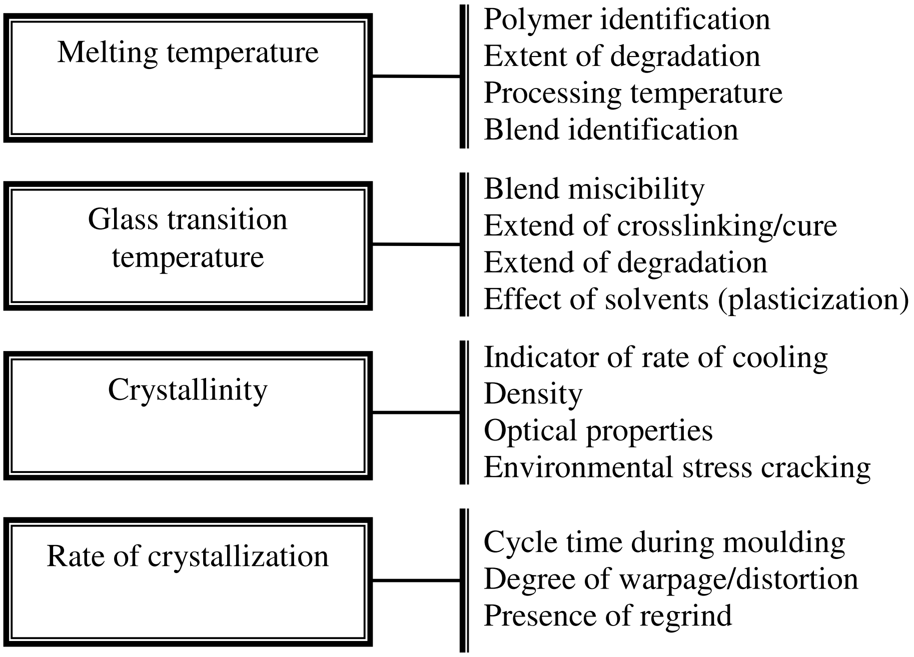


Figure 1.10 Thermal properties obtainable by DSC and their practical applicability [18]

This technique utilizes individual heaters to maintain identical temperatures for two small platinum holders, one of which includes a small polymer sample (usually about 5-10 mg) mechanically sealed in a small aluminum pan and the other includes an empty (reference) pan, as illustrated in Figure 1.11. Temperatures are measured by using identical platinum-resistance thermisters. Then, the differential power needed to maintain both the reference and sample pans at equal temperatures during a programmed heating cycle is recorded as a function of temperature [14]. A typical programmed cycle includes heating the sample at a rate of 100ºC/min to 40ºC above its T_m (or T_g) and then cooling it at a rate of 5ºC/min [18].

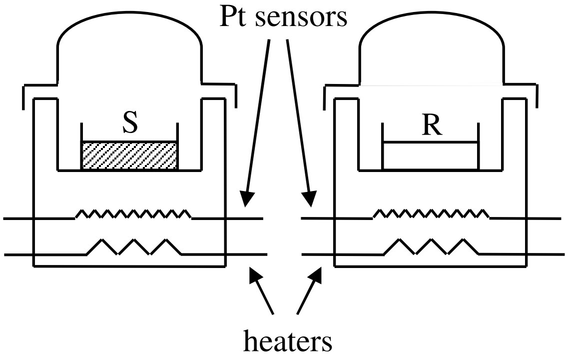


Figure 1.11 Schematic representation of a typical DSC sample cell [14]

At the beginning of the test, constant energy input is required to heat the sample at a constant rate. This forms a baseline. When a transition point is reached, the sample requires either more or less energy based on whether the change is endothermic or exothermic [16]. For instance, at the glass transition point, the heat capacity increases due to the increased molecular motions in the polymer and therefore an endothermic shift from the baseline is observed [19]. When a polymer reaches the melting point, it requires more energy to melt the crystalline structure. The area of the peak in units of energy is the enthalpy of fusion, the heat of melting. The temperature dependence of the peak and its shape inform about the degree of crystallinity, the molecular-weight distribution, degree of branching, copolymer blend ratio and processing history [16].

Above the melting temperature, the polymer will degrade at the degradation temperature (decomposition temperature) (T_d). This transition can give rise either to an endothermic peak or to an exothermic peak. For crystallizable polymers, an additional transition is observed at a temperature between T_g and T_m values. This temperature, at which ordering and production of the crystalline regions occur, is known as crystallization temperature (T_c). The polymer chains have sufficient mobility at this specific temperature to crystallize and an exothermic peak is observed [19]. A typical DSC curve obtained for a polymer sample is shown in Figure 1.12.

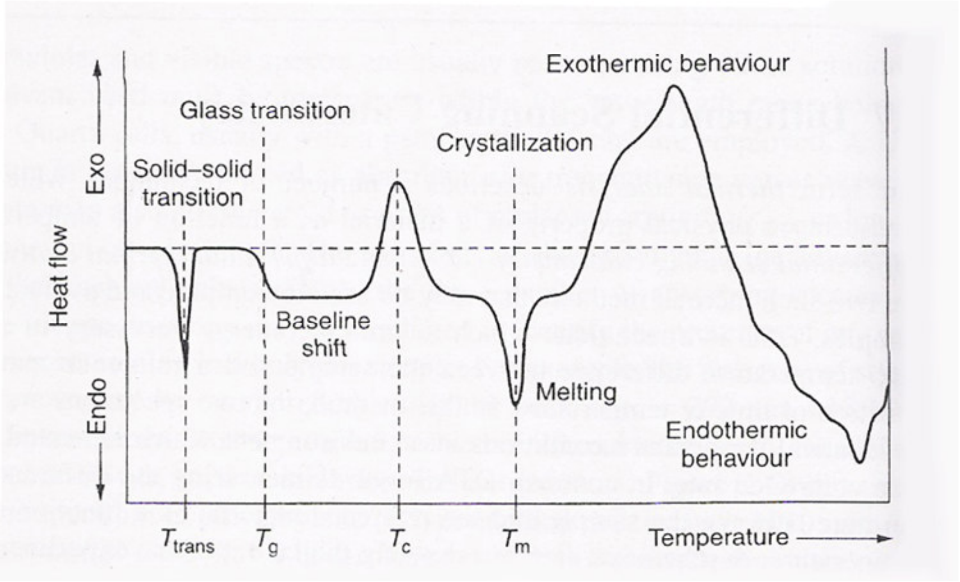


Figure 1.12 A typical DSC curve obtained for a polymer sample [19]

1.6.3 Morphological Analysis

1.6.3.1 Scanning Electron Microscopy

Scanning electron microscopy is utilized for examining the top topography of polymer surfaces due to the large depth of field that is possible. The depth of field capacity is about 300 times greater than that of a conventional optical microscope at comparable magnifications. Moreover, scanning electron microscopy has a resolution of about 3 nm, which is two orders of magnitude greater than that of the optical microscope (0.2 μm) [18].

Scanning electron microscopy can be utilized for a broad range of polymer studies and applications such as surface roughness, adhesive failures, fractures surfaces, networks and phase boundaries in blends [19]. Enhanced contrast between the reinforcement and the polymer matrix can be observed by the utilization scanning electron microscopy in the back-scatter mode. This results from atomic number contrast in the black-scattered electron image where the brightness increases with atomic number. However, scanning electron microscopy has some pitfalls such as charging, beam damage and artifacts due to metal coating [18].

Polymer samples can be mounted on metal stubs by using a conductive cement such as nail varnish containing graphite powder. Non-conductive polymer samples must be sputter-coated with gold in order to reduce the incidence of charging, which occurs due to high negative charges accumulating on the sample surface and causes bright spots on the image. While using double-sided adhesive tape to mount samples, it is necessary to add a conductive track around the edge of the sub to provide a path for the electrons to escape along [18].

In this technique, a fine electron beam with a diameter of 5-10 nm is scanned across the sample surface in synchronization with a beam from a cathode-ray tube. The scattered electrons produced cause a signal that modulates this beam. Then, an image with the above-mentioned high depth of field is obtained [19].

1.6.3.2 Attenuated Total Reflectance Spectroscopy

Attenuated total reflectance (ATR) spectroscopy uses the total internal reflection phenomenon. A beam of radiation entering a crystal undergoes total internal reflection when the angle of incidence at the interface between the sample and crystal is greater than the critical angle, where the angle is a function of the refractive indices of the two surfaces. The beam penetrates a fraction of a wavelength beyond the reflecting surface. When a material, which selectively absorbs radiation, is in close contact with the reflecting surface, the beam loses energy at the wavelength at which the material absorbs. The spectrometer measures the resultant attenuated radiation and plots its variation with wavelength and gives rise to the absorption spectral characteristics of the sample [19].

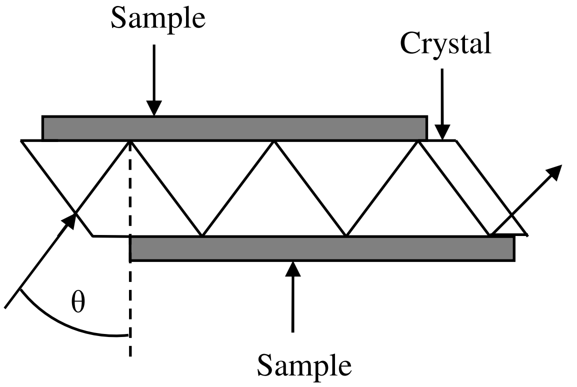


Figure 1.13 Schematic of an attenuated total reflectance cell [19]

The depth of penetration in ATR is a function of the wavelength, the refractive index of the crystal and the angle of incident radiation. The crystals used in ATR cells are made from materials which have high refractive indices, such as zinc selenide, germanium thallium iodide [19].

1.7 PREVIOUS STUDIES

In this study, it was aimed to provide antistatic character to polypropylene films by utilizing conductive fillers which function independent of humidity and eliminate the problems encountered with the use of antistatic agents, and to enhance the scratch resistance of the films by employing aromatic based additives. Previous studies on improving the antistatic ability and the scratch character of polypropylene are summarized in the following sections.

1.7.1 Improving Antistatic Ability of Polypropylene

Li et al. [8] modified a kind of inner antistatic agent by using carbon nanotubes and investigated its antistatic effect on polypropylene fibers. They synthesized carbon nanotubes by catalytic pyrolysis and prepared antistatic fibers either by mixing polypropylene with the antistatic agent and the synthesized carbon nanotubes or with antistatic agent and carbon black. They concluded that carbon nanotubes can effectively enhance the antistatic ability of polypropylene fibers when they are carried by organic antistatic agent and the antistatic effect of carbon nanotubes is higher than that of carbon black. They also concluded that the antistatic effect of carbon nanotubes can be enhanced by reducing the diameter and curvatures of carbon nanotube walls and by heat treatment.

Omastova [20] et al. prepared conducting polymer composites of polyethylene, polypropylene and poly(methyl methacrylate) with polypyrrole by chemical modification method and polypropylene and polypyrrole by mechanical mixing. They examined the effect of polymerization time, pyrrole content and temperature on conductivity of the composites. They concluded that conductivity of afore mentioned polymers can be effectively enhanced by chemical modification method and the conductivity of polypropylene-polypyrrole composites prepared by chemical modification is seven orders of magnitude higher than those of prepared by mechanical mixing. Furthermore, they determined the threshold concentration of polypyrrole for discharge of composites and the temperature limit for thermal stability of the composites.

Kandasubramanian and Gilbert [21] prepared composites of polypropylene and acrylonitrile-butadiene-styrene with nickel-coated mica fillers. They investigated the dependence of conductivity on filler concentration, amount of Ni on mica and film thickness. They concluded that conductivity increases both with increasing filler concentration and amount of Ni on mica whereas it decreases with increasing film thickness. Moreover, they concluded that better conductivity can be achieved in PP than in ABS.

1.7.2 Enhancing Scratch Resistance of Polypropylene Films

Dasari et al. [22] investigated the scratch deformation characteristics of neat and wollastonite containing polypropylenes. They concluded that density of scratch tracks is greater for neat polypropylene than wollastonite containing polypropylenes. They observed that resistance to scratch deformation decreases with the following sequence: coated and coupled wollastonite containing PP, neat PP, fine wollastonite containing PP, coarse wollastonite containing PP and coated wollastonite containing PP.

Chu et al. [23] investigated the test methods used to quantify the extent of scratch and mar damage and the effect of different mineral fillers on the scratch and mar resistance of pigmented mineral-filled polypropylene. They concluded that wollastonite can reduce the scratch depth and visibility whereas talc is not very efficient for this purpose. They also concluded that addition of an interface modifier and lubricant can further reduce scratch depth and whitening. Moreover, they obtained a correlation between scratch visibility and scratch hardness based on scratch depth measurements.

Thridandapani et al. [24] investigated the surface deformation during scratching of neat polypropylene and polypropylene-clay nanocomposites. They concluded that nanoclay has a significant effect on modulus, yield strength, elastic recovery and resistance to mechanically induced scratch damage. They also observed that in polypropylene – clay nanocomposites the severity of the scratch deformed region is considerably reduces. They also concluded that the scratch hardness is a true reflection of resistance to scratch deformation.

CHAPTER 2

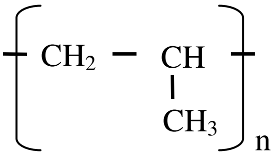
EXPERIMENTAL

2.1 MATERIALS

2.1.1 Materials Utilized in Antistatic Experiments

2.1.1.1 Polypropylene Powder

Polypropylene powder, which was used as polymer matrix in antistatic experiments, was purchased from Borealis Polymers, Belgium. Chemical structure of polypropylene is given in Figure 2.1.



$$\left[-CH_2 - \underset{\displaystyle CH_3}{\overset{}{CH}} - \right]_n$$

Figure 2.1 Structure of polypropylene

2.1.1.2 Pyrrole

The conductive filler utilized in this study was pyrrole, which was purchased from Sigma-Aldrich Co., USA. Chemical structure and basic properties of pyrrole are given in Figure 2.2 and Table 2.1, respectively.

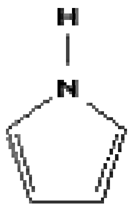


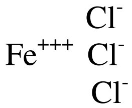
Figure 2.2 Chemical structure of pyrrole

Table 2.1 Properties of pyrrole

Property	**Value**	**Unit**
Molecular weight	67.09	g/mol
Melting point	-23	°C
Boiling point (at 769 mmHg)	129-131	°C
Flash point	36	°C
Density	0.966	g/cm^3

2.1.1.3 Iron (III) Chloride

Iron (III) chloride used in this study was obtained from ACROS Organics, Belgium. Iron (III) chloride is readily soluble in water and liquids which have donor properties, such as alcohols, ketones, ethers, nitriles and amines, whereas it is slightly soluble in nonpolar solvents such as benzene and hexane [25]. Chemical structure and properties of iron (III) chloride are given in Figure 2.3 and Table 2.2, respectively.



$$\begin{matrix} & Cl^- \\ Fe^{+++} & Cl^- \\ & Cl^- \end{matrix}$$

Figure 2.3 Chemical structure of iron (III) chloride

Table 2.2 Properties of iron (III) chloride

Property	**Value**	**Unit**
Molecular weight	162.21	g/mol
Sublimation temperature	305	ºC
Boiling point (at 760 mmHg)	332	ºC
Specific gravity	2.9	-
pH (0.1 M aqueous solution)	2.0	-
Solubility in water (at 20ºC)	920	g/l

2.1.1.4 Methanol

Methanol, which was the solvent utilized in this study, was obtained from ACROS Organics, Belgium. Chemical structure and basic properties of methanol are given in Figure 2.4 and Table 2.3, respectively.

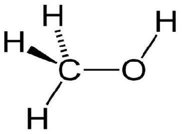


Figure 2.4 Chemical structure of methanol

Table 2.3 Properties of methanol

Property	**Value**	**Unit**
Molecular weight	32.04	g/mol
Melting point	-98	ºC
Boiling point (at 760 mmHg)	64.7	ºC
Flash point	12	ºC
Specific gravity	0.791	
Viscosity (at 20ºC)	0.55	cP

2.1.2 Materials Utilized in Anti-Scratch Experiments

2.1.2.1 Pelletized Polypropylene

Pelletized polypropylene was utilized as the polymer matrix in all of the prepared materials. Pelletized PP, which has a trade name of MH 418, was purchased from PETKIM, Izmir. Chemical structure and basic properties of the pelletized polypropylene are given in Figure 2.1 and Table 2.4, respectively.

Table 2.4 Properties of palletized polypropylene

Property	**Value**	**Unit**	**Test Method**
Melt flow rate (2160 g, 230ºC)	4.0 – 6.0	g/10 min	ASTM D1238
Tensile strength at yield	350	kg/cm^2	ASTM D638
Tensile strength at break	430	kg/cm^2	ASTM D638
Color B 10 D 65	1.8	-	Hunter Lab. CQ

2.1.2.2 Maleic Anhydride Grafted Polypropylene

Maleic anhydride grafted polypropylene adds polarity to polypropylene matrices, improves its reactivity and therefore achieves compatibility in polypropylene based materials. Maleic anhydride grafted polypropylene, which has a trade name of EXXELOR PO 1015, was supplied by ExxonMobil Chemical, Belgium. Chemical structure of maleic anhydride and basic properties of maleic anhydride grafted polypropylene are given in Figure 2.5 and Table 2.5, respectively.

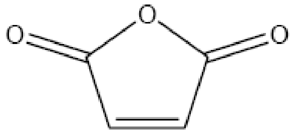


Figure 2.5 Chemical structure of maleic anhydride

Table 2.5 Properties of maleic anhydride grafted polypropylene

Property	Value	Unit	Test Method
Maleic anhydride graft level	0.25-0.5	%	FTIR EPK-04 QT-02
Melt flow index (1.2 kg, 190°C)	22	g/10 min	ASTM D1238
Melt flow rate (2.16 kg, 230°C)	~150	g/10 min	ASTM D1238
Density	0.9	g/cm^3	DIN 53479
Melting point	138	°C	DSC
Volatiles	0.2 max.	%	AM-S 350.03
Color	30 max.	Yellowness index pellet	ASTM E313-96

2.1.2.3 Naphthalene Derivatives

Three different naphthalene derivatives, namely 1,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene and 2,7-dihydroxynaphthalene, were utilized in this study and they were purchased from ACROS Organics, Belgium. Chemical structures and basic properties of 1,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene and 2,7-dihydroxynaphthalene are given in Figure 2.6, Figure 2.7, Figure 2.8 and Table 2.6, respectively.

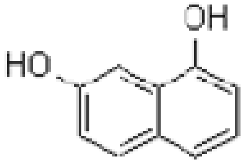


Figure 2.6 Chemical structure of 1,7-dihydroxynaphthalene

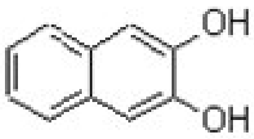


Figure 2.7 Chemical structure of 2,3-dihydroxynaphthalene

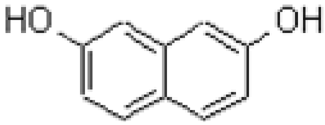


Figure 2.8 Chemical structure of 2,7-dihydroxynaphthalene

Table 2.6 Properties of naphthalene derivatives

Material	**Property**		
	Molecular weight	**Melting point**	**Flash point**
1,7-dihydroxynaphthalene	106.17 g/mol	178-182ºC	252ºC
2,3-dihydroxynaphthalene	106.17 g/mol	162-166ºC	175ºC
2,7-dihydroxynaphthalene	106.17 g/mol	184-189ºC	-

2.1.2.4 p-Phenylene Diamine

p-Phenylene diamine used in this study was purchased from Sigma-Aldrich Co., USA. Chemical structure and basic physical and chemical properties of p-phenylene diamine are illustrated in Figure 2.9 and Table 2.7, respectively.

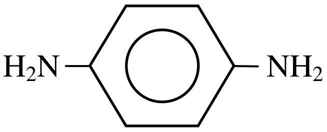


Figure 2.9 Chemical structure of p-phenylene diamine

Table 2.7 Physical and chemical properties of p-phenylene diamine

Property	**Value**	**Unit**
Molecular weight	108.14	g/mol
pH (at 20ºC, 50 g/l)	9	
Melting point	141	ºC
Boiling point (at 760 mmHg)	267	ºC
Flash point	110	ºC
Vapor pressure (at 100ºC)	1.08	mmHg
Vapor density	3.7	g/l
Bulk density	600	kg/l
Solubility (in water, 20ºC)	10	mg/ml

2.1.2.5 Hydroquinone

Hydroquinone utilized in this study was purchased from Merck Schuchardt OHG, Germany. Chemical structure and basic physical and chemical properties of hydroquinone are given in Figure 2.10 and Table 2.8, respectively.

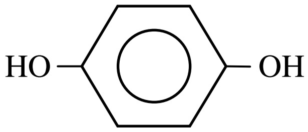


Figure 2.10 Chemical structure of hydroquinone

Table 2.8 Physical and chemical properties of hydroquinone

Property	**Value**	**Unit**
Molecular weight	110.11	g/mol
pH (at 20°C, 70 g/ml H_2O)	3.75	
Melting point	172	°C
Boiling point	287	°C
Flash point	165	°C
Relative vapor density	3.81	
Density (25°C)	1.358	g/cm^3
Bulk density	~600	kg/m^3
Solubility (in water, 25°C)	70	g/l

2.2 EXPERIMENTAL PROCEDURE

2.2.1 Antistatic Experiments

2.2.1.1 Preparation of Polypropylene – Polypyrrole Composites

Polypropylene – polypyrrole composites were prepared by chemical modification. Initially, polypropylene particles were dispersed in 160 ml of water – methanol mixture with a volume ratio of 2.5. Then, $FeCl_3$ was added. Next, a certain amount of pyrrole was dissolved in methanol and added dropwise under vigorous stirring for 5 hours. The molar ratio of $FeCl_3$ to pyrrole was kept constant as 2.3. The pyrrole concentrations were taken to be 2%, 5%, 7% and 9%. Finally, the reaction product was filtered, washed with distilled water and methanol and dried in a vacuum oven at 50°C. The experimental procedure for preparation of polypropylene – polypyrrole composites is illustrated in Figure 2.11.

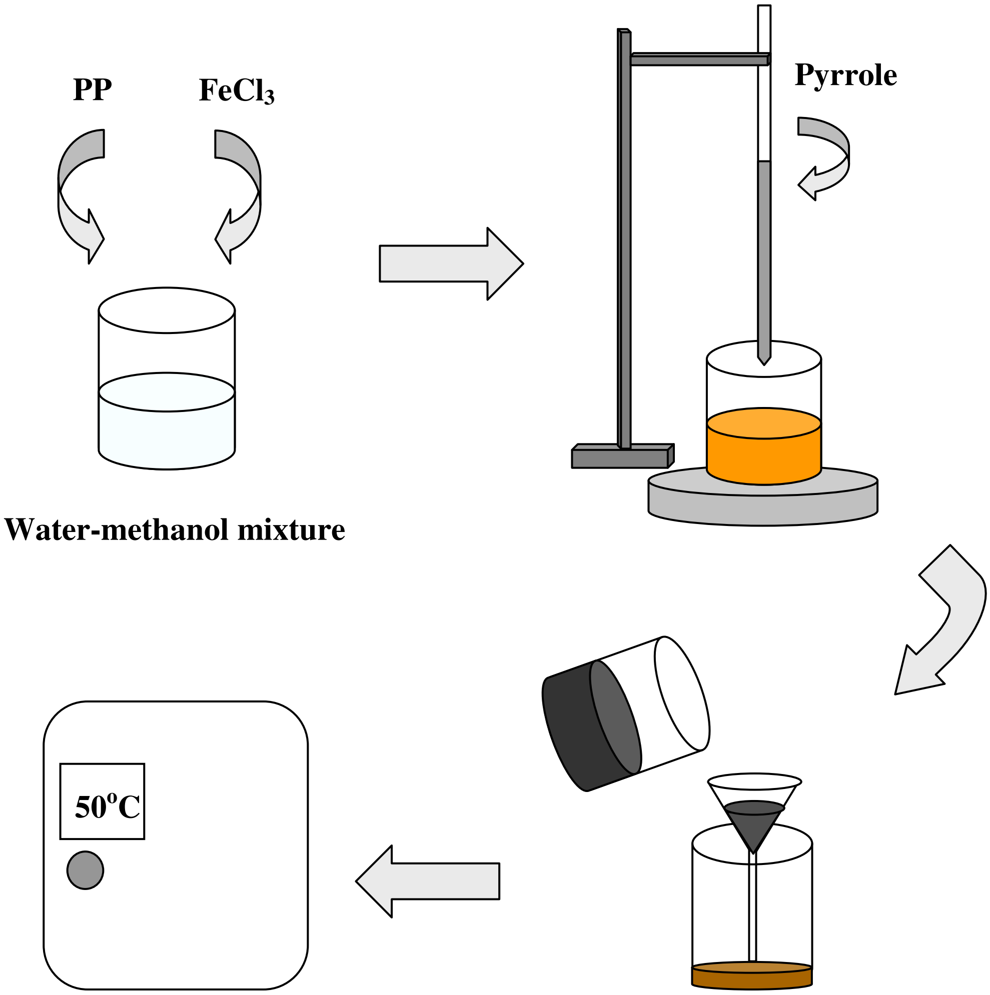


Figure 2.11 Schematic of preparation of polypropylene - polypyrrole composites

2.2.1.2 Conductivity Measurement

The electrical conductivities of the prepared composites were measured by using Keithley 2400 Sourcemeter. At least six copper wire pieces were fixed into the prepared polypropylene - polypyrrole composites with different pyrrole content and the samples were compression molded for 6 minutes at 230ºC. Then, the probes of the sourcemeter were attached to either two of the copper wires embedded in the films and resistivity values were directly obtained by the provided computer software. Three measurements were taken for each sample.

2.2.2 Anti-Scratch Experiments

2.2.2.1 Preparation of Materials

Polypropylene based materialss were prepared by using an internal mixer, namely Brabender Plasti-Corder Torque Rheometer, PLV-151. Polypropylene, maleic anhydride grafted polypropylene and one of aromatic structured additives mentioned above were mixed in a beaker and fed to the internal mixer simultaneously. The operating temperature, speed and process time were determined as 200-210°C, 60 rpm and 15 minutes, respectively. The prepared materials were dried in a vacuum oven at 50ºC. The compositions of the prepared materials are listed in Table 2.9.

2.2.2.2 Preparation of the Films

The prepared materials were compression molded by using a laboratory scale press, namely Rucker PHI, in order to obtain samples both for scratch test and tensile test. The blends were preheated for 10 minutes at 230ºC and then molded for 3 minutes with a pressure of 20 bars. The films were immersed in cold water when they are removed from the press. The films prepared for the scratch test had dimensions of 15 cm × 15 cm × 1 mm whereas the films prepared for the tensile test had dimensions of 11 cm × 11 cm × 1 mm.

2.2.2.3 Scratch Test

The prepared films were scratched with constant loads of 100 g and 200 g by using Heidon 18L Scratch Resistance Tester.

Table 2.9 Compositions of the prepared materials (wt%)

Sample no	**Polypropylene**	**Maleic anhydride grafted PP**	**1,7-dihydroxynaphthalene**	**2,3-dihydroxynaphthalene**	**2,7-dihydroxynaphthalene**	**p-phenylene diamine**	**hydroquinone**
1	97	1.5	1.5	-	-	-	-
2	95	2.5	2.5	-	-	-	-
3	92	4	4	-	-	-	-
4	92	6	2	-	-	-	-
5	97	1.5	-	1.5	-	-	-
6	95	2.5	-	2.5	-	-	-
7	92	4	-	4	-	-	-
8	92	6	-	2	-	-	-
9	97	1.5	-	-	1.5	-	-
10	95	2.5	-	-	2.5	-	-
11	92	4	-	-	4	-	-
12	92	6	-	-	2	-	-
13	97	1.5	-	-	-	1.5	-
14	95	2.5	-	-	-	2.5	-
15	92	4	-	-	-	4	-
16	92	6	-	-	-	2	-
17	97	1.5	-	-	-	-	1.5
18	95	2.5	-	-	-	-	2.5
19	92	4	-	-	-	-	4
20	92	6	-	-	-	-	2

2.2.3 Characterization Experiments

2.2.3.1 Tensile Test

Prior to performing tensile test, five dog bone shaped specimens for each material, neat polypropylene and maleic anhydride grafted polypropylene were prepared. The shape and dimensions of the specimens are illustrated in Figure 2.12 and Table 2.10, respectively. Tensile test was performed according to ASTM D638M-91a (Standard Test Method for Tensile Properties of Plastics) by using a Lloyd LR 5 K computer controlled tensile test machine. The crosshead speed of the machine was set at the rate of 5 cm/min.

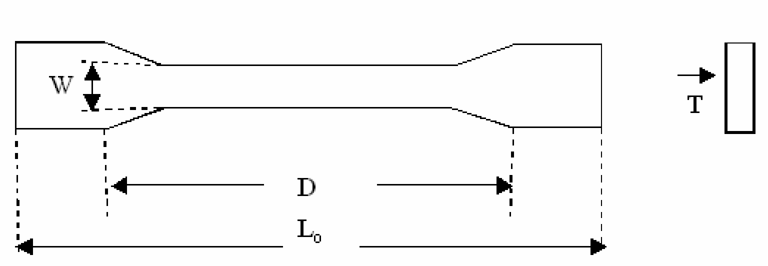


Figure 2.12 Tensile test specimen

Table 2.10 Tensile test specimen dimensions

Symbol	Specimen dimensions (mm)
W, Width of narrow section	3.0
D, Distance between grips	50.0
L_0, Total length of specimen	100.0
T, Thickness of specimen	1.0

2.2.3.2 Differential Scanning Calorimetry

Differential scanning calorimetry analysis was performed by 91OS Differential Scanning Calorimeter in order to observe the possible changes in glass transition and melting temperatures due to the presence of aromatic based additives.

Approximately 5 mg of each sample were prepared for the analysis. The samples were heated from -100ºC to 250ºC at a rate of 10ºC/min. The thermograms were recorded under nitrogen atmosphere.

2.2.3.3 Scanning Electron Microscopy

Films of neat polypropylene and the prepared polypropylene based materials, which had been scratched with constant loads, were examined by a JEOL JSM-6400 Scanning Electron Microscope. The scratched surfaces were coated with a thin layer of gold in order to provide conductive surfaces. SEM photographs were taken at ×300 magnification.

2.2.3.4 Microscopy

Scratch widths of polypropylene and polypropylene based materials were investigated by a TOPCON T.U.M measuring microscope. Three measurements were taken for each sample.

2.2.3.5 Attenuated Total Reflectance Spectroscopy

Attenuated Total Reflectance analysis was performed by IRPRESTIGE 21 Spectrophotometer. Very small pieces of films with a thickness of 1 mm were prepared prior to the analysis. Wavenumbers vs. percent transmittance data were obtained directly by the provided computer software.

Figure 2.13 Schematic of attenuated total reflectance spectroscopy

CHAPTER 3

RESULTS AND DISCUSSION

3.1 ANTISTATIC PROPERTY

Pyrrole, which is a conductive filler, was used in order to provide antistatic character to the polypropylene films. Polypropylene - polypyrrole composites containing 2%, 5%, 7% and 9% pyrrole were synthesized by chemical modification. The main reason for utilizing polypropylene powder in the synthesis of these composites was to provide the adsorption of pyrrole on polypropylene surface and prevent the dispersion of pyrrole in bulk polypropylene. The electrical conductivities of the prepared composites were measured by using Keithley 2400 Sourcemeter. Effect of pyrrole content on the conductivity of polypropylene films is shown in Figure 3.1.

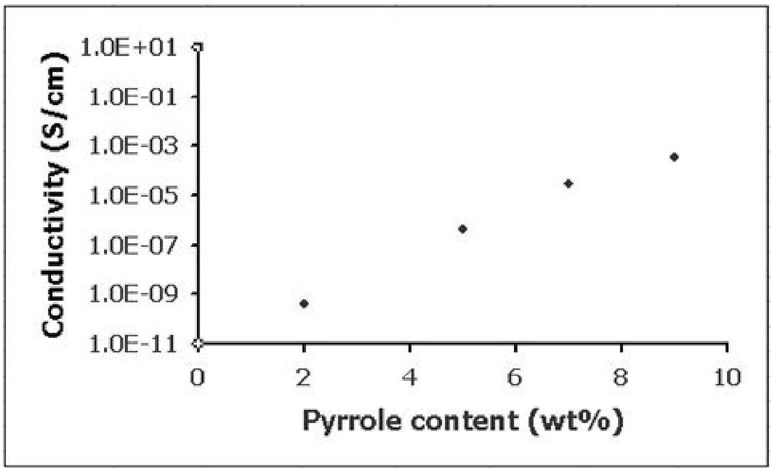


Figure 3.1 Effect of pyrrole content on the conductivity of polypropylene films

Figure 3.1 illustrates that conductivity of polypropylene films increases with increasing pyrrole concentration. Based on the surface resistivity scale given in Figure 3.2, 2% of pyrrole is sufficient to provide antistatic character to polypropylene films. Moreover, polypropylene films achieve conductive character when the pyrrole content exceeds 7%.

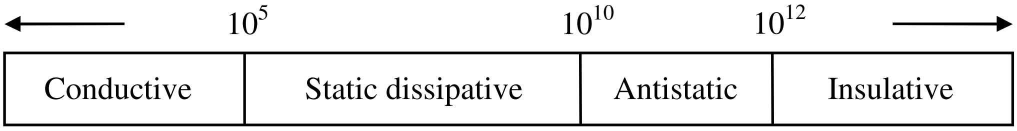


Figure 3.2 Surface resistivity scale (ohm/sq) [26]

3.2 ANTI-SCRATCH PROPERTY

3.2.1 Morphological Analysis

Scanning electron microscopy (SEM) analysis was performed in order to observe the surface morphology of the scratch damaged regions of neat and additive containing polypropylene films, which were scratched with constant loads of 100 g and 200 g. Compositions of the samples that were analyzed by SEM are given in Table 3.1. All SEM micrographs are presented at x300 magnification.

Table 3.1 Compositions of the samples in SEM analysis (wt%)

Sample	**1**	**2**	**3**	**4**	**5**
Polypropylene	100	92	92	92	92
Maleic anhydride grafted polypropylene	-	6	6	6	6
1,7-Dihydroxynaphthalene	-	2	-	-	-
2,3-Dihydroxynaphthalene	-	-	2	-	-
2,7-Dihydroxynaphthalene	-	-	-	2	-
p-Phenylene diamine	-	-	-	-	2

Figure 3.3 illustrates the scratch damaged regions of neat polypropylene films whereas Figures 3.4-3.7 illustrate the scratch damaged regions of polypropylene based materials containing 1,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,7-dihydroxynaphthalene and p-phenylene diamine as additives, respectively.

It can be clearly observed from the figures that the scratch tracks were formed consecutively in a zig-zag manner both in neat PP and additive containing PP films, which were scratched with a load of 100 g. Additive containing PP films, which were scratched with a load of 200 g, showed the same zig-zag manner. However, neat polypropylene film, which was scratched with a load of 200 g, showed a somewhat desultory behavior.

The consecutive zig-zag nature of the scratch tracks can be attributed to the stick-slip motion between the tip and the surface of the material. In scratch test, a hard object such as an indenter or a stylus is pressed onto the material surface under a normal load and moved by a horizontal force in order to form a groove. Based on the loading system, the groove is usually not smooth and includes deep indents connected by shallower grooves of non-uniform depths [27]. In the stick-slip process, there is no relative motion between the two contact surfaces during the stick stage. However, the indenter applies stress on the polymer surface and therefore the material beneath the indenter is deformed. The horizontal or tangential stress is less than the critical stress; however, it increases with time. When the stress applied on the polymer surface exceeds the critical stress, the slip stage begins and lasts until the stress decreases below the critical stress. When the stress reduces below the critical stress, the indenter and the polymer surface stick again. During the slip stage, the material accumulates ahead of the indenter. Consequently, the periodic scratch tracks demonstrate sequential accumulation and release of tangential force [11].

Figures 3.3-3.7 illustrate that both the neat PP and additive containing PP films have apparent boundaries between the scratch and the unscratched area. There is not a considerable difference between the sharpness of the boundaries observed in the samples. However, the boundary between the scratch and the film surface in the material containing 2,7-dihydroxynaphthalene as the additive is slightly blunter as it can be seen in Figure 3.6. The distinct boundary between the scratch and the unscratched area indicates that the material is deformed mainly in a plastic manner whereas indistinctness of the boundary implies that the material is deformed mainly in an elastic manner with little plastic flow [28].

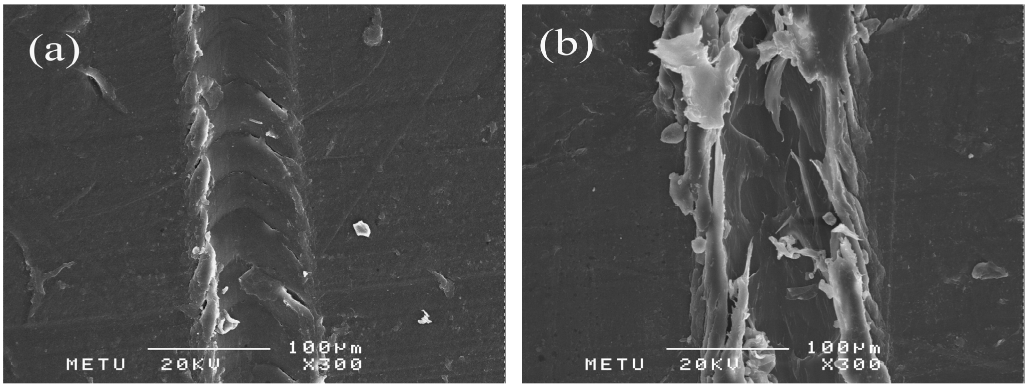


Figure 3.3 SEM micrographs of scratched polypropylene (a) with a load of 100 g (b) with a load of 200 g

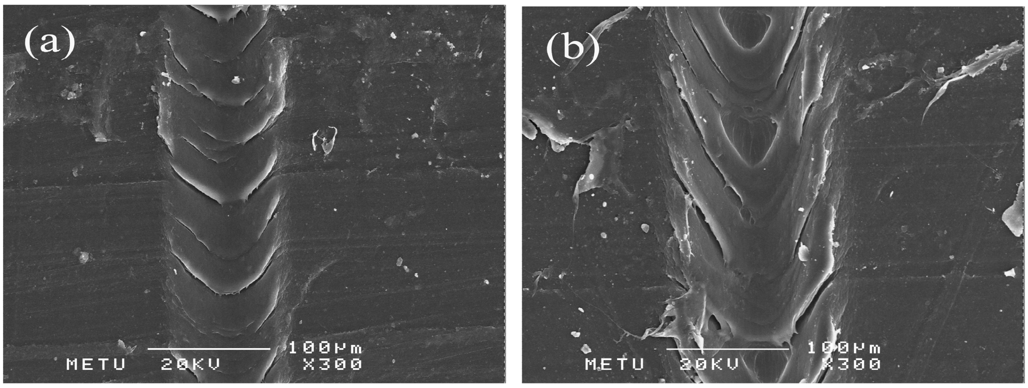


Figure 3.4 SEM micrographs of scratched film containing 1,7-dihydroxynaphthalene (a) with a load of 100 g (b) with a load of 200 g

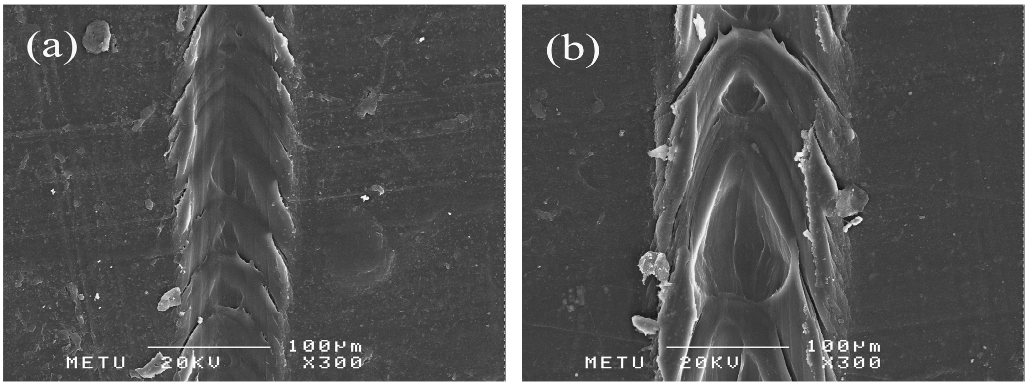


Figure 3.5 SEM micrographs of scratched film containing 2,3-dihydroxynaphthalene (a) with a load of 100 g (b) with a load of 200 g

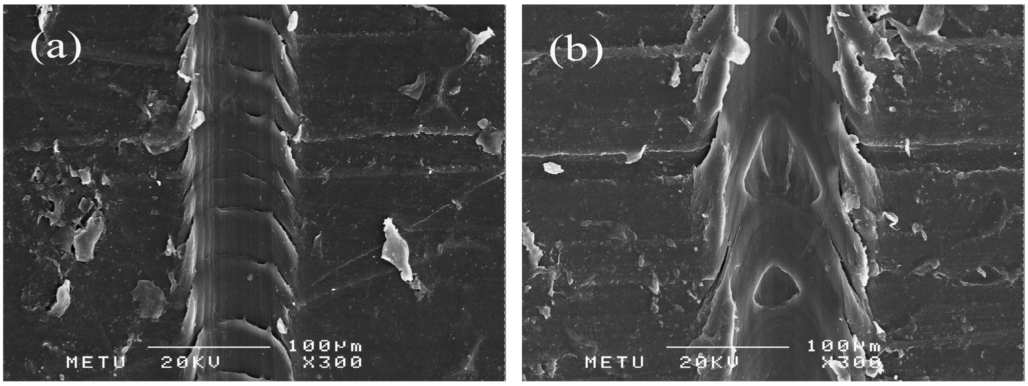


Figure 3.6 SEM micrographs of scratched film containing 2,7-dihydroxynaphthalene (a) with a load of 100 g (b) with a load of 200 g

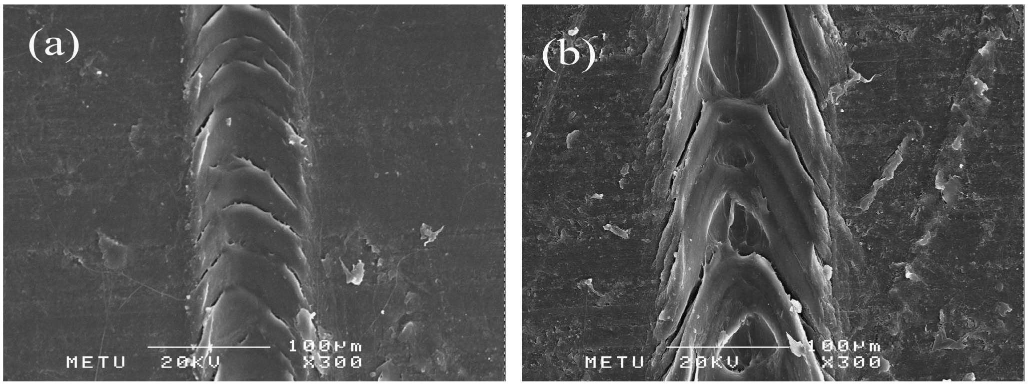


Figure 3.7 SEM micrographs of scratched film containing p-phenylene diamine (a) with a load of 100 g (b) with a load of 200 g

Scratch hardness is one of the characteristics of the material which indicates its scratch deformation resistance. Like indentation hardness, scratch hardness is a measure of force applied to the sample per unit area and it can be calculated as follows [11]:

$$H_{scratch} = \frac{L_{scratch}}{A} \tag{3.1}$$

where $H_{scratch}$ is the scratch hardness, $L_{scratch}$ is the applied load and A is the load supporting area. The load supporting area is $\pi w^2/4$ for a conical indenter, where w is the scratch width. Consequently, Eq. 3.1 can be rewritten as follows [11]:

$$H_{scratch} = \frac{4L_{scratch}}{\pi w^2} \tag{3.2}$$

In order to determine the scratch hardness of polypropylene based materials, scratch widths of each sample were obtained by a measuring microscope. Then, scratch hardness of the materials were calculated by using Eq. 3.2. The compositions of the samples that were investigated by the measuring microscope and the scratch width and scratch hardness of each sample are given in Table 3.2 and Table 3.3, respectively.

As Table 3.3 clearly demonstrates, scratch width of the polypropylene film decreases and therefore its scratch hardness increases significantly with the insertion of PP-*g*-MA and the aromatic based additives. It was observed that the materials containing 2% of aromatic based additive and 6% PP-*g*-MA have the highest scratch hardness values both for the samples scratched with a load of 100 g and 200 g. This may be due to the higher cross-linking achieved with increasing amount of maleic anhydride. In addition, the material containing 2% 1,7-dihydroxynaphthalene and 6% PP-*g*-MA introduces the highest enhancement in scratch hardness by more than 60%.

It was also observed that the effect of additive concentration on the scratch hardness varies according to the additive type. In the materials containing equal amounts of PP-*g*-MA and 1,7-dihydroxynaphthalene or 2,3-dihydroxynaphthalene, scratch hardness increases with increasing additive content. On the other hand, in the materials containing equal amounts of PP-*g*-MA and 2,7-dihydroxynaphthalene, p-phenylene diamine or hydroquinone, scratch hardness first increases and then decreases with increasing additive content.

Table 3.2 Compositions of the samples investigated with microscope (wt%)

Sample no	**Polypropylene**	**Maleic anhydride grafted PP**	**1,7-dihydroxynaphthalene**	**2,3-dihydroxynaphthalene**	**2,7-dihydroxynaphthalene**	**p-phenylene diamine**	**hydroquinone**
1	97	1.5	1.5	-	-	-	-
2	95	2.5	2.5	-	-	-	-
3	92	4	4	-	-	-	-
4	92	6	2	-	-	-	-
5	97	1.5	-	1.5	-	-	-
6	95	2.5	-	2.5	-	-	-
7	92	4	-	4	-	-	-
8	92	6	-	2	-	-	-
9	97	1.5	-	-	1.5	-	-
10	95	2.5	-	-	2.5	-	-
11	92	4	-	-	4	-	-
12	92	6	-	-	2	-	-
13	97	1.5	-	-	-	1.5	-
14	95	2.5	-	-	-	2.5	-
15	92	4	-	-	-	4	-
16	92	6	-	-	-	2	-
17	97	1.5	-	-	-	-	1.5
18	95	2.5	-	-	-	-	2.5
19	92	4	-	-	-	-	4
20	92	6	-	-	-	-	2

Table 3.3 Scratch width and scratch hardness of PP and PP based materials

Material	1st scratch*		2nd scratch*	
	Scratch width (μm)	Scratch hardness (kg/mm^2)	Scratch width (μm)	Scratch hardness (kg/mm^2)
PP	79	20.4	142	12.6
1	74	23.3	126	16.0
2	73	23.9	131	14.8
3	71	25.3	124	16.6
4	62	33.1	110	21.0
5	77	21.5	136	13.8
6	72	24.6	138	13.4
7	67	28.4	125	16.3
8	65	30.1	115	19.3
9	69	26.7	126	16.0
10	74	23.3	135	14.0
11	70	26.0	123	16.8
12	69	26.7	120	17.7
13	67	28.4	124	16.6
14	72	24.6	132	14.6
15	65	30.1	118	18.3
16	63	32.1	114	19.6
17	68	27.5	123	16.8
18	72	24.6	131	14.8
19	66	29.2	126	16.0
20	63	32.1	113	19.9

*1st and 2nd scratches represent the scratches formed with a load of 100 g and 200 g, respectively.

3.2.2 Mechanical Analysis

Tensile test was performed in order to examine the effects of additive type and concentration on the mechanical properties of polypropylene based materials. Young's modulus, tensile strength and elongation at break values of each sample were obtained by means of stress-strain curves and compared with those of neat polypropylene.

Figures 3.8-3.12 present the effect of additive concentration on Young's modulus of the polypropylene based materials containing 1,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, p-phenylene diamine and hydroquinone as additives, respectively. As it can be seen from Figures 3.8-3.12, insertion of the additives enhances Young's modulus of polypropylene in all materials except for the material containing hydroquinone as additive.

Effect of 1,7-dihydroxynaphthalene content on the Young's modulus of the polypropylene based materials is illustrated in Figure 3.8. The material including 1.5% additive gives the highest Young's modulus value. As the additive content increases, Young's modulus first decreases and then increases again. The same behavior is observed in the materials containing 2,3-dihydroxynapthalene and 2,7-dihydroxynaphthalene as shown in Figure 3.9 and 3.10. On the other hand, Young's modulus decreases with increasing additive content in the materials including p-phenylene diamine and hydroquinone as shown in Figure 3.11 and 3.12. This may result from the softening effect of maleic anhydride grafted polypropylene, which can be observed better when the materials consisting of same percentage of PP but different percentages of maleic anhydride grafted PP and additive are compared.

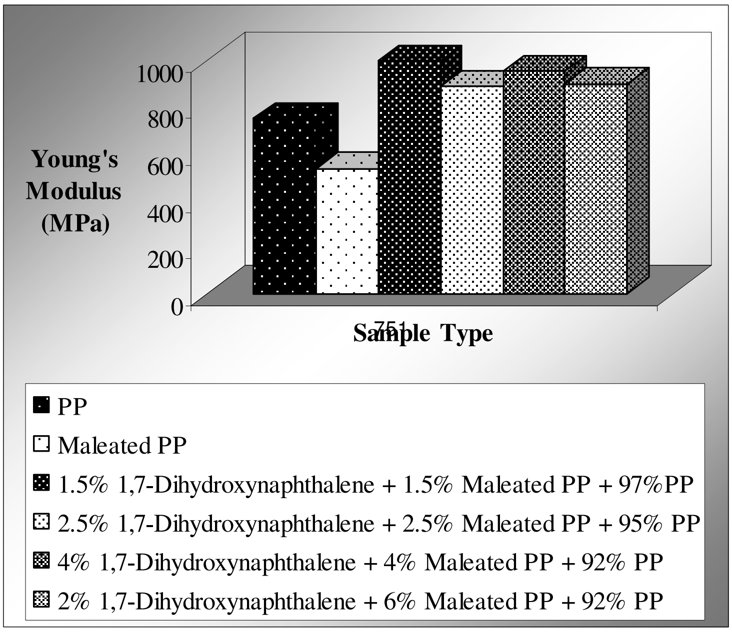


Figure 3.8 Effect of 1,7-dihydroxynaphthalene concentration on Young’s Modulus of the polypropylene based materials

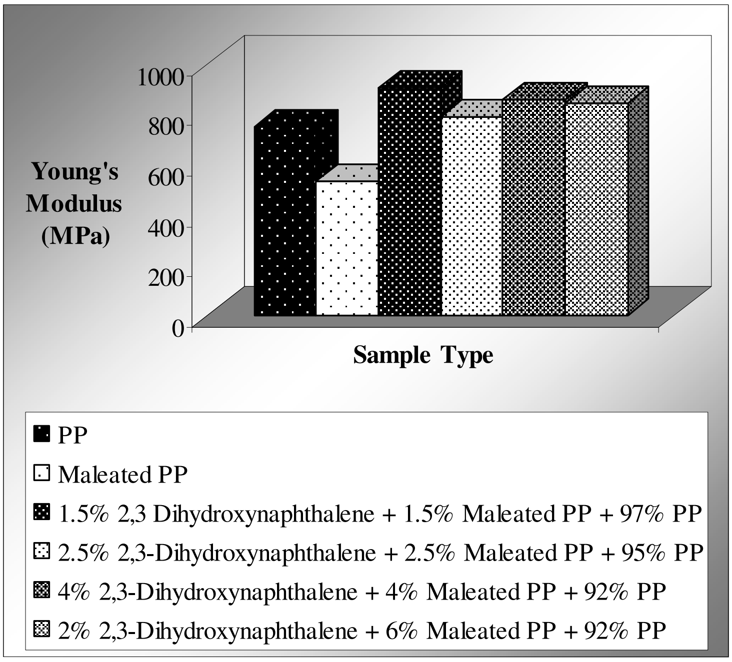


Figure 3.9 Effect of 2,3-dihydroxynaphthalene concentration on Young’s Modulus of the polypropylene based materials

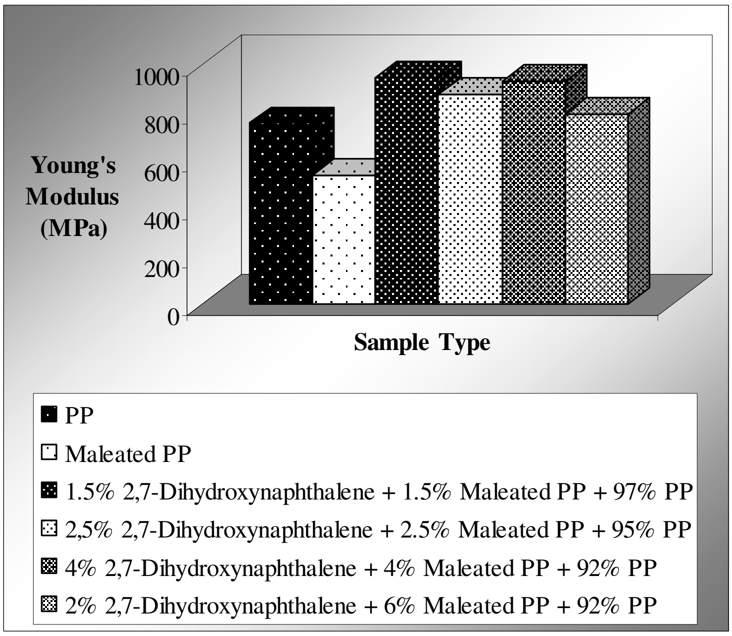


Figure 3.10 Effect of 2,7-dihydroxynaphthalene concentration on Young's Modulus of the polypropylene based materials

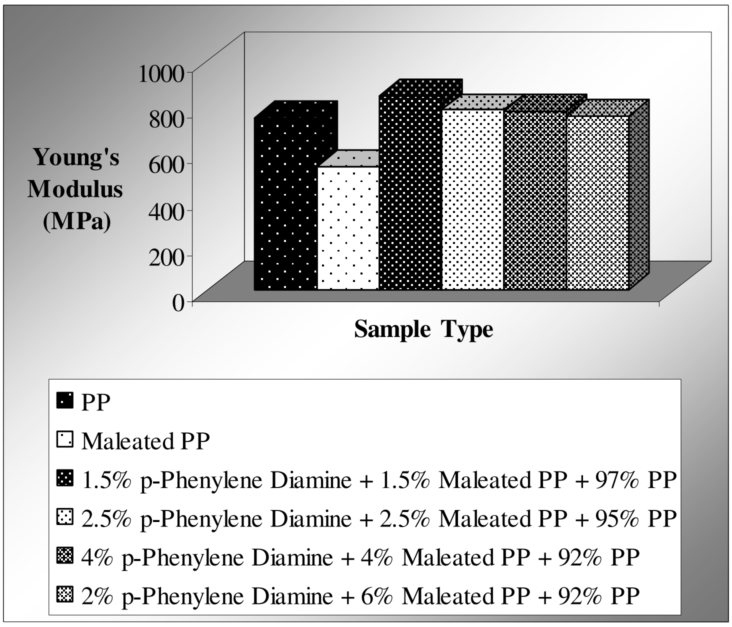


Figure 3.11 Effect of p-phenylene diamine concentration on Young's Modulus of the polypropylene based materials

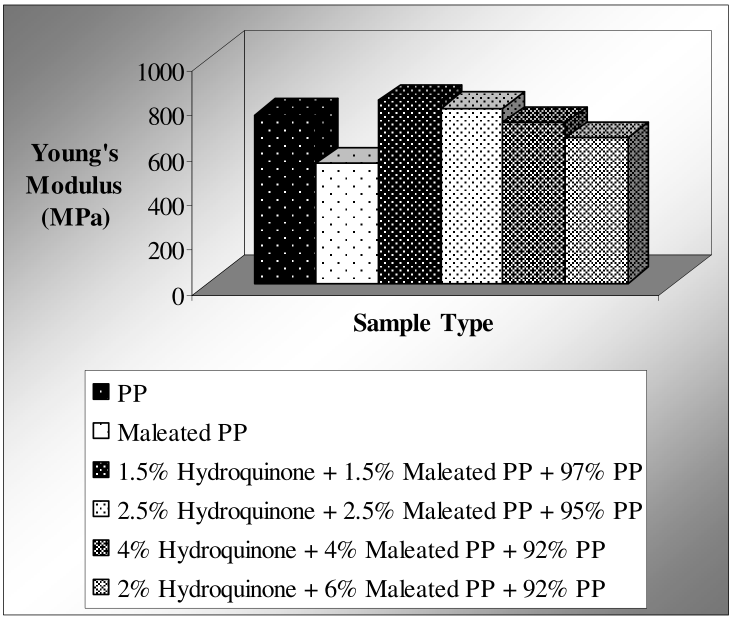


Figure 3.12 Effect of hydroquinone concentration on Young's Modulus of the polypropylene based materials

As illustrated in Figure 3.13, the highest enhancement in Young's modulus is achieved in the materials containing 1,7-dihydroxynaphthalene, followed by those containing 2,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene and p-phenylene diamine. This may be attributed to the fact that modulus is strongly dependent on the stiffening groups on the polymer chain backbone or side chain. Naphthalene derivates have greater stiffening effect than that of p-phenylene diamine. Moreover, the difference between the effects of the naphthalene derivatives on Young's modulus can be due to the fact that the positions of the functional groups in 1,7-dihydroxynaphthalene and 2,7-dihydroxynaphthalene make the intermolecular attractions easier. On the other hand, in 2,3-dihydroxynaphthalene, intermolecular attractions are limited because of steric hindrance.

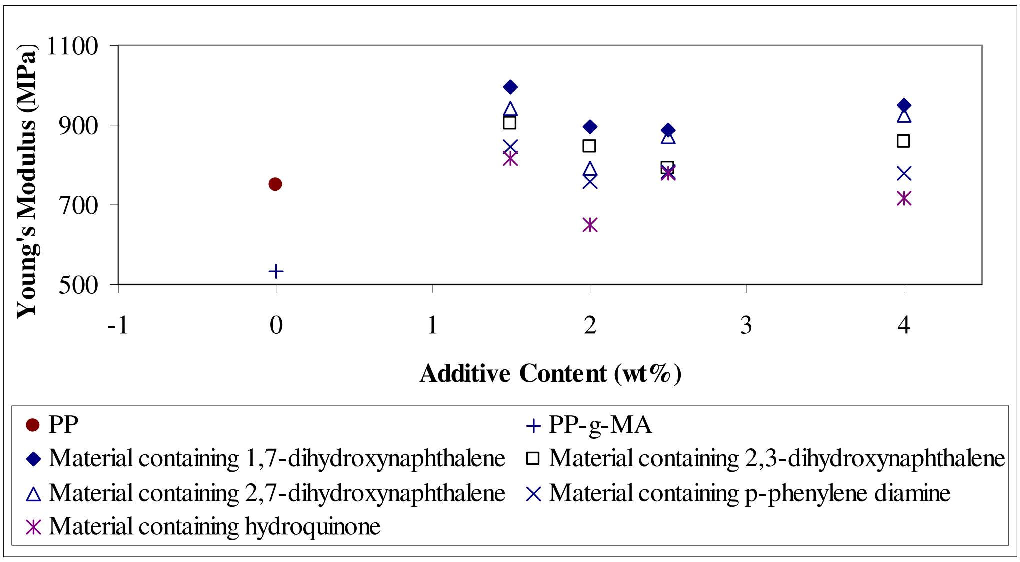


Figure 3.13 Effect of additive type and concentration on Young's Modulus of the polypropylene based materials

The effect of additive concentration on the tensile strength of the polypropylene based materials involving 1,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, p-phenylene diamine and hydroquinone as additives are presented in Figures 3.14-3.18, respectively. The figures clearly demonstrate that tensile strengths of all materials are much higher than that of neat polypropylene regardless of the additive type.

The additive content does not influence the tensile strength significantly in the materials including 1,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene and p-phenylene diamine. However, tensile strength decreases considerably when the additive content is increased from 1.5% to 2.5% in the materials containing 2,7-dihydroxynapthalene and hydroquinone.

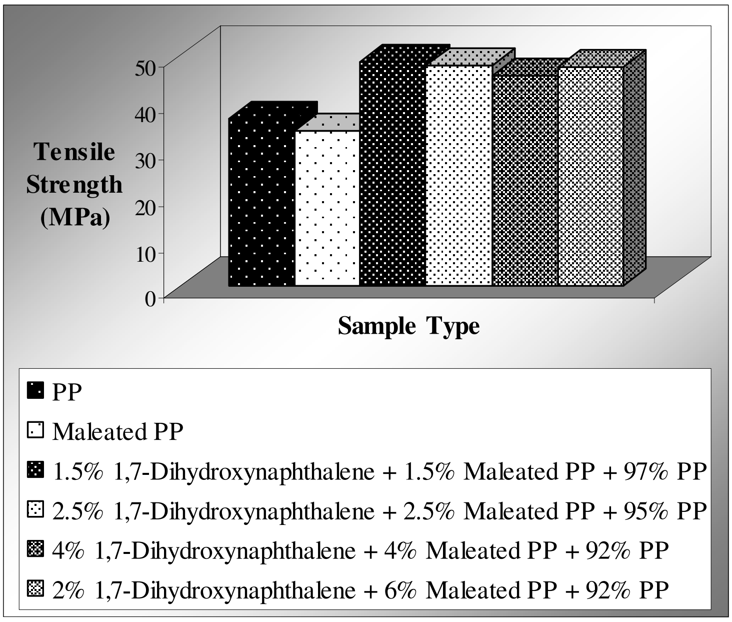


Figure 3.14 Effect of 1,7-dihydroxynaphthalene concentration on the tensile strength of the polypropylene based materials

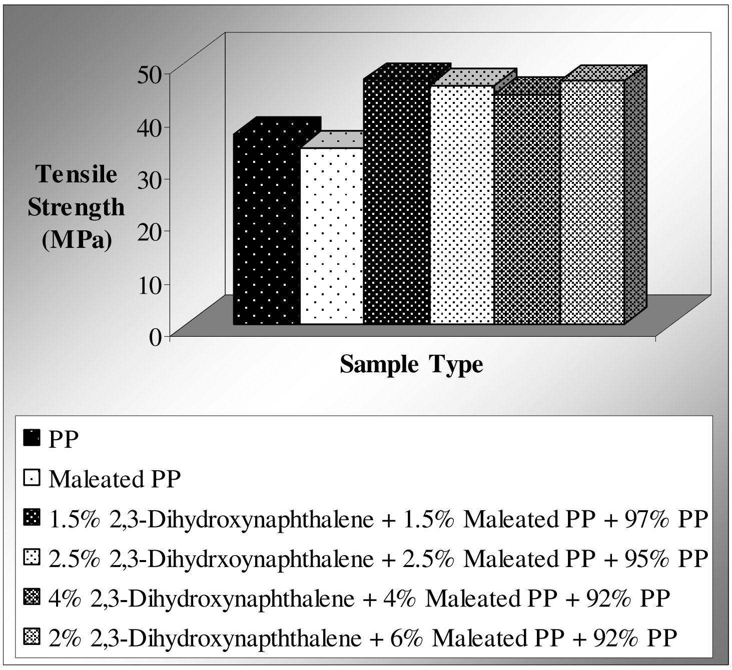


Figure 3.15 Effect of 2,3-dihydroxynaphthalene concentration on the tensile strength of the polypropylene based materials

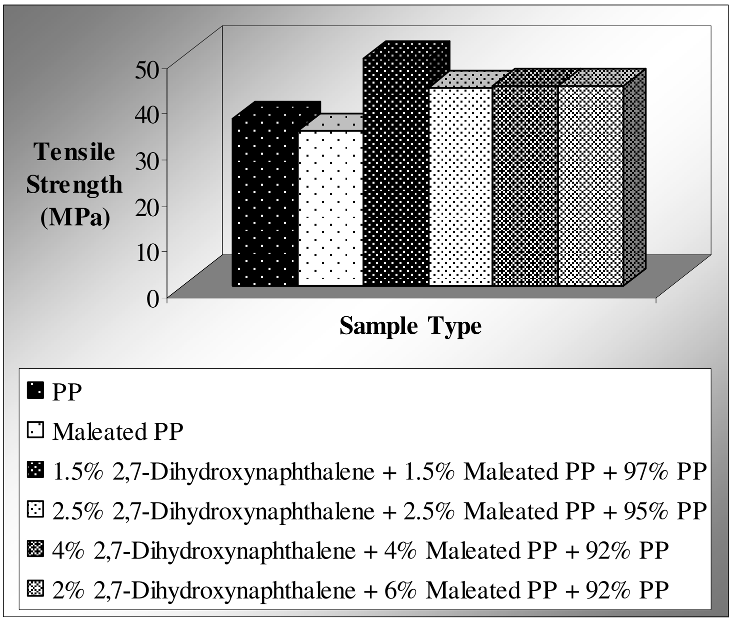


Figure 3.16 Effect of 2,7-dihydroxynaphthalene concentration on the tensile strength of the polypropylene based materials

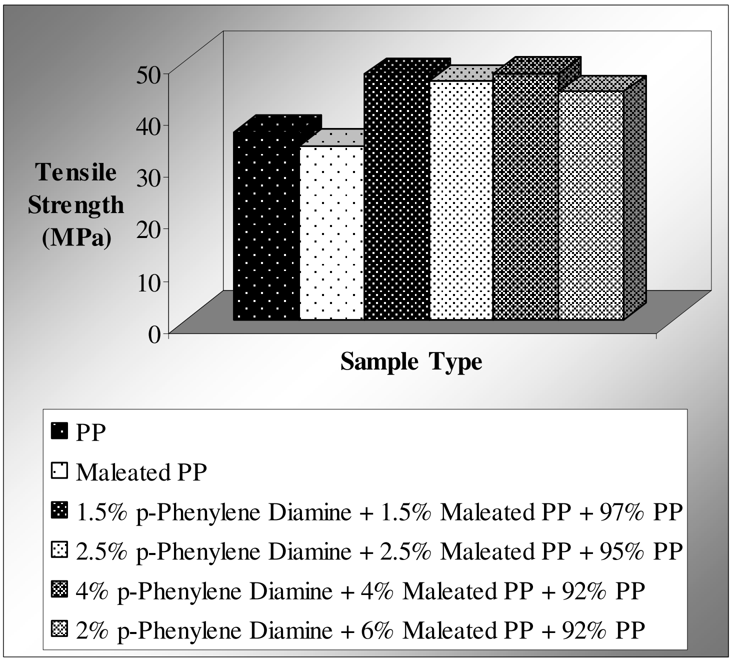


Figure 3.17 Effect of p-phenylene diamine concentration on the tensile strength of the polypropylene based materials

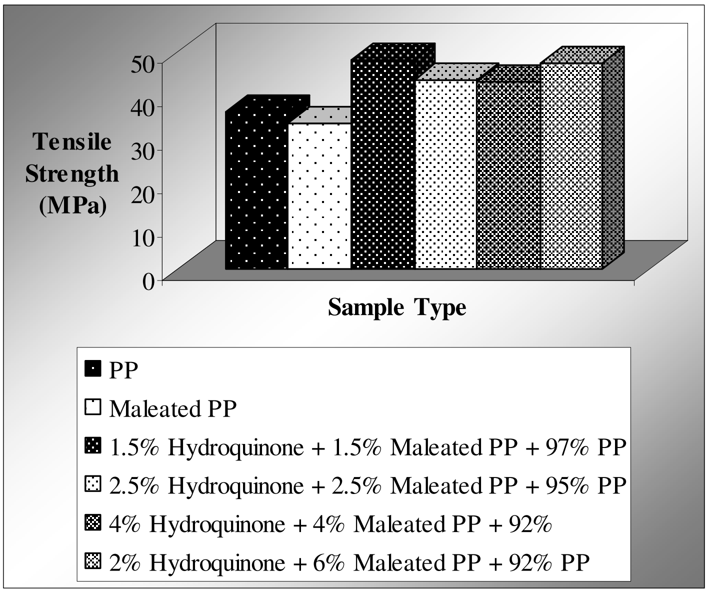


Figure 3.18 Effect of hydroquinone concentration on the tensile strength of the polypropylene based materials

The largest increase in the tensile strength is observed in the polypropylene based materials including 1,7-dihydroxynaphthalene, followed by p-phenylene diamine, 2,3-dihydroxynaphthalene, hydroquinone and 2,7-dihydroxynaphthalene as shown in Figure 3.19.

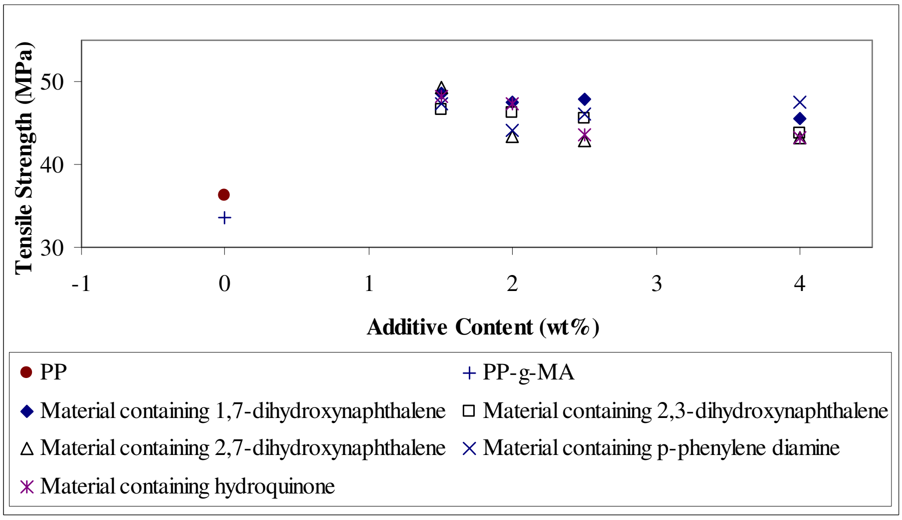


Figure 3.19 Effect of additive type and concentration on the tensile strength of the polypropylene based materials

Elongation at break indicates the ductility and toughness of the material. Figures 3.20-3.24 demonstrate the effect of additive concentration on elongation at break of the polypropylene based materials containing 1,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, p-phenylene diamine and hydroquinone as additives, respectively. As it can be seen from the figures, each material containing a different additive shows a different trend with increasing concentration. However, it is obvious that elongation at break values are significantly enhanced with the insertion of the additives. This significant increase in elongation at break values may result from the possible bonding between the end groups of the additives and the ester group of the maleic anhydride grafted PP and therefore formation of crosslinks.

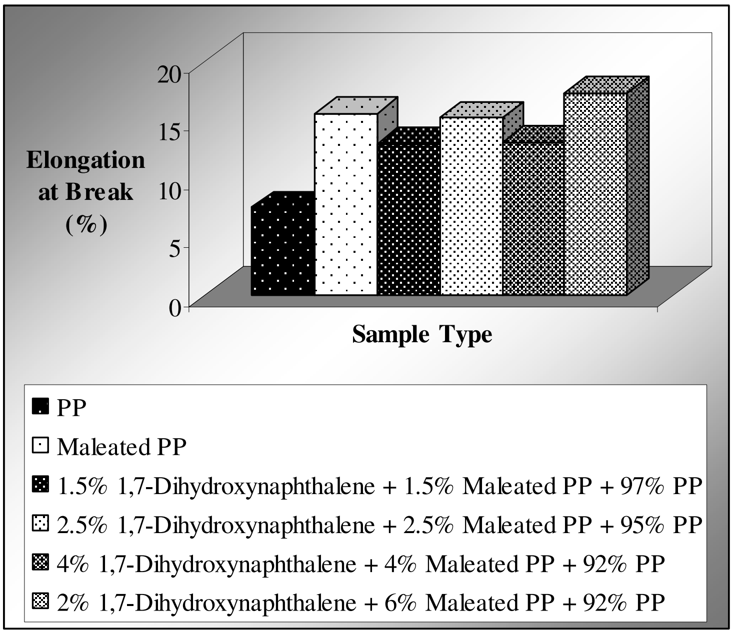


Figure 3.20 Effect of 1,7-dihydroxynaphthalene concentration on the elongation at break of the polypropylene based materials

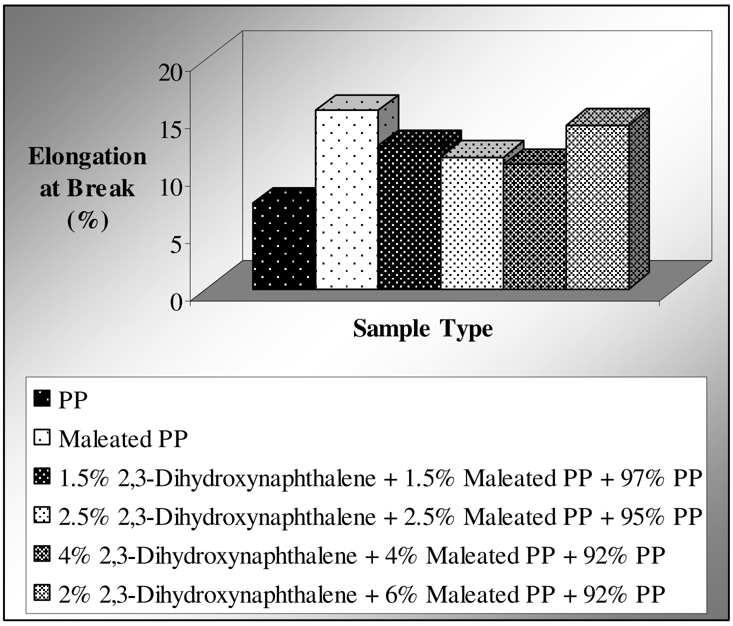


Figure 3.21 Effect of 2,3-dihydroxynaphthalene concentration on the elongation at break of the polypropylene based materials

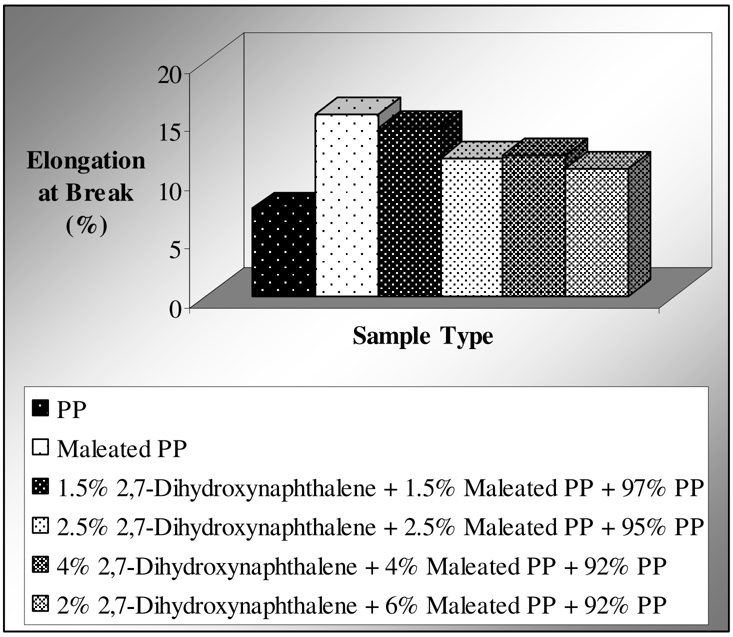


Figure 3.22 Effect of 2,7-dihydroxynaphthalene concentration on the elongation at break of the polypropylene based materials

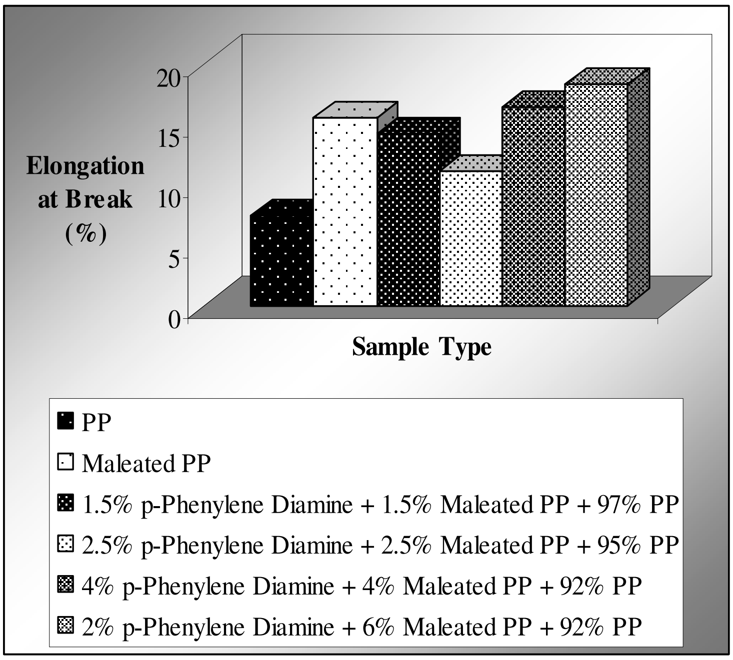


Figure 3.23 Effect of p-phenylene diamine concentration on the elongation at break of the polypropylene based materials

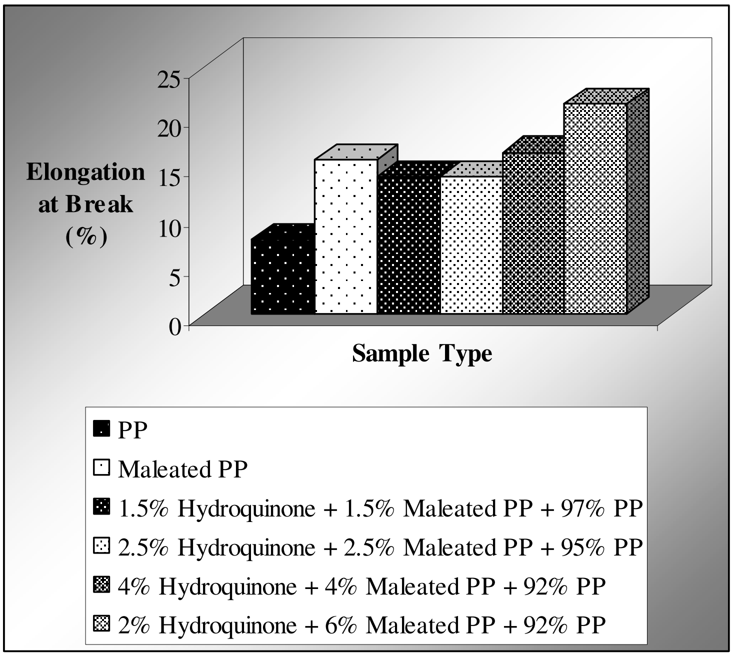


Figure 3.24 Effect of hydroquinone concentration on the elongation at break of the polypropylene based materials

Figure 3.25 illustrates that different additives enhance the elongation at break value most at each concentration. For instance, p-phenylene diamine has the highest contribution to the elongation at break when it is inserted 1.5% and 4%. On the other hand, the material containing hydroquinone has the highest elongation at break at 2% whereas the material containing 1,7-dihydroxynaphthalene has the highest value at 2.5%.

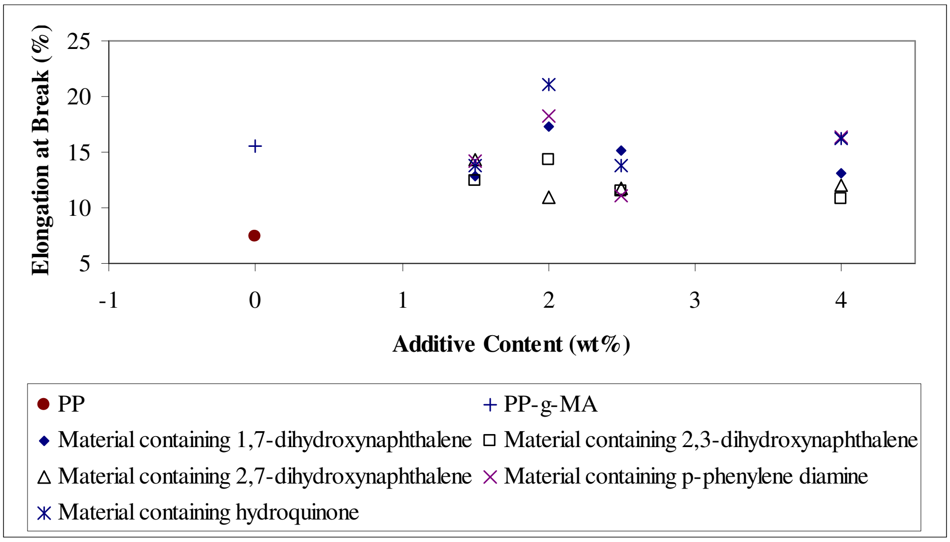


Figure 3.25 Effect of additive type and concentration on the elongation at break of the polypropylene based materials

Young's modulus, tensile strength and elongation at break data for all materials and representative stress-strain curves for PP, PP-*g*-MA and PP based materials are given in Appendix B.

3.2.3 Attenuated Total Reflectance Measurements

Attenuated total reflectance (ATR) measurements were performed in order to observe the possible bond formation between the end groups of the additives and the ester group of maleic anhydride grafted PP. The compositions of the samples that were analyzed by ATR are given in Table 3.4.

The obtained ATR spectra of PP, PP-*g*-MA and PP based materials are very similar to each other. Thus, the possible bond formations could not be observed by this analysis. ATR spectra of PP-g-MA and the polypropylene based materials are illustrated in Appendix C.

Table 3.4 Compositions of the samples in ATR measurements (wt%)

Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Polypropylene	100	-	92	92	92	92	92
Maleic anhydride grafted polypropylene	-	100	4	4	4	4	4
1,7-Dihydroxynaphthalene	-	-	4	-	-	-	-
2,3-Dihydroxynaphthalene	-	-	-	4	-	-	-
2,7-Dihydroxynaphthalene	-	-	-	-	4	-	-
p-Phenylene diamine	-	-	-	-	-	4	-
Hydroquinone	-	-	-	-	-	-	4

3.2.4 Thermal Analysis

Differential scanning calorimetry analysis was performed in order to observe the possible changes in melting temperature of the polypropylene based materials. Bulky substituent groups which enhance the stiffness of the polymer are expected to increase the melting temperature.

Polypropylene utilized in this study has a melting temperature of 166.90ºC. In addition, maleic anhydride grafted polypropylene, which was utilized in all the materials as a compatibilizer, has a melting temperature of 146.41ºC.

Compositions of the samples that were analyzed by differential scanning calorimetry are given in Table 3.5.

Table 3.5 Compositions of the samples in DSC analysis (wt%)

Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Polypropylene	100	-	95	95	95	95	95
Maleic anhydride grafted polypropylene	-	100	2.5	2.5	2.5	2.5	2.5
1,7-Dihydroxynaphthalene	-	-	2.5	-	-	-	-
2,3-Dihydroxynaphthalene	-	-	-	2.5	-	-	-
2,7-Dihydroxynaphthalene	-	-	-	-	2.5	-	-
p-Phenylene diamine	-	-	-	-	-	2.5	-
Hydroquinone	-	-	-	-	-	-	2.5

DSC curves for PP, PP-*g*-MA and polypropylene based materials containing 1,7-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, p-phenylene diamine and hydroquinone are given in Appendix D. The expected melting temperatures of the materials were calculated by the rule of mixtures and both the theoretical and the experimental melting temperatures are given in Table 3.6.

Table 3.6 Theoretical and experimental melting temperatures of the materials

Additive Type	**Melting Temperature (°C)**	
	Theoretical	**Experimental**
1,7-Dihydroxynaphthalene	166.75	165.73
2,3-Dihydroxynaphthalene	166.40	166.53
2,7-Dihydroxynaphthalene	166.90	167.39
p-Phenylene diamine	165.68	165.45
Hydroquinone	166.49	167.85

As it can be seen from Table 3.6, the experimental melting temperatures are consistent with the expected values. The experimental melting temperatures of the materials containing 2,3-dihydroxynaphthalene and p-phenylene diamine are very close to the theoretical values. In the materials containing hydroquinone and

2,7-dihydroxynapththalene the observed melting temperatures were higher than the expected values whereas in the materials containing 1,7-dihydroxynaphthalene the experimental result was lower than the theoretical value.

The crystallinity of polymers can be calculated by using DSC curve and employing the following equation [19]:

$$\%\,\text{crystallinity} = 100\frac{\Delta \text{H}}{\Delta \text{H}_c} \tag{3.3}$$

where ΔH is the enthalpy change of the sample, ΔH_c is the enthalpy change of 100% crystalline sample.

% Crystallinity of each material was calculated by using Eq. 3.3. Enthalpy change of 100% crystalline polypropylene was taken as 207 J/g [29] and enthalpy changes of the samples were obtained from DSC curves. % Crystallinity of the materials are given in Table 3.7.

Table 3.7 % Crystallinity of the materials

Material	% Crystallinity
PP	40.4
Material containing 1,7-dihydroxynaphthalene	45.3
Material containing 2,3-dihydroxynaphthalene	43.4
Material containing 2,7-dihydroxynaphthalene	35.7
Material containing p-phenylene diamine	32.6
Material containing hydroquinone	31.1

Number of chains per unit area to support a stress is higher in the crystalline areas than in the amorphous areas since the polymer chains are more closely packed in the crystalline areas. Moreover, since they are in close and regular contact over relatively long distances in the crystallites, the secondary forces holding them together are cumulatively greater than in the amorphous regions. Consequently, crystallinity can significantly increase the strength and rigidity of a polymer [30]. As it can be seen from Table 3.7, there is an increase in the % crystallinity of the materials containing 1,7-dihydroxynaphthalene and 2,3-dihydroxynaphthalene. On the contrary, there is a decrease in the % crystallinity of the materials containing 2,7-dihydroxynaphthalene, phenylene diamine and hydroquinone. The increase in the % crystallinity of the materials containing 1,7-dihydroxynaphthalene and 2,3-dihydroxynaphthalene is consistent with the increase in the tensile strength and Young's modulus of the materials.

CHAPTER 4

CONCLUSIONS

The objective of this study was to provide antistatic character to polypropylene films by utilizing conductive fillers which function independent of humidity and to enhance the scratch resistance of the films by employing aromatic based additives.

Conductivity measurement results demonstrated that electrical conductivity of polypropylene films are greatly enhanced with the addition of conductive filler, pyrrole by chemical modification. It was concluded that 2% of pyrrole is adequate to provide antistatic character to polypropylene films. Moreover, conductive character was achieved when the pyrrole content exceeds 7%. It was also concluded that electrical conductivity of polypropylene films increases with increasing pyrrole content.

Scanning electron microscopy analysis illustrated that scratch tracks are formed consecutively in a zig-zag manner both in neat PP and additive containing PP films due to the stick-slip process. Furthermore, the observed distinct boundary between the scratch and the unscratched area indicates that plastic deformation occurs during the scratch process of polypropylene films.

The measurements performed with the microscope demonstrated that scratch width of polypropylene films decreases and therefore scratch hardness of the films increases considerably with the insertion of the additives. It was concluded that the composites consisting of 92% polypropylene, 2% of aromatic based additive and 6% PP-*g*-MA have the highest scratch hardness values both for the samples scratched with a load of 100 g and 200 g. Furthermore, the material consisting of 92% polypropylene, 2% 1,7-dihydroxynaphthalene and 6% PP-*g*-MA increases the scratch hardness by more than 60%.

Based on the tensile test results, it was concluded that Young's modulus, which is an indication of hardness, is enhanced with the insertion of additives except for hydroquinone. It was also concluded that maximum tensile strength and elongation at break values increase significantly with the insertion of the additives regardless of the additive type.

According to DSC analysis results, it was concluded that the experimental melting temperatures of the polypropylene based materials are consistent with the theoretical values. Moreover, % crystallinity increased in the materials containing 1,7-dihydroxynaphthalene and 2,3-dihydroxynaphthalene, whereas it decreased in the materials containing 2,7-dihydroxynaphthalene, p-phenylene diamine and hydroquinone.

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APPENDIX A

PRE-EXPERIMENTS

A.1 Anti-Static Experiments

Initially, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDT/PSS), which has a conductivity of 10 S/cm, was thought to be utilized in this study in order to provide antistatic property to polypropylene films. PEDT/PSS was mixed with polyvinyl alcohol solution and then with polypropylene powder in order to provide the coating of polypropylene with PEDT/PSS. The obtained blend was compression molded for 6 minutes at 230ºC and the conductivity was measured by four-probe method. However, conductivity could not be achieved in the prepared films. Following that, PEDT/PSS was dried and the 0.5% solid PEDT/PSS was mixed with polypropylene by twin-screw extruder. The blend was compression molded for 6 minutes at 230ºC. Then, the conductivity of the film was measured both by four-probe method and Keithley 2400 Sourcemeter. However, homogeneous distribution of PEDT/PSS in the film could not be succeeded and conductivity of about 10^{-11} S/cm was achieved only at the regions where PEDT/PSS particles aggregated. Preparation of homogeneous blends was very difficult since the amount of PEDT/PSS was very small when compared with the capacity of the feeder of the extruder. PEDT/PSS could not be used to achieve antistatic character because a suitable method could not be found to mix it with polypropylene properly.

Secondly, ionic liquids, which are molten organic salts, were considered to be alternatives to provide antistatic property. Tetrabutylammonium tetrafluoroborate, which is an ionic liquid with a melting point of 160°C, and tetrabutylammonium perchlorate, which is an ionic liquid with a melting point of 210°C, were dissolved in dimethylformamide and dried in vacuum oven. It was observed that the materials have considerable conductivity when they are in molten state. Moreover, 4% of each ionic liquid was mixed with polypropylene by Brabender Plasti-Corder Torque Rheometer, PLV-151. The conductivities of the prepared blends were measured by Keithley 2400 Sourcemeter and found to be approximately 10^{-11} S/cm. The results corresponded to the antistatic region illustrated in Figure 3.2. Thus, ionic liquids were considered to be promising conductive fillers. However, further study on ionic liquids could not be performed since the materials could not be supplied.

A.2 Anti-Scratch Experiments

Initially, aromatic structured liquid crystalline polymer was considered to be employed to enhance the scratch resistance of the polypropylene films. Maleic anhydride grafted polypropylene was also thought to be utilized in order to provide the bonding between liquid crystalline polymer and polypropylene by the reaction of hydroxyl end groups and ester group.

Liquid crystalline polymer (LCP), which consists of 60% para-amino benzoic acid and 40% polyethylene terephthalate, was synthesized in our laboratory. Two materials, one composed of 30% liquid crystalline polymer and 70% maleic anhydride grafted polypropylene and the other composed of 50% liquid crystalline polymer and 50% maleic anhydride grafted polypropylene were prepared by twin-screw extruder. Then, these materials were mixed with polypropylene by twin-screw extruder in the ratios of 0.5%, 1% and 2%. Temperature profile and speed of the extruder were adjusted as 200°C, 220°C, 220°C, 220°C, 220°C and 100 rpm, respectively.

Tensile test was performed in order to investigate the mechanical properties of the prepared materials. Young’s modulus, tensile strength and elongation at break values of polypropylene, PP-*g*-MA and the prepared materials are given in Table A.1.

Table A.1 Mechanical properties of PP, PP-*g*-MA and PP-PP-*g*-MA-LCP mixtures

Material	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
PP	1001	49	9
PP-*g*-MA	787	38	11
99.5% PP + 0.35% PP-*g*-MA+ 0.15% LCP	1261	50	12
99% PP+ 0.7% PP-*g*-MA + 0.3% LCP	1014	49	13
98% PP+ 1.4% PP-*g*-MA + 0.6% LCP	964	45	14

As shown in Table A.1, Young's modulus of polypropylene increased significantly with the addition of 0.15% liquid crystalline polymer and increased slightly with the addition of 0.3% liquid crystalline polymer. Tensile strength and elongation at break values were also enhanced.

Although liquid crystalline polymer was considered to be promising to improve the scratch resistance of polypropylene films, we could not perform further study due to the lack of the material.

APPENDIX B

MECHANICAL TESTING RESULTS

B.1 Young's Modulus, Tensile Strength and Elongation at Break Data

Table B.1 Arithmetic means and standard deviations of Young's modulus values of PP, PP-g-MA and polypropylene based materials

Material	**Young's Modulus (MPa)**	
	Arithmetic mean	**Standard deviation**
PP	751	106
PP-*g*-MA	535	89
1	995	76
2	886	84
3	952	51
4	897	32
5	906	101
6	790	90
7	858	87
8	844	62
9	940	86
10	872	91
11	924	45
12	790	79
13	846	113
14	784	106
15	780	62
16	758	114
17	816	68
18	780	79
19	718	80
20	648	99

Table B.2 Arithmetic means and standard deviations of tensile strength values of PP, PP-*g*-MA and polypropylene based materials

Material	**Tensile Strength (MPa)**	
	Arithmetic mean	**Standard deviation**
PP	36.2	3.8
PP-*g*-MA	33.5	2.1
1	48.6	1.1
2	47.8	1.0
3	45.5	1.2
4	47.5	0.9
5	46.5	2.6
6	45.5	1.3
7	43.8	1.8
8	46.3	1.5
9	49.3	2.0
10	43.0	2.5
11	43.3	2.6
12	43.5	2.5
13	47.4	0.7
14	46.0	2.8
15	47.5	1.7
16	44.1	1.9
17	48.1	1.8
18	43.5	1.1
19	43.2	2.7
20	47.3	2.1

Table B.3 Arithmetic means and standard deviations of elongation at break values of PP, PP-*g*-MA and polypropylene based materials

Material	**Elongation at Break (%)**	
	Arithmetic mean	**Standard deviation**
PP	7.5	1.3
PP-*g*-MA	15.5	2.6
1	12.9	2.4
2	15.1	1.1
3	13.1	3.0
4	17.2	3.6
5	12.4	1.8
6	11.5	2.8
7	10.8	1.4
8	14.3	2.5
9	14.3	3.8
10	11.8	1.9
11	12.0	3.4
12	10.9	1.9
13	14.2	3.9
14	11.1	1.8
15	16.4	3.6
16	18.3	3.7
17	13.8	1.8
18	13.8	3.2
19	16.2	3.8
20	21.1	3.9

B.2 Stress – Strain Curves

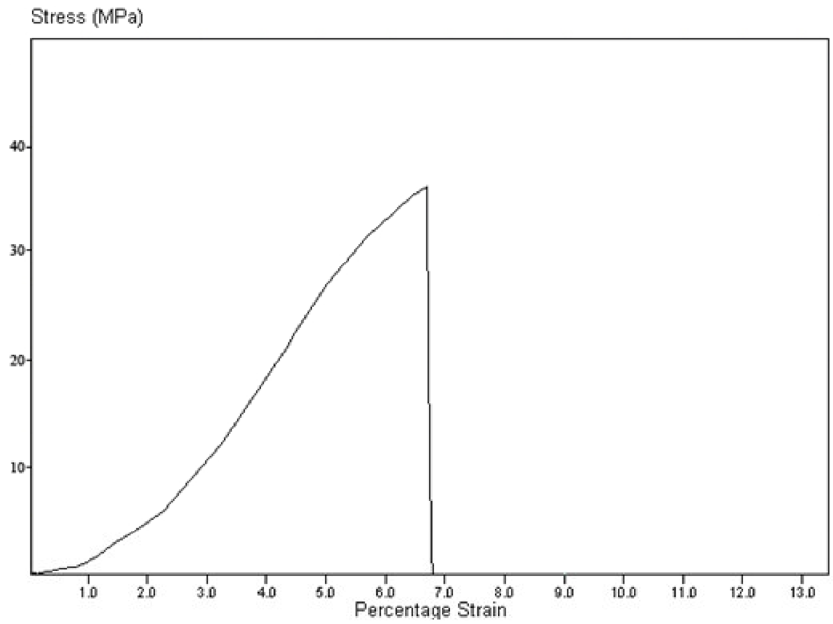


Figure B.1 Stress-strain curve of polypropylene

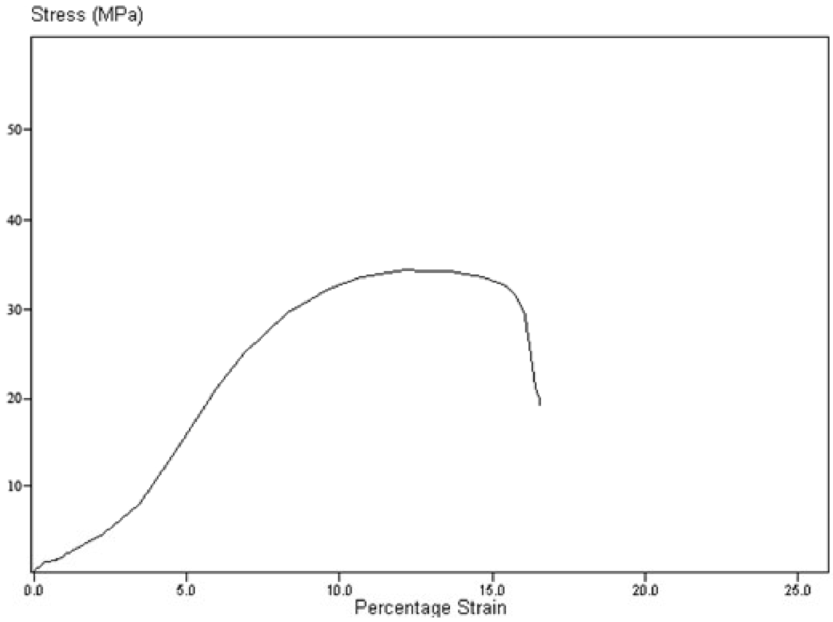


Figure B.2 Stress-strain curve of PP-*g*-MA

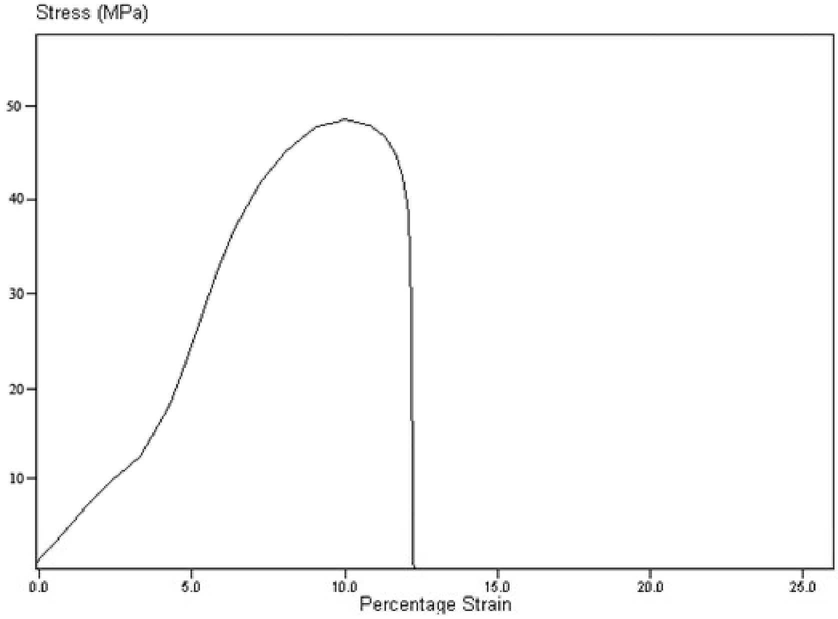


Figure B.3 Stress-strain curve of polypropylene based material containing 1.5% 1,7-dihydroxynaphthalene

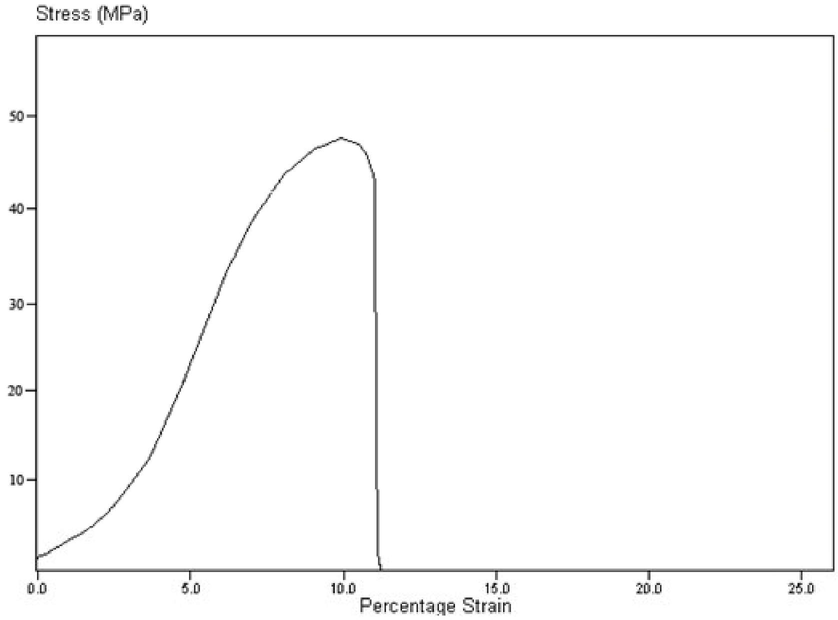


Figure B.4 Stress-strain curve of polypropylene based material containing 1.5% 2,3-dihydroxynaphthalene

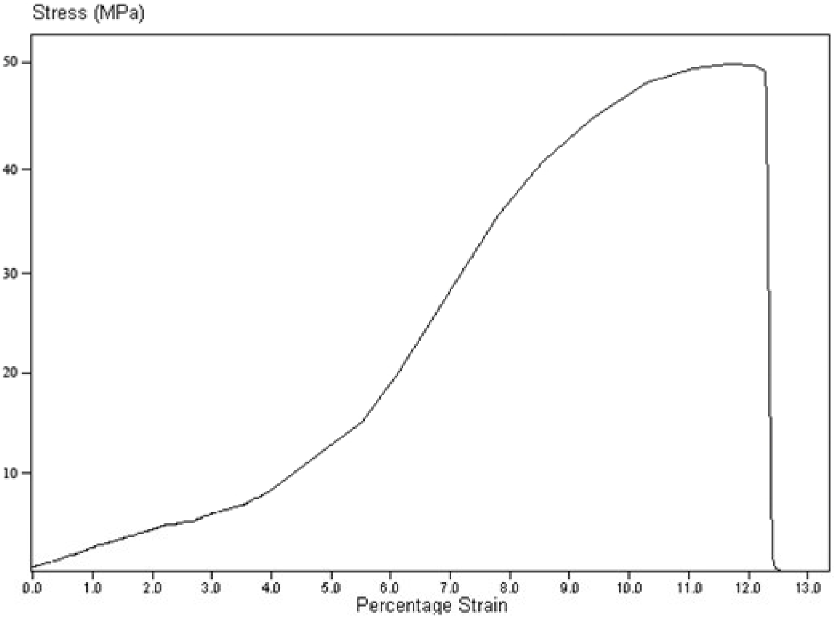


Figure B.5 Stress-strain curve of polypropylene based material containing 1.5% 2,7-dihydroxynaphthalene

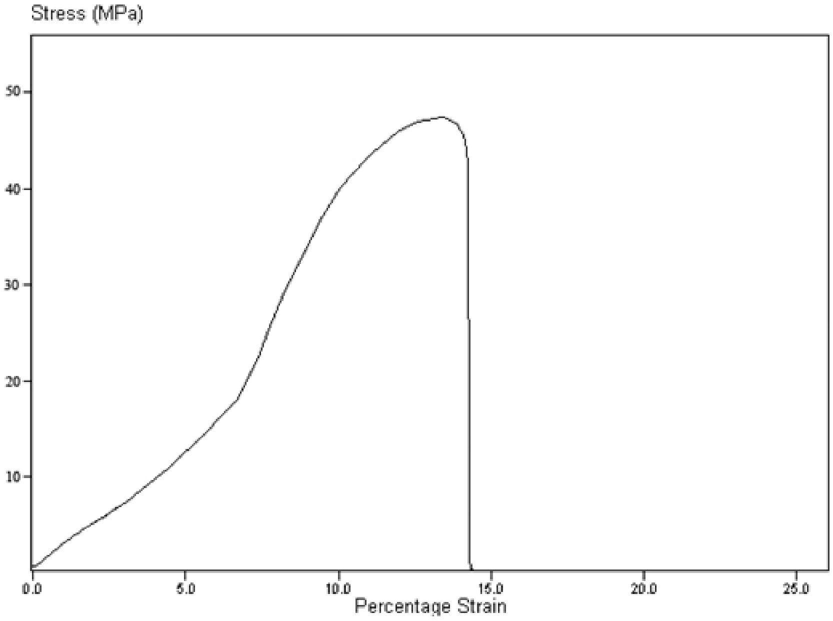


Figure B.6 Stress-strain curve of polypropylene based material containing 1.5% p-phenylene diamine

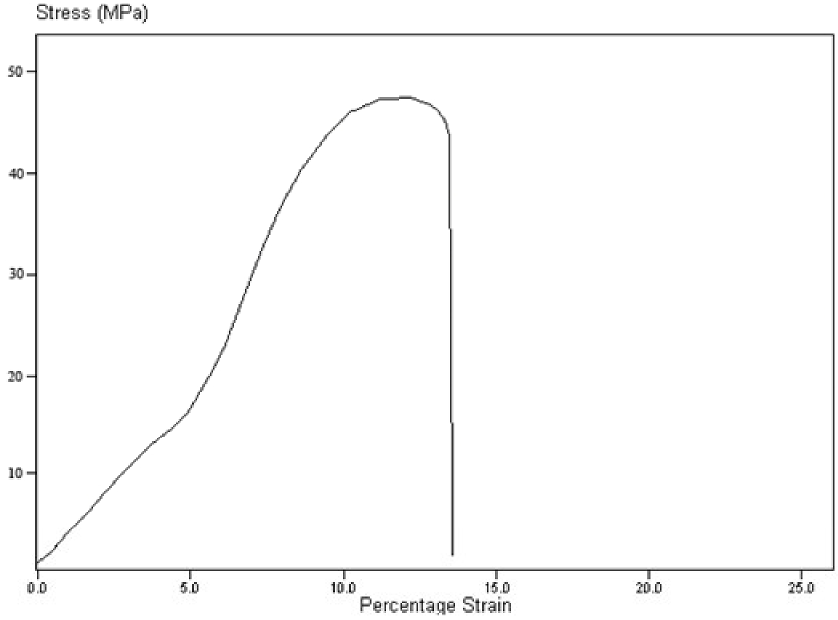


Figure B.7 Stress-strain curve of polypropylene based material containing 1.5% hydroquinone

APPENDIX C

ATR SPECTRA

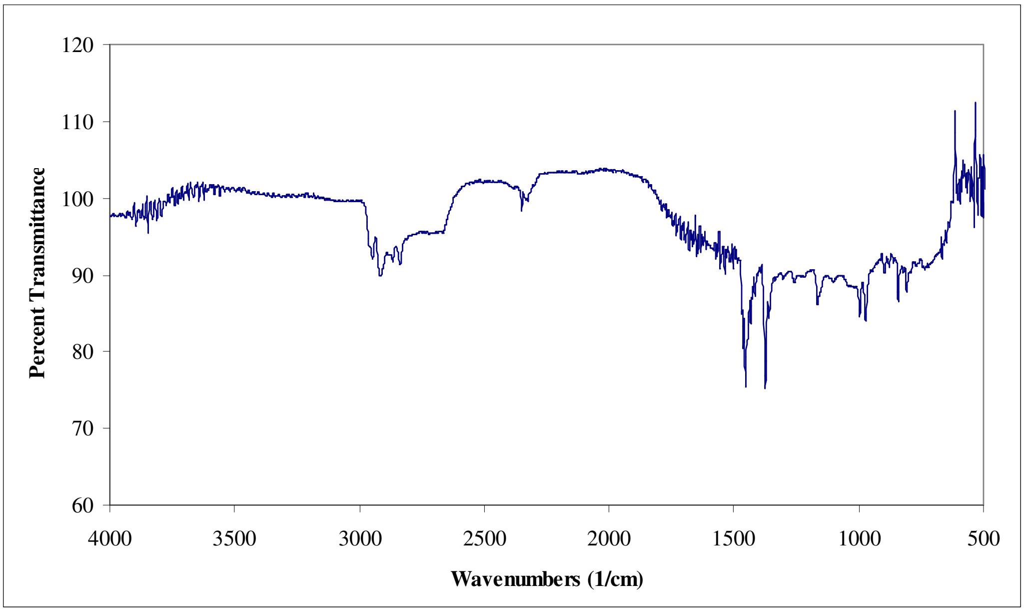


Figure C.1 ATR spectra of PP-*g*-MA

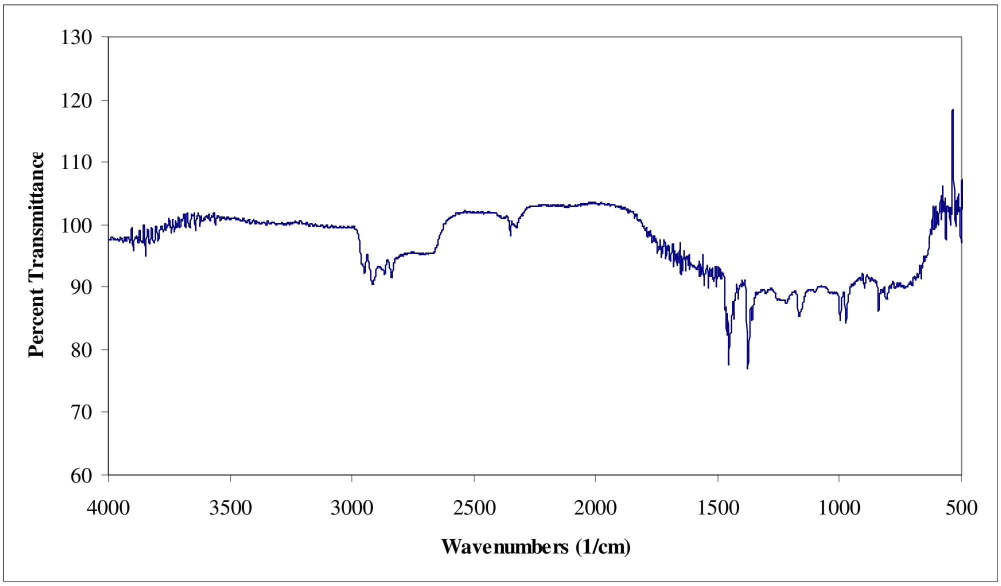


Figure C.2 ATR spectra of the material containing 1,7-dihydroxynaphthalene

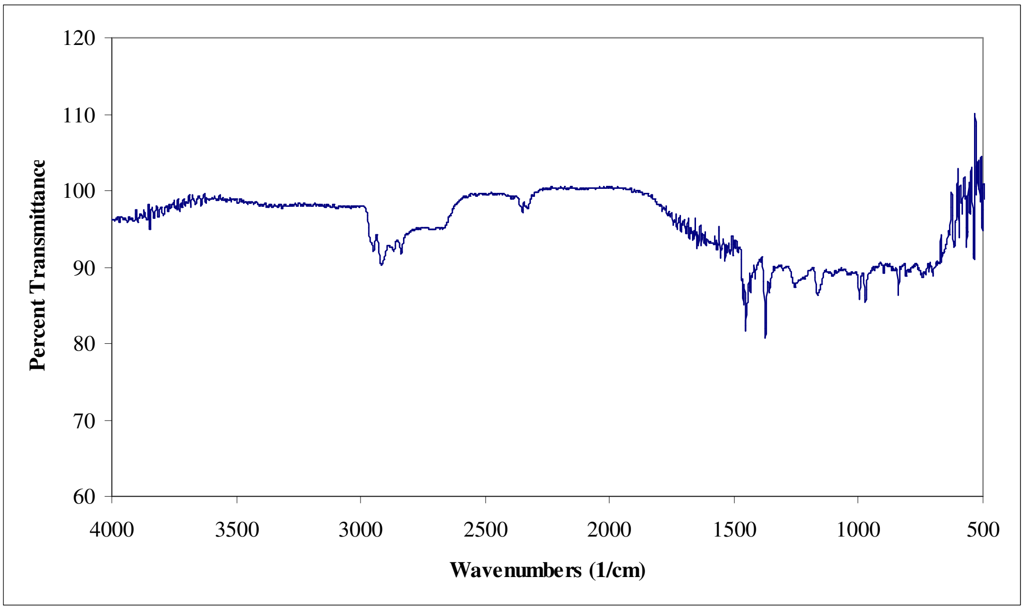


Figure C.3 ATR spectra of the material containing 2,3-dihydroxynaphthalene

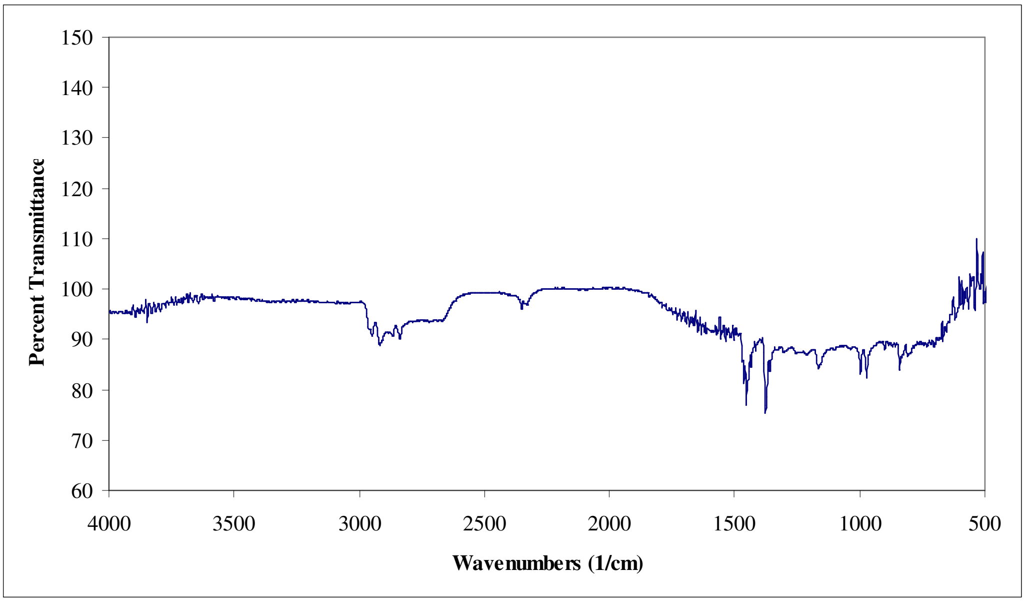


Figure C.4 ATR spectra of the material containing 2,7-dihydroxynaphthalene

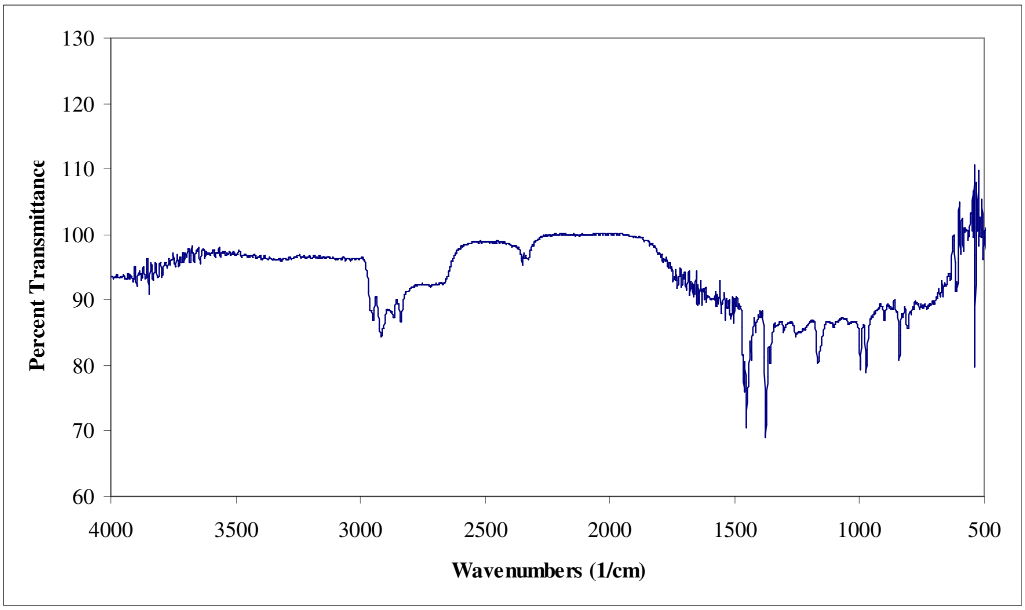


Figure C.5 ATR spectra of the material containing p-phenylene diamine

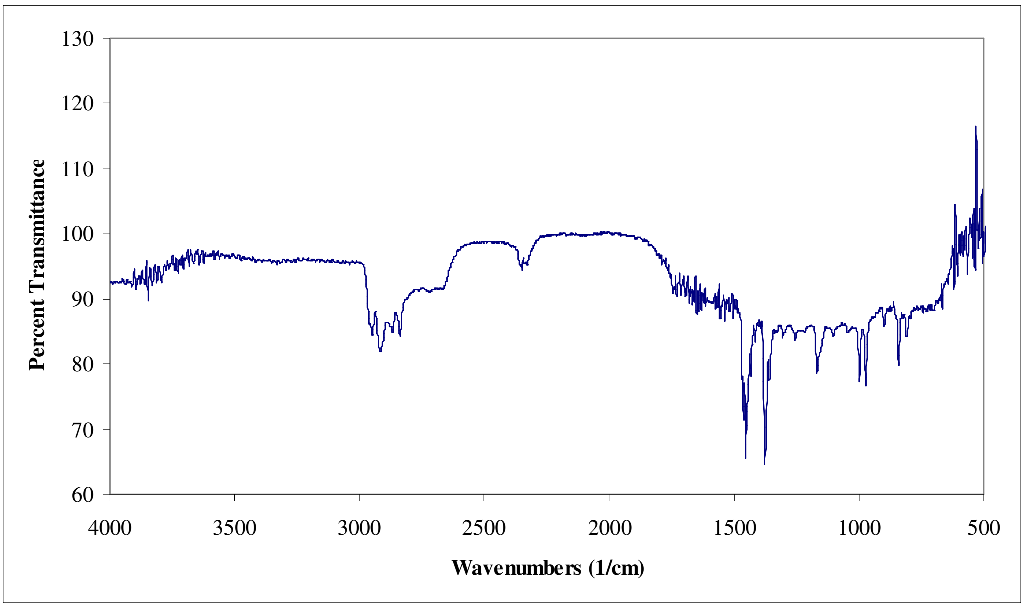


Figure C.6 ATR spectra of the material containing hydroquinone

APPENDIX D

DSC THERMOGRAMS

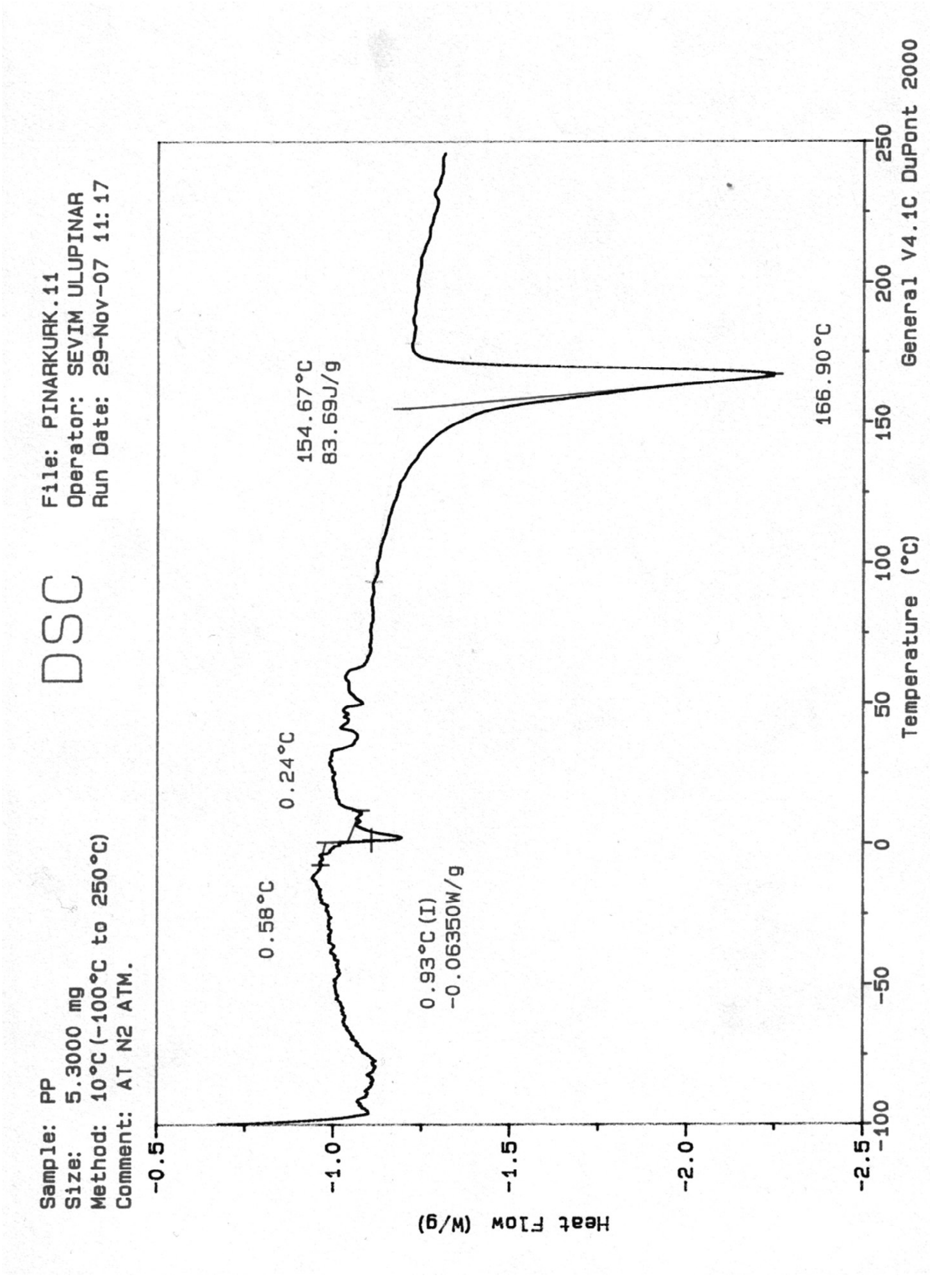


Figure D.1 DSC thermogram of polypropylene

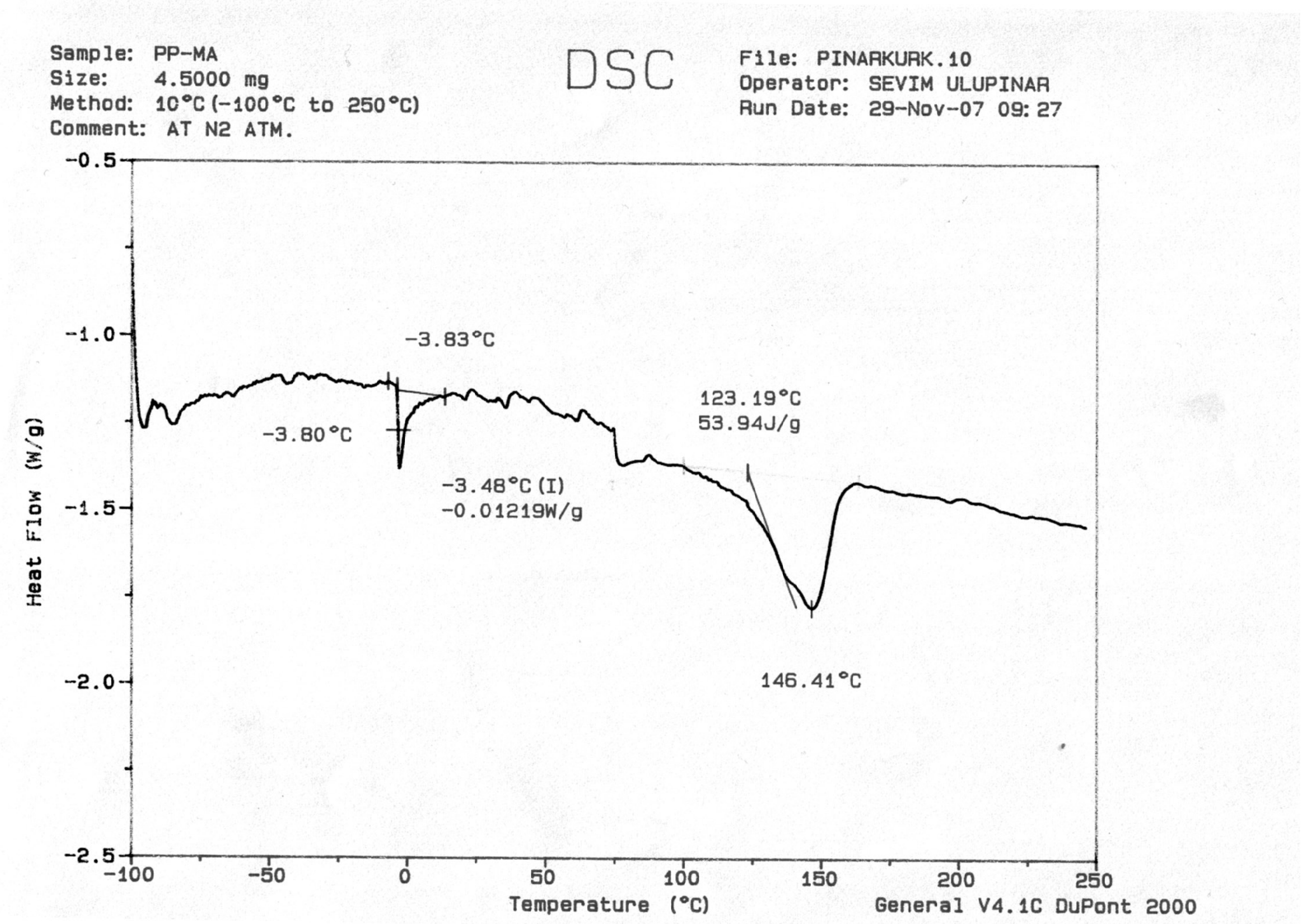


Figure D.2 DSC thermogram of maleic anhydride grafted polypropylene

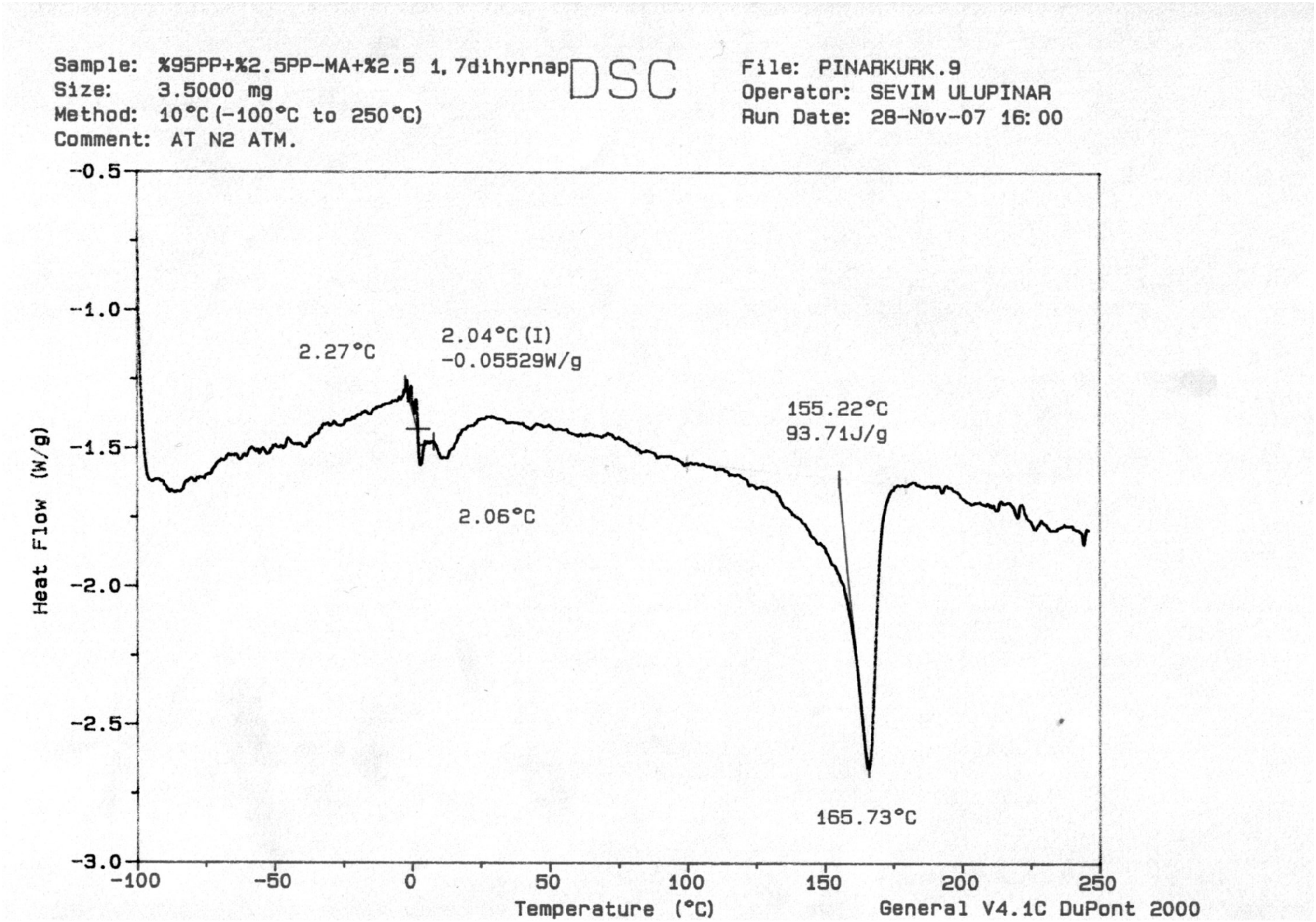


Figure D.3 DSC thermogram of the material containing 1,7-dihydroxynaphthalene

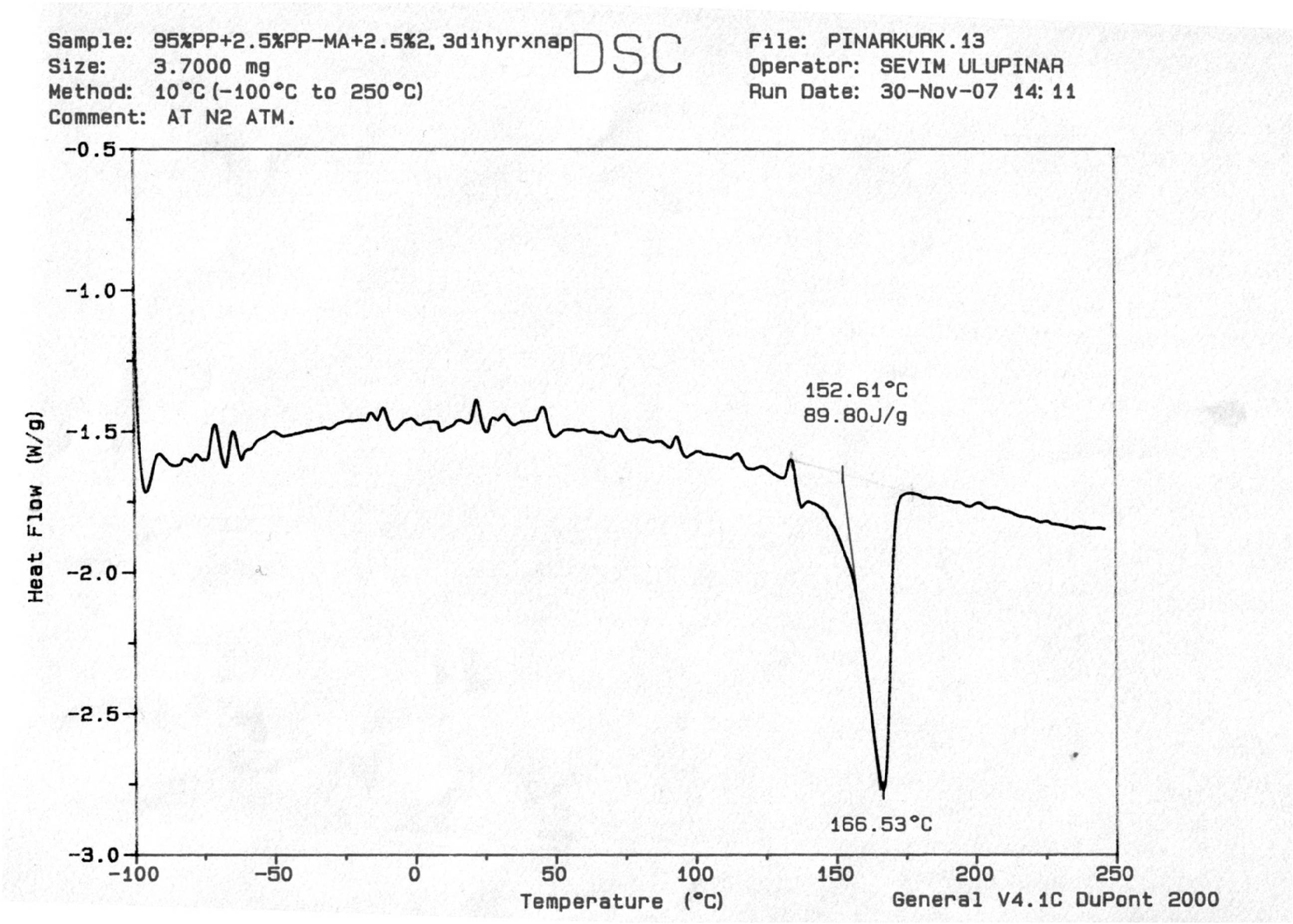


Figure D.4 DSC thermogram of the material containing 2,3-dihydroxynaphthalene

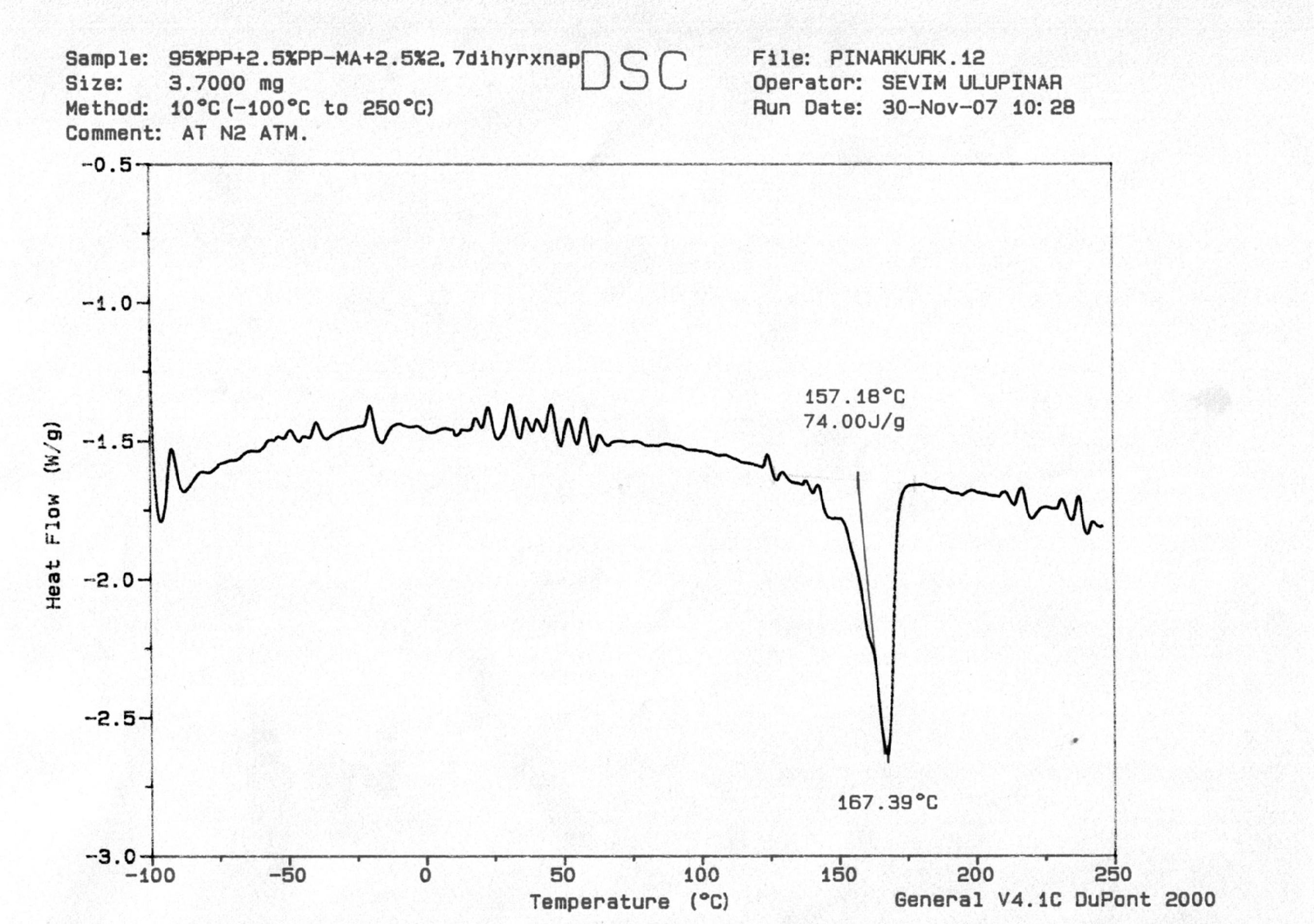
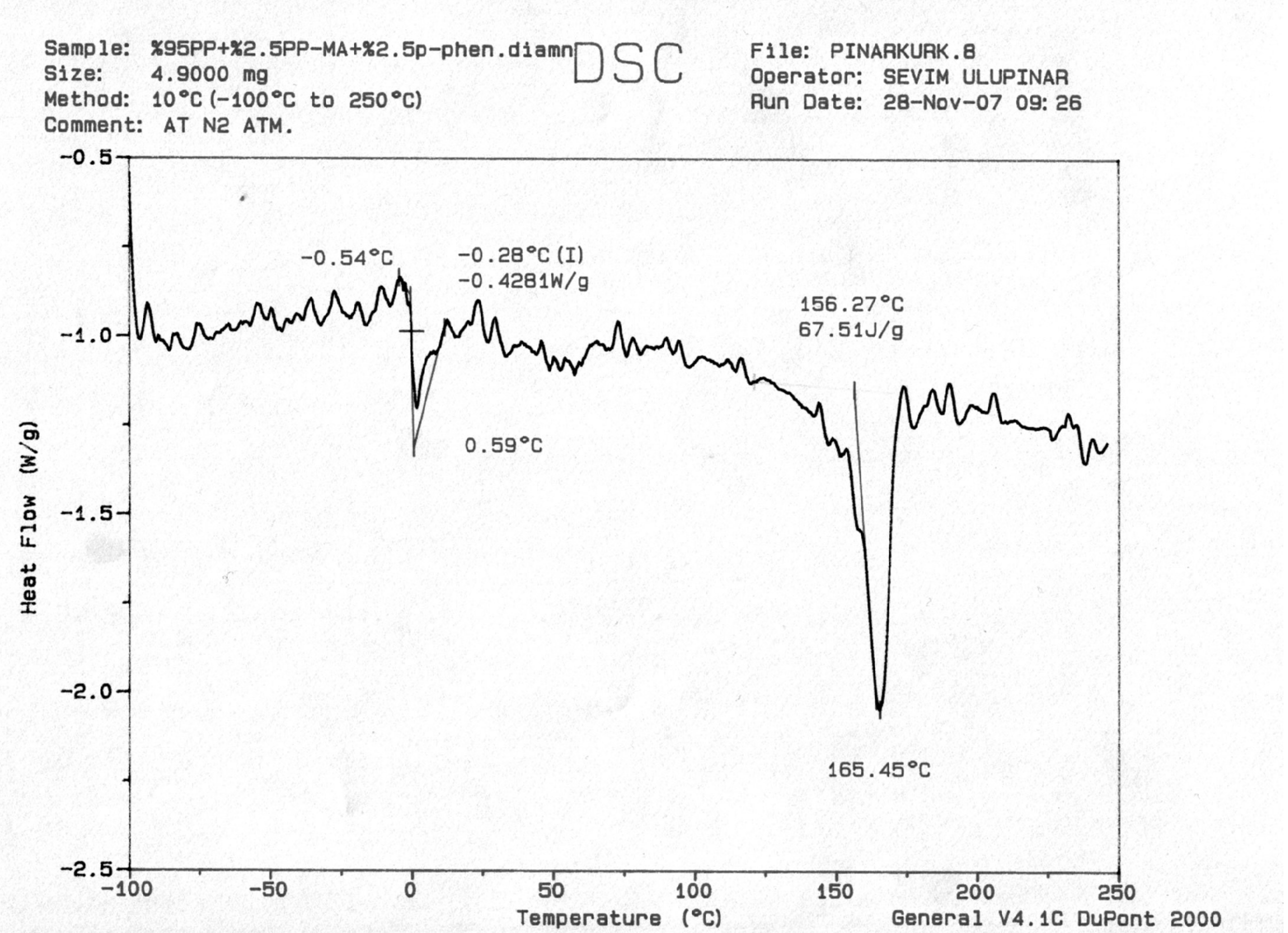


Figure D.5 DSC thermogram of the material containing 2,7-dihydroxynaphthalene



Sample: %95PP+%2.5PP-MA+%2.5p-phen.diamn
Size: 4.9000 mg
Method: 10°C(-100°C to 250°C)
Comment: AT N2 ATM.

File: PINARKURK.8
Operator: SEVIM ULUPINAR
Run Date: 28-Nov-07 09:26

Figure D.6 DSC thermogram of polypropylene based material containing p-phenylene diamine

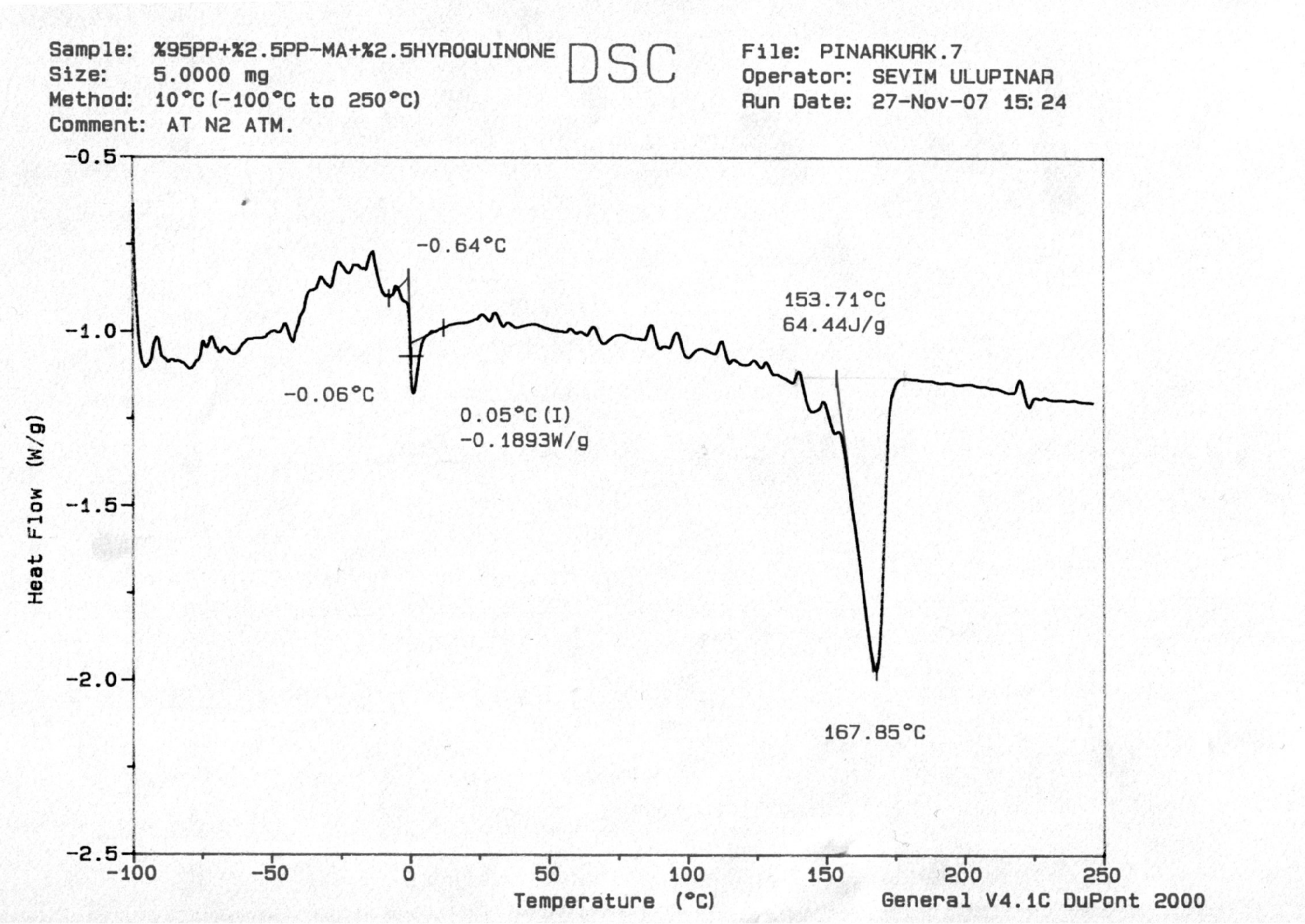


Figure D.7 DSC thermogram of the material containing hydroquinone