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MARMARA UNIVERSITY
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PRODUCTION OF ABS WIRE MATERIAL FOR RAPID
PROTOTYPING MACHINES

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ACCEPTANCE AND APPROVAL DOCUMENT

**PRODUCTION OF ABS WIRE MATERIAL FOR RAPID PROTOTYPING
MACHINES**

The jury established by the Executive Board of the INSTITUTE FOR GRADUATE STUDIES IN PURE AND APPLIED SCIENCES on (Resolution no:.....) has accepted Mr. ÖZGÜR KIRELLİ's thesis titled “Production of Supply Material for of ABS Wire Material for Rapid Prototyping Machine” as Master of Science thesis in Master Science of Mechanical Engineering.

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APPROVAL

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ABSTRACT

Production of ABS Wire Material for Rapid Prototyping Machine

Our aim is producing of supply materials for Rapid Prototyping machine and improving materials properties . With the production of supply material in Turkey, which is exported, costs are decreased and escape from foreign dependence.

This thesis investigates processes of support material and using of these materials in rapid prototyping machine. For production and selection to right material, we have to get information about production, processing and using of ABS (Acrylonitrile Butadiene Styrene).

First, general information about polymers is given in Theoretical Investigation. Then, thermoplastics are described in detail. Hereafter, detailed information is given about ABS. At the end of the theoretical investigation part, process of Rapid Prototyping process FDM (Fused Deposition Modeling) and extrusion process of ABS will be explained.

There are a lot of important points for production of supply material. We have to select the right material. There are too many types of material that used in Rapid Prototyping Machine. And there are a lot of important points such as Tensile strength, tensile modulus, elongation, melting temperature and mold flow index. Another point is smooth surfaces on these molds. Rough surfaces prevent ejection of the injection molded part and play a role in the overall quality of the final part.

In experimental study, experiments are made on samples which have different properties. We produced ABS material for rapid prototyping machine. First, we purchased raw ABS materials from producers. That is the most important point which effects overall process. Then, we made extrusion process with extrusion machine. We have to know the physical properties of material to using in machine. Prototyping process is very sensitive process which can be affected by many disturbances. When we know physical values of samples of ABS, we realize the production is good or not.

ÖZET

Hızlı Prototipleme Makineleri için ABS Tel Malzeme Üretimi

Tezin amacı Hızlı prototipleme makinelerinde kullanılan maddelerin Türkiye’de üretilmesi ve kullanılan malzemelerin iyileştirilmesidir. Amacımız, Yurtdışından ithal edilen malzemelerin Türkiye’de üretilmesiyle beraber; maliyetlerinin düşürülmesi ve dışa bağımlılıktan kurtulunması, kullanılan malzemelerin iyileştirilerek daha iyi ürünler üretilmesi.

Bu tez hızlı prototipleme makinelerinde kullanılan malzemelerin üretimini ve kullanımını incelemektedir. Doğru malzemeyi seçip ondan gerekli boyutlarda malzemeyi üretebilmek için, prototip makinelerinde hammadde olarak kullanılan malzeme ABS (Acrylonitrile Butadiene Styrene) ‘nin üretimi, işlenmesi ve kullanımı hakkında bilgi sahibi olmak gerekiyor.

Tezde öncelikle polimerler hakkında teorik incelemelere yer verildi. Ondan sonra polimerlerin, ABS’inde içinde olduğu, termoplastikler anlatıldı. ABS’nin üretim methotları kullanım alanları ve özellikleri incelendi. Teorik inceleme kısmının en sonunda, hızlı prototipleme yöntemlerinden tezle ilgili olan yöntem FDM (Fused Deposition Modelling) ayrıntılı olarak anlatıldı. Bu kısımda son olarak, hızlı prototipleme makinelerinde kullanılmak için ABS malzemeyi işlediğimiz ekstrüzyon incelendi. Tezin deneyler ve sonuçları kısmında, değişik firmalardan alınan değişik özelliklere sahip ABS örneklerine testler yapıldı. Böylelikle istenilen malzemenin özelliklerini ve firmalardan alınan ABS’ lerin arasında karşılaştırma imkanı doğdu. Bu testlerle malzemelerin içerikleri, çekme mukavemeti, sertliği, erime sıcaklıkları ve akış endeksleri incelendi. Bir diğer önemli özellik olan yüzey pürüzsüzlüğü yapılan kalıplar ve hassas ekstrüzyon işlemiyle elde edildi. Böylelikle doğru malzemeyi seçip bundan istenilen boyutlarda malzeme çekildi. Hızlı prototipleme makinesinde denenip sonuçları irdelendi.

Hızlı prototipleme işlemi çok hassas bir işlem olduğundan kullanılan malzeme birinci öncelikle işlemin ve sonucun kalitesini etkileyen etmendir. Malzemelerin fiziksel ve termal özelliklerini bilip karşılaştırma imkanımız olduğunda bu işlem için kullanılması gereken doğru ABS malzemeyi seçmiş, böylelikle tezimizin amacına ulaşmış olduk.

06, 2008

Özgür KIRELLİ

SYMBOLS

E	: Young's Modulus
F	: Force
T_m	: Melting Temperature
T_g	: Glass Transition Temperature
W	: Load
ρ	: Density

ABBREVIATIONS

ABS	: Acrylonitrile Butadiene Styrene
DTUL	: Deflection Temperature Under Load
FDM	: Fused Deposition Modeling
H₂O	: Dihidrogen Monoksit (Water)
IV	: INTRINSIC VISCOSITY
HDT	: The Heat Deflection Temperature
LOI	: The Limited Oxygen Index
MPa	: Mega Pascal
MFI	: Mold Flow Index
PC	: Polycarbonate
Psi	: Pounds per square inch
PVB	: Polyvinyl Butyral
PVC	: Polyvinyl Butyral Chloride
RP	: Rapid Prototyping
UV	: Ultraviolet Rays

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I. INTRODUCTION

The fused deposition modeling (FDM) is one of the most widely used rapid prototyping systems in the world. The main reasons of its increasing popularity and use have been its reliability, safe and simple fabrication process, low cost of material, and the availability of a variety of building thermoplastics. Ever since the first FDM system was launched in early 1990s, the Stratasys Inc has been marketing improved FDM systems on a regular basis. However, research has also been going on in universities and research institutions around the world to increase its applications, to develop new materials and to improve the FDM process [1].

The FDM systems, developed by Stratasys Inc, currently fabricate parts in elastomers, Acrylonitrile Butadiene Styrene (ABS) and investment casting wax using the layer by layer deposition of extruded material through a nozzle using feedstock filaments from a spool. Most of the parts fabricated in these materials can be used for design verification, form and fit checking and patterns for casting processes and medical application. New materials for FDM are needed to increase its application domain especially in rapid tooling and rapid manufacturing areas. ABS material can be produced in feed stock filament form of required size, strength and properties in Turkey.

Our aim is producing of supply materials for Rapid Prototyping (RP) machine and improving materials properties and its using in Turkey. With the production of supply material in Turkey, which is exported, costs are decreased and escape from foreign dependence.

This thesis investigates processes of support material and using of these materials in rapid prototyping machine. For production and selection to right material, we have to get information about production, processing and using of ABS.

First, general information about polymers is given in Theoretical Investigation. Then, thermoplastics are described in detail. Hereafter, detailed information is given about ABS. At the end of the theoretical investigation part, process of Rapid Prototyping process FDM and extrusion process of ABS will be explained.

There are a lot of important points for production of supply material. We have to select the right material. There are too many types of material that used in Rapid Prototyping Machine. And there are a lot of important points such as Tensile strength, tensile modulus, elongation, melting temperature and mold flow index. Another point is smooth surfaces on these molds. Rough surfaces prevent ejection of the injection molded part and play a role in the overall quality of the final part.

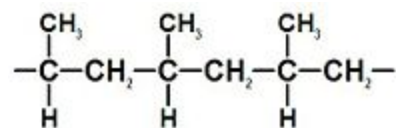
In experimental study, experiments are made on samples which have different properties. We produced ABS material for rapid prototyping machine. First, we purchased raw ABS materials from producers. That is the most important point which effects overall process. Then, we made extrusion process with extrusion machine. We have to know the physical properties of material to using in machine. Prototyping process is very sensitive process which can be affected by many disturbances. When we know physical values of samples of ABS, we realize the production is good or not.

II. GENERAL BACKGROUND

II.1 POLYMERS

A polymer is a substance composed of molecules with large molecular mass composed of repeating structural units, or monomers, connected by covalent chemical bonds. The word is derived from the Greek, πολυ, polu, "many"; and μέρος, meros, "part". Well known examples of polymers include plastics, DNA and proteins. A simple example is polypropylene whose repeating unit structure is shown at right.

Polypropylene



Poly (1-methylethylene) except where noted otherwise, data are given for materials in their standard state (at 25 °C, 100 kPa)

Figure II.1

While "polymer" in popular usage suggests "plastic", the term actually refers to a large class of natural and synthetic materials with a variety of properties and purposes. Natural polymer materials such as shellac and amber have been in use for centuries. Biopolymers such as proteins (for example hair, skin and part of the bone structure) and nucleic acids play crucial roles in biological processes. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper. Typical synthetic polymers are Bakelite, neoprene, nylon, polyvinyl chloride (PVC), polystyrene, polyacrylonitrile and polyvinyl butyral (PVB). Polymers are studied in the fields of polymer chemistry and polymer science [2].

II.1.1 Polymer Structure

The structural properties of a polymer relate to the physical arrangement of monomers along the backbone of the chain. Structure has a strong influence on the other properties of a polymer. For example, a linear chain polymer may be soluble or insoluble in water depending on whether it is composed of polar monomers (such as ethylene oxide) or nonpolar monomers (such as styrene). On the other hand, two samples of natural rubber may exhibit different durability even though their molecules comprise the same monomers. Polymer scientists have developed terminology to precisely describe both the nature of the monomers as well as their relative arrangement [6]:

II.1.2 Polymer properties

Types of polymer 'properties' can be broadly divided into several categories based upon scale. At the nano-micro scale are properties that directly describe the chain itself. These can be thought of as polymer structure. At an intermediate mesoscopic level are properties that describe the morphology of the polymer matrix in space. At the macroscopic level are properties that describe the bulk behavior of the polymer.

The bulk properties of a polymer are those most often of end-use interest. These are the properties that dictate how the polymer actually behaves on a macroscopic scale [6].

II.1.2.1 Crystallinity

When applied to polymers, the term crystalline has a somewhat ambiguous usage. In some cases, the term crystalline finds identical usage to that used in conventional crystallography. For example, the structure of a crystalline protein or polynucleotide, such as a sample prepared for x-ray crystallography, may be defined in terms of a conventional unit cell composed of one or more polymer molecules with cell dimensions of hundreds of angstroms or more.

A synthetic polymer may be described as crystalline if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually

arising from intramolecular folding and/or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely crystalline[1].

II.1.2.2 Tensile strength

The tensile strength of a material quantifies how much stress the material will endure before failing [4] [5]. This is very important in applications that rely upon polymer's physical strength or durability. For example, a rubber band with a higher tensile strength will hold a greater weight before snapping. In general tensile strength increases with polymer chain length [2].

II.1.2.3 Young's Modulus of elasticity

Young's Modulus quantifies the elasticity of the polymer. It is defined, for small strains, as the ratio of rate of change of stress to strain. Like tensile strength this is highly relevant in polymer applications involving the physical properties of polymers, such as rubber bands [2].

II.1.2.4 Transport Properties

Transport properties such as diffusivity relate to how rapidly molecules move through the polymer matrix. These are very important in many applications of polymers for films and membranes[3].

II.1.2.5 Melting point

The term "melting point" when applied to polymers suggests not a solid-liquid phase transition but a transition from a crystalline or semi-crystalline phase to a solid amorphous phase. Though abbreviated as simply " T_m ", the property in question is more properly called the "crystalline melting temperature". Among synthetic polymers, crystalline melting is only discussed with regards to thermoplastics, as thermosetting polymers will decompose at high temperatures rather than melt [6].

II.1.2.6 Boiling point

The boiling point of a polymer substance is never defined due to the fact that polymers will decompose before reaching theoretical boiling temperatures.

II.1.2.7 Glass transition temperature

A parameter of particular interest in synthetic polymer manufacturing is the glass transition temperature (T_g), which describes the temperature at which amorphous polymers undergo a second order phase transition from a rubbery, viscous amorphous solid to a brittle, glassy amorphous solid. The glass transition temperature may be engineered by altering the degree of branching or cross-linking in the polymer or by the addition of plasticizer [6].

In general, polymeric mixtures are far less miscible than mixtures of small molecule materials. This effect is a result of the fact that the driving force for mixing is usually entropics, not energetics. In other words, miscible materials usually form a solution not because their interaction with each other is more favorable than their self-interaction but because of an increase in entropy and hence free energy associated with increasing the amount of volume available to each component. This increase in entropy scales with the number of particles (or moles) being mixed. Since polymeric molecules are much larger and hence generally have much higher specific volumes than small molecules, the number of molecules involved in a polymeric mixture are far less than the number in a small molecule mixture of equal volume. The energetics of mixing, on the other hand, are comparable on a per volume basis for polymeric and small molecule mixtures. This tends to increase the free energy of mixing for polymer solutions and thus make solvation less favorable. Thus, concentrated solutions of polymers are far rarer than those of small molecules.

In dilute solution, the properties of the polymer are characterized by the interaction between the solvent and the polymer. In a *good solvent*, the polymer appears swollen and occupies a large volume. In this scenario, intermolecular forces between the solvent and monomer subunits dominate over intramolecular interactions. In a *bad solvent* or

poor solvent, intramolecular forces dominate and the chain contracts. In the *theta solvent*, or the state of the polymer solution where the value of the second virial coefficient becomes 0, the intermolecular polymer-solvent repulsion balances exactly the intermolecular monomer-monomer attraction. Under the theta condition the polymer behaves like an ideal random coil [6].

II.1.2.8 Chain length

Polymer bulk properties are strongly dependent upon their structure and mesoscopic behavior. A number of qualitative relationships between structure and properties are known.

Increasing chain length tends to decrease chain mobility, increase strength and toughness, and increase the glass transition temperature (T_g). This is a result of the increase in chain interactions such as Van der Waals attractions and entanglements that come with increased chain length. These interactions tend to fix the individual chains more strongly in position and resist deformations and matrix breakup, both at higher stresses and higher temperatures. Chain length is related to melt viscosity roughly as $1:10^{3.2}$, so that a tenfold increase in polymer chain length results in a viscosity increase of over 1000 times [5].

II.1.3 Chemical properties of polymers

The attractive forces between polymer chains play a large part in determining a polymer's properties. Because polymer chains are so long, these interchain forces are amplified far beyond the attractions between conventional molecules. Different side groups on the polymer can lend the polymer to ionic bonding or hydrogen bonding between its own chains. These stronger forces typically result in higher tensile strength and melting points.

The intermolecular forces in polymers can be affected by dipoles in the monomer units. Polymers containing amide or carbonyl groups can form hydrogen bonds between adjacent chains; the partially positively charged hydrogen atoms in N-H groups of one

chain are strongly attracted to the partially negatively charged oxygen atoms in C=O groups on another. These strong hydrogen bonds, for example, result in the high tensile strength and melting point of polymers containing urethane or urea linkages. Polyesters have dipole-dipole bonding between the oxygen atoms in C=O groups and the hydrogen atoms in H-C groups. Dipole bonding is not as strong as hydrogen bonding, so a polyester's melting point and strength are lower than Kevlar's (Twaron), but polyesters have greater flexibility.

Ethene, however, has no permanent dipole. The attractive forces between polyethylene chains arise from weak van der Waals forces. Molecules can be thought of as being surrounded by a cloud of negative electrons. As two polymer chains approach, their electron clouds repel one another. This has the effect of lowering the electron density on one side of a polymer chain, creating a slight positive dipole on this side. This charge is enough to actually attract the second polymer chain. Van der Waals forces are quite weak, however, so polyethene can have a lower melting temperature compared to other polymers [9].

II.1.4 Polymer characterization

The characterization of a polymer requires several parameters which need to be specified. This is because a polymer actually consists of a statistical distribution of chains of varying lengths, and each chain consists of monomer residues which affect its properties.

A variety of lab techniques are used to determine the properties of polymers. Techniques such as wide angle X-ray scattering, small angle X-ray scattering, and small angle neutron scattering are used to determine the crystalline structure of polymers. Gel permeation chromatography is used to determine the number average molecular weight, weight average molecular weight, and polydispersity. Thermal properties such as the glass transition temperature and melting point can be determined by differential scanning calorimetry and dynamic mechanical analysis. Pyrolysis followed by analysis of the fragments is one more technique for determining the possible structure of the polymer[9].

II.1.5 Polymer degradation

Polymer degradation is a change in the properties - tensile strength, colour, shape, etc - of a polymer or polymer based product under the influence of one or more environmental factors such as heat, light or chemicals. It is often due to the hydrolysis of the bonds connecting the polymer chain, which in turn leads to a decrease in the molecular mass of the polymer. These changes may be undesirable, such as changes during use, or desirable, as in biodegradation or deliberately lowering the molecular mass of a polymer. Such changes occur primarily because of the effect of these factors on the chemical composition of the polymer. Ozone cracking and UV degradation are specific failure modes for certain polymers[6].

The degradation of polymers to form smaller molecules may proceed by random scission or specific scission. The degradation of polyethylene occurs by random scission - that is by a random breakage of the linkages (bonds) that hold the atoms of the polymer together. When heated above 450 Celsius it degrades to form a mixture of hydrocarbons. Other polymers - like polyalphanaphthylstyrene - undergo 'specific' chain scission with breakage occurring only at the ends. They literally unzip or depolymerize to become the constituent monomer[6].

However the degradation process can be useful from the view points of understanding the structure of a polymer or recycling/reusing the polymer waste to prevent or reduce environmental pollution. Polylactic acid and Polyglycolic acid, for example, are two polymers that are useful for their ability to degrade under aqueous conditions. A copolymer of these polymers is used for biomedical applications such as hydrolysable stitches that degrade over time after they are applied to a wound. These materials can also be used for plastics that will degrade over time after they are used and will therefore not remain as litter.

II.1.6 Polymerization

In polymer chemistry, polymerization is a process of reacting monomer molecules together in a chemical reaction to form three-dimensional networks or polymer chains [7]. There are many forms of polymerization and different systems exist to categorize them.

The main categories are

- Chain-growth polymerization
- Step-growth polymerization

In chemical compounds, polymerization occurs via a variety of reaction mechanisms which vary in complexity due to functional groups present in reacting compounds[8] and. In more straightforward polymerization, alkenes, which are a relatively stable due to σ bonding between carbon atoms form polymers through relatively simple radical reactions; conversely, more complex reactions such as those that involve substitution at the carbonyl atom require more complex synthesis due to the way in which reacting molecules polymerize.[8]

As alkenes can be formed in somewhat straightforward reaction mechanisms, they form useful compounds such as polyethylene and polyvinyl chloride (PVC) when undergoing radical reactions, which are produced in high tonnages each year due to their usefulness in manufacturing processes of commercial products, such as piping, insulation and packaging. Polymers such as PVC are generally referred to as "**singular**" polymers as they consist of repeated long chains or structures of the same monomer unit, whereas polymers that consist of more than one molecule are referred to as "**co-polymers**".

Other monomer units, such as formaldehyde hydrates or simple aldehydes, are able to polymerize themselves at quite low temperatures ($>-80^{\circ}\text{C}$) to form trimers;[8] molecules consisting of 3 monomer units which can cyclize to form ring cyclic structures, or undergo further reactions to form tetramers, or 4 monomer-unit

compounds. Further compounds either being referred to as oligomers in smaller molecules. Generally, because formaldehyde is an exceptionally reactive electrophile it allows nucleophilic addition of hemiacetal intermediates, which are generally short lived and relatively unstable "mid stage" compounds which react with other molecules present to form more stable polymeric compounds.

Polymerization that is not sufficiently moderated and proceeds at an undesirably fast rate can be very hazardous. This phenomenon is known as Hazardous polymerization and can cause fires and explosions[9].

II.1.6.1 Chain-growth

Chain-growth polymerization or addition polymerization involves the linking together of molecules incorporating double or triple chemical bonds. These unsaturated *monomers* (the identical molecules which make up the polymers) have extra internal bonds which are able to break and link up with other monomers to form the repeating chain. Addition polymerization is involved in the manufacture of polymers such as polyethylene, polypropylene and polyvinyl chloride (PVC). A special case of addition polymerization leads to living polymerization[8].

The main characteristics are:

Polymerization process takes place in three distinct steps:

1. Chain initiation, usually by means of an initiator which starts the chemical process. Typical initiators include any organic compound with a labile group: e.g. azo (-N=N-), disulfide (-S-S-), or peroxide (-O-O-).

2. Chain propagation[8]

3. Chain termination, [8]which occurs either by **combination** or **disproportionation**. Termination, in radical polymerisation, is when the free radicals combine and is the end of the polymerisation process.

- Some side reactions may occur, such as: chain transfer to monomer, chain transfer to solvent, and chain transfer to polymer.

- Unlike condensation polymerisation (also known as step-growth polymerization):
 - high molecular weight polymer is formed at low conversion
 - no small molecules, such as H_2O , are eliminated in this process
- New monomer adds on the growing polymer chain via the reactive active centre which can be a
 - free radical in free radical addition polymerisation
 - carbocation in cationic addition polymerisation
 - carbanion in anionic addition polymerisation
 - organometallic complex in coordination polymerisation
- The monomer molecule can be a
 - unsaturated compound like ethylene or acetylene which make them reactive, see vinyl polymer
 - Alicyclic compound, see ring-opening polymerisation
- Given special reactants and reaction conditions an addition polymerization can be considered a living polymerization.
- Above a certain **ceiling temperature**, no polymerisation occurs[8].

In the polymerization of ethylene, its pi bond is broken and these two electrons rearrange to create a new propagating center like the one that attacked it. The form this propagating center takes depends on the specific type of addition mechanism. There are several mechanisms through which this can be initiated. The free radical mechanism was one of the first methods to be used. Free radicals are very reactive atoms or molecules which have unpaired electrons. Taking the polymerization of ethylene as an example, the free radical mechanism can be divided in to three stages: chain initiation, chain propagation and chain termination[9].



Polymerization of ethylene

Figure II.2

Free radical addition polymerization of ethylene must take place at high temperatures and pressures, approximately 300°C and 2000 At. While most other free radical polymerizations do not require such extreme temperatures and pressures, they do tend to lack control. One effect of this lack of control is a high degree of branching. Also, as termination occurs randomly, when two chains collide, it is impossible to control the length of individual chains. A newer method of polymerization similar to free radical, but allowing more control involves the Ziegler-Natta catalyst especially with respect to polymer branching [9].

Other forms of addition polymerization include cationic addition polymerization and anionic addition polymerization. While not used to a large extent in industry yet due to stringent reaction conditions such as lack of water and oxygen, these methods provide ways to polymerize some monomers that cannot be polymerized by free radical methods such as polypropylene. Cationic and anionic mechanisms are also more ideally suited for living polymerizations, although free radical living polymerizations have also been developed[9].

II.6.2 Step-growth

Step growth polymers are defined as polymers formed by the stepwise reaction between functional groups of monomers. Most step growth polymers are also classified as condensation polymers, but not all step growth polymers (like polyurethanes formed from isocyanate and alcohol bifunctional monomers) release condensates. Step growth polymers increase in molecular weight at a very slow rate at lower conversions and only reach moderately high molecular weights at very high conversion (*i.e.* >95%).

To alleviate inconsistencies in these naming methods, adjusted definitions for condensation and addition polymers have been developed. A condensation polymer is defined as a polymer that involves elimination of small molecules during its synthesis, or contains functional groups as part of its backbone chain, or its repeat unit does not contain all the atoms present in the hypothetical monomer to which it can be degraded [7].

II.2 ENGINEERING THERMOPLASTICS

II.2.1 Introduction

The development of plastic materials is one of the most successful stories of the twentieth century. In the sixties, plastics represented a small fraction of the total annual consumption of materials, but 20 years later they surpassed metallic materials (mostly iron-based) in terms of consumed volume. At the end of the century, plastics reached the astonishing total amount of 150 million metric tons produced per year. Of this amount, 70% is comprised by the so-called commodity plastics, 11% by thermoset resins, 7% by elastomers, and 12% by engineering thermoplastics[9].

The definition of engineering plastics is rather arbitrary. In the last edition of this encyclopedia they were defined as thermoplastic resins, neat or filled, which maintain dimensional stability and most mechanical properties above 100°C and below 0°C. In such a definition, engineering plastics are obviously intended as engineering thermoplastics and the terms are used interchangeably. They encompass plastics that can be formed into parts suitable for bearing loads and able to withstand abuse in thermal environments traditionally tolerated by metals, ceramics, glass, and wood. A more general definition defines *engineering plastics* as those *high performance materials that provide a combination of high ratings for mechanical, thermal, electrical, and chemical properties*. This article adopts this latter definition, with the following three restrictions: [9] thermoplastics considered here are generally produced on an industrial scale; [10] with some exceptions, their predominant application is as solid parts or films, not fibers or cellular materials; and [11] sophisticated derivations of commodities, like reinforced, widely used in engineering applications are excluded. Following these guidelines, Table 1 was compiled; occasionally, copolymers, blends, and reinforced polymers are included. The materials have been arbitrarily grouped by considering the most representative heteroatom present in their chemical structure.

These materials are discussed in general in this article and in more detail in articles devoted to the various polymers. Cross references are provided. The selection of polymer families treated here is somewhat arbitrary. For instance, fluoropolymers are more functional materials than engineering materials, and acrylic resins suffer enough

thermal instability to be considered by some authors as outside the border of engineering plastics. However, PTFE (together with some copolymers) and PMMA have been considered because of their notoriety and some specific engineering applications.

Table II.1 Relationships Between Polymer Properties and Morphology

Relationships between Polymer Properties and Morphology		
Property	Crystalline	Amorphous
Light transmission	High	None to low
Solvent resistance	High	Low
Lubricity	High	Low
Dimensional stability	High	Low
Mold shrinkage	High	Low
Resistance to dynamic fatigue	High	Low
Facility to form high strength fibers	High	None
Thermal expansion coefficient	High	Low
Melting temperature	Sharp	Absent
Dependence of properties on temperature	High	Low

In Table II.1, the qualitative dependence of some properties of polymeric materials as a function of their morphological state is reported. Such properties are determined directly or indirectly by the different response of chains to solicitations (chemical, thermal, and so on) when they are in an ordered arrangement or in a random one. Totally crystalline (100%) polymers are impossible to obtain because of the unavoidable presence of chain folds; further, the crystallinity degree can change under the effect of thermal, mechanical, or chemical operations.

II.2.2 History of development of Thermoplastics

The development of engineering thermoplastics began in the thirties and is still continuing. The first patent on polyamide (nylon) was obtained by Carothers in 1931. Before the second World War, acrylic and polyester resins were discovered, as well as styrene-based copolymers (ABS) and PTFE. The latter was brought to full production in 1950 as Teflon by DuPont. In the same year, polycarbonates were introduced by General Electric and acetal resins by Celanese. In the period of 1960–1980, most of the actual high performance polymers were developed, among them were polyimides, PES, PPS, PEEK, and PEI, as well as other engineering resins such as PPO and PBT. At that time, the potential of development of novel engineering plastics was overestimated, and when it was realized that the volume growth was not so fast, the introduction of new families slowed down. Several factors contributed to this change of attitude, from the growing of costs necessary for the introduction of a new material, to a lower demand of materials studied for structural applications, and finally to the competition of tailored grades of existing polymers (also commodity plastics, like PP), new blends, and reinforced materials. Furthermore, the time from the invention of a new polymer structure to the achievement of the industrial stage remained quite high (10– 12 years), in spite of the experience accumulated in such processes. Thus, from an originally forecasted 25% of the whole plastics market, engineering plastics cover only 10% roughly. It remains true that the growth rate is higher than that of commodities, but this expands their total fraction only very slowly. In Figure II.3, the chronological development of commercial thermoplastic polymers is sketched, taking into account commodities nearer to engineering polymers (in properties) [11,12]. The figure shows that most of the engineering thermoplastics were introduced industrially in the 1950–1980 period. The new flourishing in the nineties was partly enhanced by some particular events, like the development of metallocene catalysts, which rendered convenient the fabrication of new materials like sPS and COCs, and the availability of the monomer for PEN.

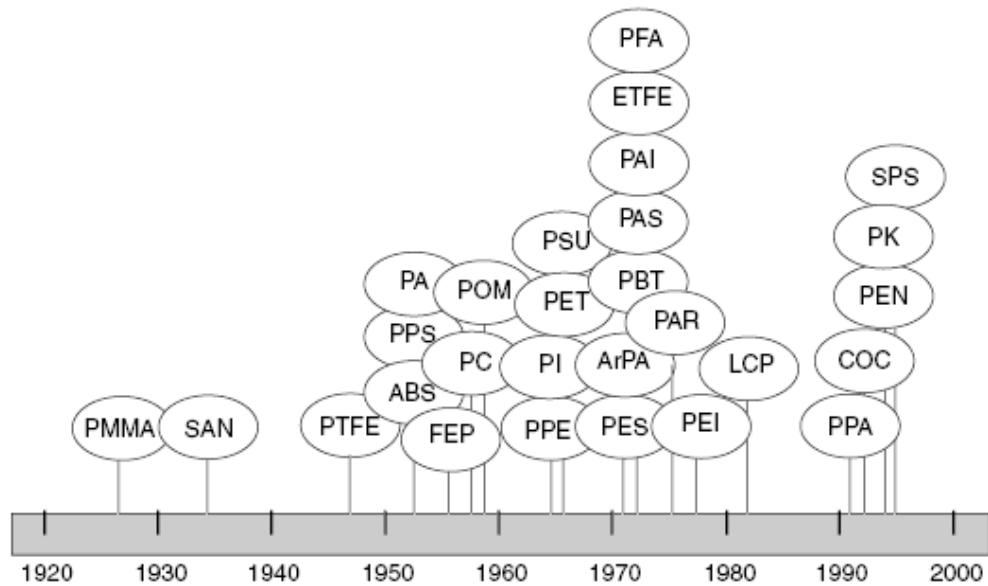


Figure II.3 The Historical Development of Synthetic Thermoplastic Resins.

The reported years indicate the presumed entry in the market. [6]

Table 2 reports for each polymer family the most important producers and corresponding trade names, with the aim of helping the reader to identify materials. Some books are dedicated to this task [12–15], which is complicated by ongoing mergers and selling of operations, resulting in changed connections between producers and trade names.

II.2.3 Properties of Thermoplastics

Some material properties are intrinsic to the chemical substance under investigation; others depend on the processing operation, which confers a shape and orientation to the material. Because some processing is often necessary to prepare testing specimens, intrinsic properties can be difficult to measure. Some properties acquire relevance only when the final article is manufactured and strictly depend on the specific use of the article. Properties have been distinguished as performance, maintenance, or aesthetic properties [9]; however, this classification is extremely subjective. Herein, mainly intrinsic and processing properties are considered, divided into four conventional groups: physical, electrical, thermal, and mechanical. Several of such properties change remarkably depending on the morphology (amorphous or semicrystalline materials) or

for the presence of fillers and reinforcing fibers. It is impossible to report the properties of all the grades present on the market; it was estimated that more than 5300 grades of engineering plastics were offered by producers in 1997 [13]. Thus, the more representative of them are described in discussions of specific polymers. In Table II.2, the most representative properties are reported, together with the proper SI units and, if existing, the respective standard measurement method. Several books describe the methods in more detail [11,12,16].

Table II.2 Producers and Trade Names of Engineering Thermoplastics

Material ^a	Trade Name	Manufacturer
COC	Topas	Ticona
	Apel	Mitsui Petrochemical
	Zeonex ^b , Zeonor ^c	Nippon Zeon
	Arton	JSR
sPS	Questa	Dow
	Xarec	Idemitsu
POM	Delrin	DuPont
	Hostaform, Celcon	Ticona
	Ultraform	BASF
	Tenac	Asahi
PET, PBT	Iupital	Mitsubishi
	See Table 4	See Table 4
PAR	U-Polymer	Unitika ^d
	Durel	Ticona
LCP	Vectra	Ticona
	Xydar	BP Amoco
	Zenite	DuPont
	Summika	Sumitomo
PPE	Siveras	Toray
	PPO, Noryl ^e	GE Plastics
	Luranyl	BASF
	Vestoran	Degussa Huls
PC	Makrolon	Bayer
	Lexan	GE Plastics
	Calibre	Dow
	Iupilon	Mitsubishi
PK	Carilon	Shell
	Ketonex	BP Amoco
PEEK	Victrex	ICI
	Ketron	DSM
PEK	Stilan	Raytheon
	Hostatec	Ticona
	Kadel	BP Amoco
PEKK	Declar	DuPont
PEKEKK	Ultrapek	BASF
PEN	Koladex	ICI
	Hipertuf	Shell ^f
PMMA	Perspex, Diakon	ICI
	Plexiglas, Plexidur, Altuglas, Vedril	AtoHaas
	Acrifix	Rohm
	Vestiform	Huls
	Paraglas, Degalan	Degussa
	Lucryl	BASF
	Sumipex	Sumitomo
	Fortron	Ticona
PPS	Ryton	Phillips
	Supec	GE Plastics
	Tedur	Bayer
	Craston	CIBA-GEIGY
	Techtron	DSM

Table II.2 (cont'd) [7]

Material ^a	Trade Name	Manufacturer
PSU	Udel	BP Amoco
	Ultrason S	BASF
PES	Radel A	BP Amoco
	Ultrason E	BASF
	Victrax PES	ICI
	Astrel	Carborundum
PAS	Radel R	BP Amoco
ABS	See Table 5	See Table 5
SAN	Luran	Bayer
	Lustran	BASF
	Tyrl	Dow
PA	See Table 6	See Table 6
ArPA	Nomex	DuPont
	Conex	Teijin
	Kevlar	DuPont
	Twaron	Akzo
PI	Kapton, Vespel, Avimid	DuPont
	Upilex	UBE
	Kinel, Matrimid	CIBA-GEIGY
	Apical	Allied
	Aurum	Mitsui Toatsu
	Kerimid	Nyltech
	Duratron	DSM
PAI	Torlon	BP Amoco
PPA	Amodel	BP Amoco
PEI	Ultem	GE Plastics
Fluoropolymers	Teflon, Tefzel	DuPont
	Fluon	ICI
	Hostaflon	Dyneon
	Algoflon, Hyflon	Ausimont
	Neoflon, Polyflon	Daikin
	Aflon	Asahi Glass

^aSee Table 1 for explanation of acronyms.^bHomopolymer.^cCopolymer.^dCommercialized by Amoco for several years under the trade name of Ardel.^eIn blend with other polymers.^fBusiness acquired by Mossi & Ghisolfi.

II.2.3.1 Physical Properties

Physical properties include density, properties connected to their combustion tendency (flammability and oxygen index), optical properties (refractive index and yellow index), and the ability to absorb water. Density ρ , ie, the mass per unit volume, depends on the nature of atoms present in the chemical structure and the way molecules (chains) pack together. Polyolefins, composed of C and H only, have densities in the range 0.85–1; organic polymers containing heteroatoms rarely have densities higher than [2]. Conformations and crystalline phases strongly influence density. Crystalline phases are generally more dense than amorphous phases, an average ρ_c/ρ_a ratio of 1.13 ± 0.08 has been determined [9].

Table II.3 Producers and Trademarks of Thermoplastic Polyesters [6]

Producer	PET	PBT
Eastman	Ektar, Eastapak, Kodapak, Tenite, Kodar	Ektar
Allied Signal	Petra	
DuPont	Rynite, Mylar	Crastin
Dow	Lighter	
Ticona	Impet	Celanex
Hoechst	Polyclear	
Bayer		Pocan
BASF		Ultradur
GE Plastics		Valox
DSM	Arnite	Arnite
Degussa/Hüls		Vestodur
ICI	Melinar ^a , Melinex ^a	
Shell		Cleartuf ^b
Nyltech	Techster	Techster
Mitsubishi		Novadur
EMS Chemie		Grilpet

^aBusiness acquired by DuPont.

^bBusiness acquired by Mossi & Ghisolfi.

an oxygen/nitrogen mixture able to support combustion of a candle-light sample under specific test conditions. The LOI test is necessary but not sufficient for determining the

burning behavior of polymers in real conditions. For this task, specific flammability tests have been established on an empirical basis. The most widely used test is UL94, elaborated by Underwriters Laboratories, rating the ability of a material to extinguish a flame once ignited [15]. In decreasing order, the UL94 degrees are V-0, V-1, V-2, and HB, based on a specific specimen thickness.

Only a few high performance polymers, like polyetherimides, have been classified as inherently nonflammable (ie, V-0); other polymers can reach a good classification after the addition of specific additives, ie, flame-retardants, in the material formulation.

Table II.4 Producers and Trademarks of ABS Materials [7]

Producer	Pure grade	Blend with PC	Blend with PBT	Blend with PVC	Blend with others
GE Plastics	Cycolac	Cycoloy	Cycolin	Cycovin	
Dow	Magnum	Pulse			Prevail ^a
Bayer	Lustran	Bayblend			Triax ^b
	Novodur				
EniChem	Sinkral	Koblend			
Hoechst	Cevian				
Toray	Toyolac	Toyolac			
Condea	Vista			Suprel	
Shin-A	Claradex				
Nova	Cycogel				
Schulman	Polyfabs			Polyman	

^aWith polyurethane.

^bWith PA.

The refractive index n measures the deviation of light when passing through matter and is expressed as $\sin(i)/\sin(r)$, where i and r are the angles of incident light and refracted light, respectively. It is closely linked to molecular structure of polymers and contributes to their optical properties, like clarity, haze, birefringence, color, transmittance, and reflectance. Most of engineering plastics considered here are opaque and/or inherently colored, with the exceptions of PC, PMMA, and COC. For them, when used in optical applications, the yellow index (YI) is relevant. Yellow index indicates the

degree of departure of an object color from colorless or from a preferred white toward yellow and is determined from spectrophotometric data.

Water absorption indicates the increase of weight of a polymer after immersion in water under specified conditions of temperature and time. Generally, it is referred to 24 h at room temperature (23°C) and is expressed as a percentage with respect to the initial weight. If water is absorbed by a polymer, drying is required before processing operations because the presence of water at high temperature results in uncontrolled degradation of the material and consequently poor performance. This is the case of PET and other polyesters.

Some polymers like polyamides absorb water from air humidity and hold water molecules rather firmly by hydrogen bonding. Absorbed water causes a slow variation of properties like electrical characteristics, mechanical strength, and dimensions. For this reason, polymers or specific grades insensitive to water must be employed in moist environments[13].

Table II.5 : Properties, Units and Standard Methods of Measurement [7]

Properties, Units and Standard Methods of Measurement		
Property	ASTM method	ISO method
Physical properties		
Density, g/mL	D792	1183
Flammability	UL94 ^a	
Oxygen index (LOI), %	D2863	4589
Refractive index	D542	489
Yellowness index (YI)	D1925	
Water absorption (24 h, 23°C)		
Electrical properties		
Dielectric constant (1 MHz)	D150	
Dielectric strength (1 mm), kV/mm	D149	
Dissipation factor (1 kHz)	D150	
Volume resistivity (23°C, dry), Ω -cm	D150	
Thermal properties		
Glass-transition temperature (T_g), °C		
Melting temperature (T_m), °C		
Heat-deflection temperature (HDT) at 0.45 or 1.8 MPa, °C	D648	75
Specific heat capacity J/(kg·K)		
Thermal conductivity (23°C), W/(m·K)	C177	
Thermal expansion coefficient, K ⁻¹	D696	
Upper working temperature, °C		
Mechanical properties		
Elastic modulus, GPa ^b	D638	527
Tensile strength, MPa ^c	D638	527
Flexural modulus, GPa ^b	D790	178
Flexural strength, MPa ^c	D790	178
Compressive strength, MPa ^c	D638	527
Elongation at break, %	D638	527
Notched Izod impact resistance (3.2 mm), J/m ^d	D256	180
Hardness (Rockwell M or R)	D785	2039
Friction coefficient	D1894	8295
Rheological properties		
Intrinsic viscosity, Pa·s		
Melt-flow index, g/10 min	D1238	1133

^aUL94 is an Underwriters Laboratories method.^bTo convert GPa to psi, multiply by 145,000.^cTo convert MPa to psi, multiply by 145.^dTo convert J/m to lbf·ft/in., divide by 53.38.

II.2.3.2 Electrical Properties

Electrical properties include dielectric constant, dielectric strength, dissipation factor, and volume resistivity. All of them depend on temperature and water absorption. The (relative) dielectric constant is the ratio of the capacitance of a condenser formed by two metal electrodes separated by a suitable layer of the material considered and the same separated by dry air. The dielectric strength measures the dielectric breakdown resistance of a material under an applied voltage. The applied voltage value just before breakdown is divided by the specimen thickness. Thus, because the result depends on thickness, this value must be specified. The dissipation factor, also called loss tangent, measures the tangent of the difference angle between 90° (ideal angle for a perfect dielectric material) and the true angle at which an alternating current leads the voltage. It is equivalent to the ratio of current dissipated into heat and current actually transmitted. The volume resistivity is the electrical resistance of a unit cube of a given material when an electrical potential is applied to two opposite faces of the cube[14].

II.2.3.3 Thermal Properties

Thermal properties include some transitions like melting temperature and glass transition temperature, the heat deflection temperature (HDT), specific heat capacity, thermal conductivity, coefficient of thermal expansion, and upper working temperature. The melting temperature T_m is the temperature at which a solid becomes a liquid (or, on cooling, at which a liquid solidifies). For polymeric materials, T_m is often a temperature range rather than a single value; however, its point value should represent the maximum temperature at which crystallites exist. Amorphous polymers do not exhibit a T_m . The glass-transition temperature T_g is the temperature at which a solid, rigid, and brittle polymer becomes rubbery by loosening remarkably its rigidity. Mechanical properties are also reduced at T_g , and other properties like volume, thermal expansion coefficient, and specific heat capacity change noticeably. Being kinetic in nature, T_g occurs over a temperature range (depending, for instance, on cooling rate) and is hardly visible in some polymers.[12]

HDT measures the temperature at which a specimen is deformed a specific amount (eg, 0.25 mm) under a given load (usually, 0.45 or 1.82 MPa), applied in a three-point

arrangement. HDT is also called Deflection Temperature Under Load DTUL and should not be interpreted as a safe temperature for continuous operation (which is usually somewhat lower). The specific heat capacity represents the amount of heat necessary to increase the temperature of a unit mass of a substance by one degree. Depending on its definition at constant pressure or at constant volume, it is indicated as c_p or c_v , respectively. Thermal conductivity represents the amount of heat conducted per unit of time through a unit area of a material of unit thickness having a difference of one degree between its faces. The thermal expansion coefficient represents the change in volume (or length) accompanying a temperature unit variation and is of great importance in molding operations of plastic articles, having mold shrinkage as a practical effect. The upper working temperature is a purely empirical indication at which a given plastic can be expected to perform safely and satisfactorily. It is generally lower than HDT [13].

II.2.3.4 Mechanical Properties

Mechanical properties include tensile properties (modulus and strength), flexural properties (modulus and strength), compressive strength, elongation at break, impact resistance, hardness, and friction coefficient. Other relevant properties are creep and fatigue but it is difficult to find comparative data among materials.

The tensile modulus (also elastic, or Young's modulus) E is the stress-to-strain ratio within its proportional limit for a material under tensile loading (in practice, the initial slope of the stress-strain curve). The tensile strength represents the maximum tensile stress observed when the specimen is being pulled. It may or may not coincide with the ultimate strength, ie, the tensile stress at specimen failure. In tough materials it can be equal to the yield stress. The flexural modulus is the stress-to-strain ratio within its proportional limit for a material under bending load conditions. It measures the stiffness of a material. The flexural strength is the ability of a material to flex without permanent deformation or breaking. The elongation at break is equal to tensile strength at failure multiplied by 100. It is expressed as a percent of the original length of the specimen. The impact strength (or impact resistance) represents the ability of a material to resist physical breakdown when subjected to a rapidly increasing force and is accepted as a

comparison guide for toughness (see IMPACT RESISTANCE). It depends strongly on the type of test used. The most widely used test in the field of plastics is Izod; the Charpy test is less common. The Izod test requires specimens of thickness from 3.18 to 12.7 mm, preferentially notched following the test method prescriptions. A weighted pendulum arm released from a fixed height strikes the specimen in a specified way. The Izod impact energy is measured by dividing the energy lost by the pendulum (presumably absorbed by the specimen) by the specimen thickness [13].

Hardness, defined as the resistance of a material to local deformation, is connected in a complex way to mechanical properties, elasticity, and plasticity. Hardness cannot be defined unambiguously and depends strongly on the test adopted for its determination. It is usually characterized by the combination of three parameters, ie, scratch resistance, abrasion resistance, and indentation under load. For the indentation test, different Shore and Rockwell scales are in use, Rockwell M and Rockwell R being the most popular for engineering plastics [10]. The scale depends on the combination of load and indenter dimensions. The friction coefficient represents the resistance of surfaces of solid bodies in contact with each other to sliding or rolling. It is represented as $k = F/w$, where F is the force necessary to move one surface with respect to the other one, and w the load exerted on them.

II.2.3.5 Rheological Properties

Rheological properties, describing the deformation of materials under stress and concerning their flow properties, must be considered in all processing techniques for the fabrication of plastic articles. In order to give operators necessary rheological information, melt viscosity vs shear plots are commonly included in Data Sheets provided by plastics producers. Here only a few properties connected to rheology are considered, ie, intrinsic viscosity (IV) and melt-flow index (MFI). Intrinsic viscosity measures the capability of a polymer in solution to increase the viscosity of the solution itself. Because IV increases with molecular mass, it is an indication of this last property. The MFI (or simply melt index) measures the isothermal resistance to flow through an extrusion plastometer commonly referred to as melt indexer. Practically, the amount of matter forced by a given load to pass in 10 min through a standard die is determined. Melt-flow index can be considered as a single-point test (ie, resistance to flow at a single

shear rate). Every plastics processing technology operates at a defined MFI range as follows (2): 5–100 g/10 min for injection molding, 5–20 g/10 min for rotational molding, 0.5–6 g/10 min for film extrusion, and 0.1–1 g/10 min for blow molding and profile extrusion.

II.2.3.6 Chemical Resistance

Chemical resistance is less rigidly defined than the properties discussed previously. Measurement methods include immersion in selected vapors or liquids of a test specimen, then determining the variation of mechanical properties after and before treatment. Optical properties are also considered, particularly in the case of transparent materials. The test results are generally indicated as excellent, good, fair, or poor, or are given other arbitrary scale units. Chemical agents are chosen in order to simulate possible real situations: strong and weak acids, alkalis, saline solutions, hydrocarbons (aliphatic or aromatics), oils and greases, alcohols, aldehydes, ketones, etc. Engineering plastics are generally difficult to dissolve in most solvents. Strictly correlated to chemical resistance is weathering resistance, where a combination of a particular environment, temperature, time, and uv irradiation is considered, also with cyclic experiments.

II.2.4 Processing of Thermoplastics

Processing of thermoplastic materials can be classified into four main categories: extrusion, post-die processing, forming, and injection molding [9–11]. In an extruder, the polymer is melted and pumped into a shaping device called a die, through which the material is forced to assume a particular shape. The pumping action is done by a single-screw or by a twin-screw device, the configuration of which is essential for a suitable result. Extruders are very often used at the end of the polymerization reactor in order to obtain polymer pellets by chopping an extruded strand. Extruders are also currently used to mix in the proper additives for the polymer, to obtain intimately mixed polymer blends, to devolatilize the material from the monomers or solvent residues, and in some special cases as a chemical reactor (reactive extrusion). For example, polyetherimide is prepared at the industrial level by reactive extrusion. Depending on the extrusion die geometry, final articles can also be obtained, including sheets, films, pipes, rods, and

profiles of various geometries (T, double T, C, and so on). Coating on wires can be done, as well as coextrusion of two or more layers. Post-die processing includes a number of operations carried out at the exit of the extruder die in a free-surface way. Examples of such processes are fiber spinning, film blowing, and sheet forming. The shape and dimensions of the extrudate material are determined by the rheological properties of the melt, the die dimensions, the cooling conditions, and the take-up speed (relative to the extrusion rate).

Forming processes use a mold to confer the final form to the article. Blow molding is widely used in the manufacture of bottles or other containers for liquids, widely using engineering polymers like PET and PC. Essentially, an extruded cylindrical parison is inflated with a gas until it fills the mold cavity. A good equilibrium between the melt strength of the resin under low shear conditions (parison stability) and the flow properties under high shear conditions (blowing) are essential for obtaining a satisfactory result. In thermoforming, a polymer sheet is heated to a temperature above its T_g (or sometimes above T_m) and then pressed into the female part of the mold by means of a suitable plug or by vacuum pulling. Simple-shape articles such as trays can be obtained. In compression molding, an amount of polymer is heated at the proper temperature and then squeezed by means of the male part of the mold into the mold cavity. Injection molding is the most commonly used processing technique for engineering thermoplastics. Typically, the polymer pellets are melted and the melt pulled forward by means of a screw as in extrusion, so filling a mold under appropriate pressure. The shape of the mold, the number and relative location of the injection devices, and the mold cooling rate determine, together with the intrinsic properties of the material, the final quality of the molded articles. Very complex article shapes can be obtained by this technique. A viscosity of the resin around 10,000 Pa·s and a shear rate of 100 s⁻¹ are needed for a convenient operation. The main problem in injection molding is shrinkage, caused by the volume changes during transition from the melt to the solid. The typical shrinkage of semicrystalline polymers during processing is around 1–4%, compared to 0.2–0.8% for amorphous polymers (¹⁷). To reduce the problem, crystallinity could be maintained low, but this is to the detriment of mechanical properties. A compromise should be used. For polymers which crystallize slowly, like

PET, it is preferable to allow the polymer to reach the maximum crystallization degree by the use of nucleating agents. If the shrinkage amount is different in different volume portions of the fabricated part, warpage of the part itself can be observed. Interpolymer Competition The properties of engineering thermoplastics span a wide range, and there are many overlapping situations among resins. To select the right polymeric material for a specific application is a hard job because the forest of commercial polymers has become so crowded. Books have appeared to guide the materials engineer in the selection of thermoplastic materials, with the help of a dedicated software [13].

Four main groups of technical considerations must be made in order to make the right choice, ie, mechanical, electrical, environmental, and appearance. In addition, two other elements are important, ie, cost and specifications (eg, imposed by a government body or by a corporation). The environmental considerations include the operating temperature, the chemical environment, the weathering exposure, and humidity degree. The appearance includes style, shape, color, transparency, and surface finish of the fabricated object. Mechanical and electrical considerations must include both short-time and long-time values, and also the effects of environment on such properties. Also, appearance can vary under service conditions. The necessary information must be provided by different actors, that is, the material supplier, the processor, the processing equipment supplier, and the product designer/producer.

Depending on the particular application, numerous properties should be considered during the selection of the best candidate. Further, every property has a different importance, and thus a different weight on the final choice. Property values reported here are representative; several of them vary over a wide range depending on several factors, like the nature and amount of fillers, the possible occurrence of copolymerization, etc. Also, some data are not available in the current literature and others are difficult to describe with just one figure. This is particularly true for rheological data reported in data sheets as flow curves viscosity vs temperature curves, etc. Similar difficulties arise for creep curves (related to long-term mechanical resistance) and shrinkage and warpage of fabricated parts, strongly dependent on the geometry and thickness of the part itself. The internet has made it easier to access data about polymer grades actually produced

In the final selection of the best material for the fabrication of a specific object, a compromise is generally made by choosing the material which shows an optimized balance of the most relevant properties. In addition to some particular

Table II.6 Sites for Engineering Thermoplastics [20]

WWW Sites Containing Data Sheets of Engineering Thermoplastics	
URL (Uniform Resource Locator)	Information source
<i>General</i>	
http://matls.com/materials	MatWeb, the on-line
http://polydatabase.com/index2.htm	Information resource
<i>Wholesalers</i>	
http://www.boedeker.com/mguide.htm	Boedeker Plastics Inc.
http://www.goodfellow.com/static/A/start.html	Goodfellow
http://www.panpolymers.co.uk/fprodb.htm	Pan Polymers
http://members.aol.com/vpisales/tpguide.html	Venture Plastics
http://www.actech-inc.com/engmrgt.htm	Actech Inc.
http://www.plasticsandmetals.com/plastics.html	Cal Plastics and Metals
http://www.plasticeng.com/copy_of_plasticeng/engineeringmaterials.htm	Plastics Engineering Inc.
<i>Producers</i>	
http://www.dow.com/Homepage/index.html	Dow Chemicals
http://www.shellchemicals.com/home/1,1098,-1,00.html	Shell Chemicals
http://www.ticona.com/	Ticona (Celanese AG)
http://www.basf.com/	BASF
http://www.dupont.com/	DuPont
http://www.bayer.com/	Bayer
http://polymers.alliedsignal.com/	Allied Signal
http://geplastics.com/	GE Plastics
http://dsmpepp.com/	DSM

properties, like transparency and the question of processability (which involves complex issues as rheology, shrinkage, and surface finishing), in most of the applications of engineering thermoplastics, the following characteristics and properties are considered: price, mechanical properties, thermal properties, electrical properties, and chemical resistance.

The price of a thermoplastic resin is basically determined by the cost of preparation, which in turn strongly depends on the cost of reagents (monomers, catalysts, etc), the complexity of the manufacturing process, and the dimension of production plants. Aliphatic polyketones, for instance, are made from very cheap raw molecules as ethylene, propylene, and CO; their cost is determined by the need for expensive

catalysts, based on Pd complexes, and the relatively complex production plant. On the other hand, PEN, which can easily be prepared in the same reactors used for PET, suffers from the difficult availability of its basic monomer dimethyl 2,6-naphthalene dicarboxylate. Most engineering polymers contain aromatic monomers, which are difficult to synthesize and polymerize, with slow and sophisticated mechanisms (condensation, substitution, oxidative coupling).

Roughly, commodities are priced at US\$0.5–1/kg, engineering polymers in the range of US\$1–5/kg, and high performance polymers the range of US\$5–50/kg. The current prices fluctuate following market conditions and can be found as a price range, for most materials, in technical journals like *Plastics Technology*. In Figure II.4, the prices of engineering thermoplastics are reported as a function of annual production volume, confirming, with a few exceptions, the inverse relationship between the two parameters. The price is reported in U.S. cents per volume unit, more significant than the corresponding price per mass unit. The unfilled materials have a density ranging from 1.02 g/mL for COCs to 2.18 g/mL for PTFE. However, the density of most engineering thermoplastics falls around 1.15– 1.45 g/cm³. The price/volume relationship does not work when a low volume material can be produced in a captive way in a plant used also for producing a higher volume polymer. This is the case of polyarylates, some aliphatic polyamides, and polysulfones[14].

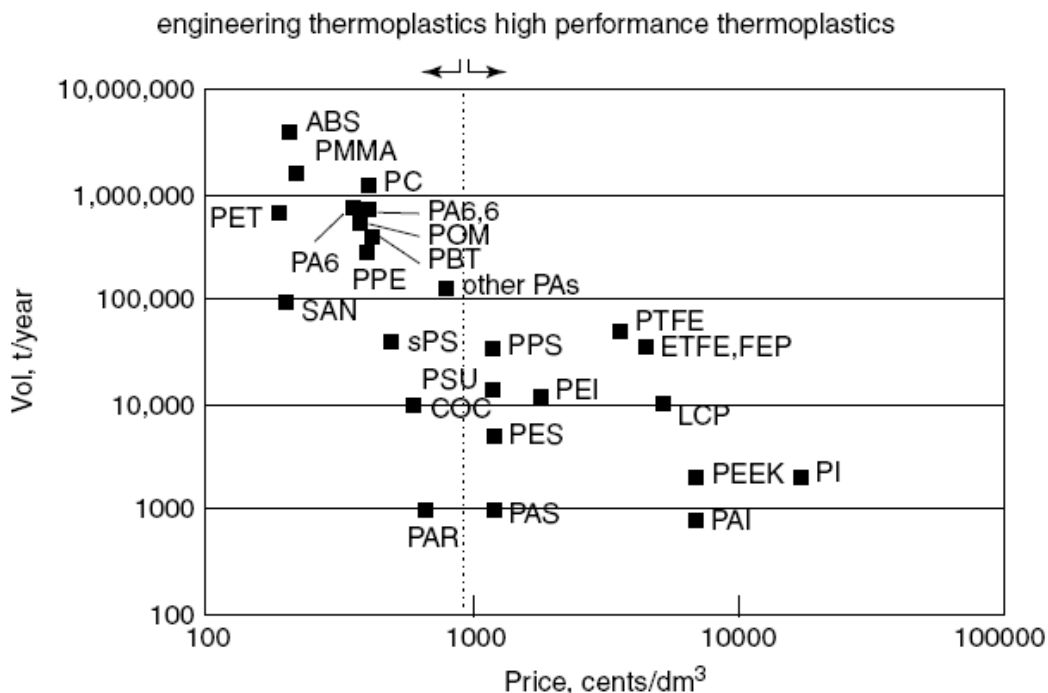


Figure II.4 Production Volumes and Prices For Volume Units For Thermoplastics [19]

Fig.II.4. Production volumes and prices for volume units for thermoplastics considered in this compilation. The dashed line represents an arbitrary border between engineering and high performance thermoplastics.

II.2.5 Summary of Mechanical, Thermal, and Electrical Properties

The most representative mechanical properties are elastic (or tensile) modulus, tensile strength, flexural modulus, and toughness. Flexural modulus is particularly interesting, because it represents the stiffness of the material; unfortunately, data are not available for all materials. However, because flexural modulus values are mostly of the same order of magnitude of tensile modulus values, the latter can be used for comparison purposes. Toughness is approximately described by Izod impact strength. Figure II.5 reports elastic moduli and Izod strengths of engineering thermoplastics.

Data ranges are particularly wide for toughness data. The figure shows that for any application, a wide number of combinations of stiffness and toughness is available in the field of engineering thermoplastics. Further, reinforcing practice with fibers, minerals, or

other fillers is largely applied in order to enhance the mechanical and thermal properties. Most of the materials treated here are offered in the market in a large number of reinforced grades. Such a practice also influences the cost of the material, and this is particularly relevant when the cost of the matrix is higher than the cost of the filler. Figure II.5 shows the increase of modulus values that can be obtained by adding glass fibers to several polymers.

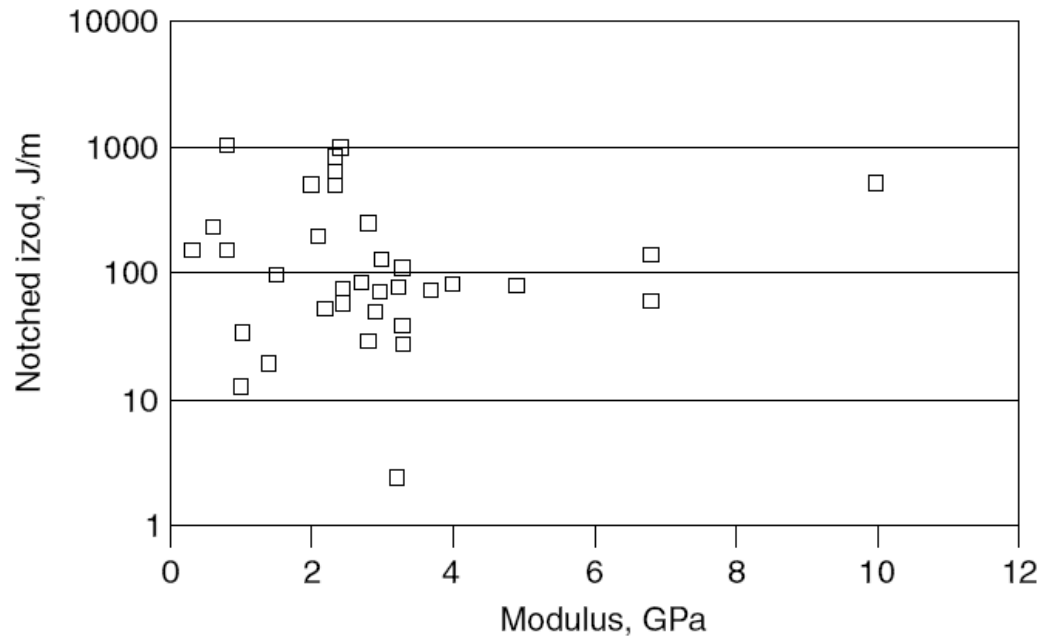


Fig. II.5 Modulus Vs Notched Izod Of Engineering Thermoplastics. [19]

Heat-deflection temperature does not correspond to the practical use temperature; however, it has been widely used in the plastics industry to compare the physical response of materials to temperature at a single-load level. In Figure II.5, HDT vs tensile strengths at two different loads are reported. Both groups of data roughly show a proportional trend that can be ascribed to the fact that in many cases the molecular structure of the chain influences, in the same sense, the mechanical and thermal properties.

The electrical properties of engineering thermoplastics are generally excellent. In specific applications, like cable and wire coatings, electrical or electronic parts, etc,

demanding values are requested. On the other side, electrical conductivity can be increased by adding particular fillers like metallic powders.[17]

Chemical Resistance. Chemical resistance belongs to environmental considerations because the accidental or expected exposure of a material to the action of chemicals or solvents can have relevant short-and long-term influence

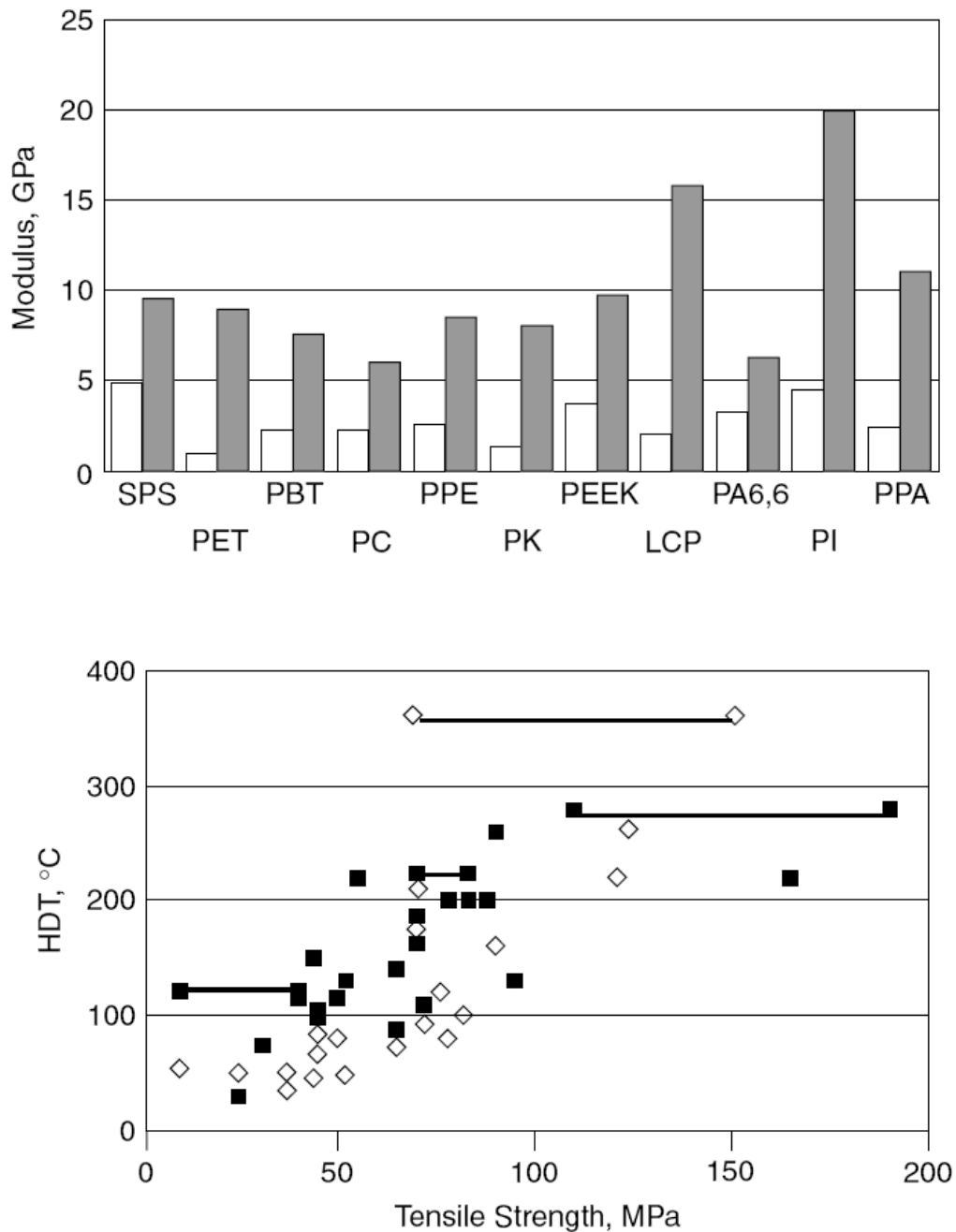


Figure.II.6. Tensile strength vs HDT of engineering thermoplastics. [17]

Table II.7 Chemical Resistance of Engineering Thermoplastics [7]

Material	Ketones	Acid		Alkali	Alcohol	Hydrocarbons (aromatic)	Greases and oil
		Dilute	Conc.				
sPS	G	G	G	G	F	G	G
POM		P	P	G	G	G	F/G
PET		G	P	G	F	G	G
PBT		G	F	G	G	G	G
PEN		G	F	G	G	G	G
PAR				F	F	F	F
LCP	G	F	G	F	G	G	G
PPE		F/G	G	F	P	F	F
PC		F/G	P	G	P	G	P
PK	G	P	G	F	G	G	G
PEEK	G	F	G	G	G	G	G
PMMA	G	F	G	F	P	P	P
PPS	G	F	G	G	G	G	G
PSU		G	G	G	P	G	P
PES		G	G	G	P	G	P
PAS		G	G	G	P	G	F
ABS		G	F		P		P
SAN		P	P	F	F	G	F
PA6,6	P	P	G	G	G	G	G
PA6	P	P	G	G	G	G	G
PA11	P/F	P	G	F	G	G	G
PA12	P/F	P	G	F	G	G	G
ArPA		F	F/G	G	G	G	G
PI	G	G	P	G	G	G	G
PAI	G	G	P	G	G	G	G
PPA	G	F	G	F	G	G	G
PEI		G	F/G		G		
F-polymers	G	G	G	G	G	G	G

^aP: poor; F: fair; G: good.

Table II.7 summarizes the resistance of polymers against the most common families of chemicals and solvents. As expected, fluoropolymers show the best response against the whole range of chemicals considered. Chemical resistance values reported in the table are indicative because they can be significantly affected by exposure length and temperature. In practice, chemical resistance testing under end-use conditions is suggested.

II.2.6 The Future

Thermoplastic materials have now pervaded every important aspect of the human life, from food management (through packaging) to clothing (through synthetic fibers), ground and air transportation, office equipment, health (medical instruments and devices, artificial prostheses), entertainment (audio and video reproduction components), sports goods, and so on. Applications of thermoplastic materials, both commodities and engineering thermoplastics, will continue to expand at the expense of other materials like glass, metals, wood, and ceramics. Moreover, the time between the laboratory synthesis of a new polymer and its industrial production remains high [17], thus discouraging the introduction of new materials. The expected expansion of the engineering thermoplastics market is of the order of 12% per year in the next three years [14]. Interestingly, the most significant threat to engineering polymers comes from some commodities, like polypropylene, which in some reinforced (but also unreinforced) grades reach the performance of some engineering materials.

II.3 Introduction to ABS Resins

Acrylonitrile butadiene styrene, or **ABS**, (chemical formula $(C_8H_8 \cdot C_4H_6 \cdot C_3H_3N)_n$) ABS is an acronym for the engineering polymer acrylonitrile-butadiene-styrene. Contrary to what the name suggests, ABS is rarely made by simply reacting acrylonitrile, butadiene, and styrene; intermediate stages are usually necessary. Nor is the polymer structure homogenous; multiple phases are usually present. In 1970, there were hundreds of patents to make ABS, 89 of which described a different series of chemical reactions. Today, it is estimated that there are over 2300 grades of ABS resins available commercially.[19] Almost all of these are produced by unique processes.

It is a copolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The proportions can vary from 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene. The result is a long chain of polybutadiene criss-crossed with shorter chains of poly(styrene-co-acrylonitrile). The nitrile groups from neighboring chains, being polar, attract each other and bind the chains together, making ABS stronger than pure polystyrene. The styrene gives the plastic a shiny, impervious surface. The butadiene, a rubbery substance, provides resilience even at low temperatures. ABS can be used between -25 and 60 °C. The properties are created by rubber toughening, where fine particles of elastomer are distributed throughout the rigid matrix.

Production of 1 kg of ABS requires the equivalent of about 2 kg of oil for raw materials and energy. It can also be recycled

End products made from ABS have properties passed on from each of the three components.

- Acrylonitrile makes the plastic hard, heat resistant and chemical resistant.
- Styrene adds rigidity, strength, and processibility.
- Butadiene makes the plastic more elastic, increasing the impact performance and toughness of the plastic[11].

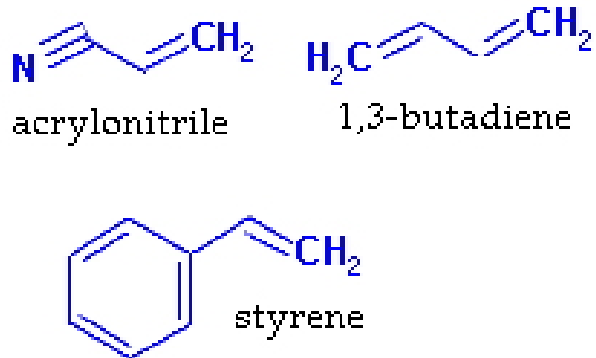


Figure II.7 Monomers in ABS polymer [11]

II.3.1 Properties of ABS

The mechanical properties of ABS are comparable to resins that cost far more. It is easy to process in standard injection molding, extrusion, thermoforming, and blow molding machines, which make up the majority of the plastic processing sales volume. It has high gloss, can be easily colored, has minimal shrinkage during molding, and is scratch-resistant making it aesthetically pleasing both after processing and through the life of the part.[9] It is considered to be one of the most versatile engineering thermoplastic resins.[11] Common ABS products are telephones and computer housings, appliance housings, helmets, automotive panels, and pipe.

With all the benefits of ABS come a few drawbacks. First, ABS degrades when exposed to heat, light, and oxygen. Without any modifications, this excludes ABS resins from use in outdoor or other harsh environments. With the addition of stabilizers, pigments, or protective coatings, this problem can be partially overcome.[11] However, added steps and materials increase processing time and cost of manufacturing. For this reason, the primary uses of ABS are found indoors or in UV protected environments.

Another disadvantage of ABS is that nearly all grades are opaque. This problem has been partially overcome by newer grades of ABS that graft methyl methacrylate onto a special styrene-butadiene substrate, which makes the polymer transparent. This special modification makes these polymers more expensive than standard ABS. It has found limited use in medical applications.

Major disadvantage of ABS is its susceptibility to degradation during processing. When many thermoplastics are exposed to heat (near melting temperature), they may bend or stretch, but they suffer little chemical degradation. Polyethylene is an example of such a plastic. ABS, on the other hand, will slowly degrade over time.[9] Its mechanical properties are reduced as it is exposed to high temperatures, as in processing. ABS has a strong thermal history, meaning that there is a limit to the number of times it can be reprocessed without significant loss of mechanical properties.[11] Because of the short cycle times in injection molding, extruding, and blow molding, this only becomes a factor in regrind or recycling. However, in rotational molding, with inherently long heating cycles, this disadvantage is important.

II.4 DESCRIPTION OF THE FDM

Created in 1989 by Scott Crump, Fused Deposition Modeling, or FDM, was one of the first commercially viable rapid prototyping technologies. Now a part of Stratasys Inc., [19] FDM has become an ideal solution for a diverse range of prototyping needs.

Today there is an array of materials available for extrusion in the various FDM machines they include: ABS plastic, polycarbonate, polyphenylsulfone, and proprietary UV plastic. Depending on the machine used objects can be as large as 59.9 x 50.0 x 59.9 cm. Default coloration for the material is white or clear. ABS can be ordered in any custom pantone color or in any of the 5 basic colors including black, red, blue, green, and yellow. In addition to the model material the FDM process also uses a temporary break away or water soluble support material laid down to attach the model to the build platform and bolster interior parts, negative space, holes, overhangs, and undercuts. The cost of material varies slightly depending on the quantity purchased and the vendor but averages USD 250 per cartridge for both model and support. With 878 cubic centimeters in a new cartridge the cost of material to build models is approximately USD 0.27 per cubic centimeter.

The FDM process begins with a three-dimensional model. This model must be completed, without geometry issues such as flipped “normals” or “naked edges”, within a solid or modeling environment such as Auto CAD, PRO E, or Rhinoceros (Figure II.8). The native three-dimensional model file format is then exported as a Stereolithography or STL file format extension. The STL file is then opened in Catalyst (Figure II.9), the software package supplied with the FDM Dimension modeler, so it can be prepared for prototyping. Once in Catalyst the model can be oriented either by surface selection or degree input to minimize supports, thus minimizing cost and time of build. Depending on the degree of detail and function of the model build style can be changed from draft to standard resulting in slice layers that are .33 and .245 mm respectively. The model’s interior style can be built “solid” with no hollow interior space or “sparse” where minimal scaffolding like threads are build within internal spaces

resulting in a semi-hollow part, again affecting cost and build time. After selecting the build and support style for the model an analysis procedure begins resulting in the establishment of a CMB file. The CMB file consists of multiple standard files generated by creating slices, supports, boundary curves, and tool paths for the model.

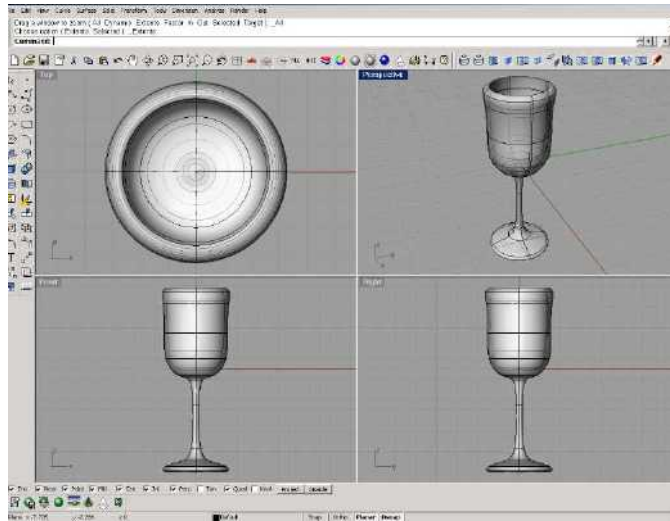


Figure II.8: Three-dimensional model of a wine glass as seen in Rhinoceros

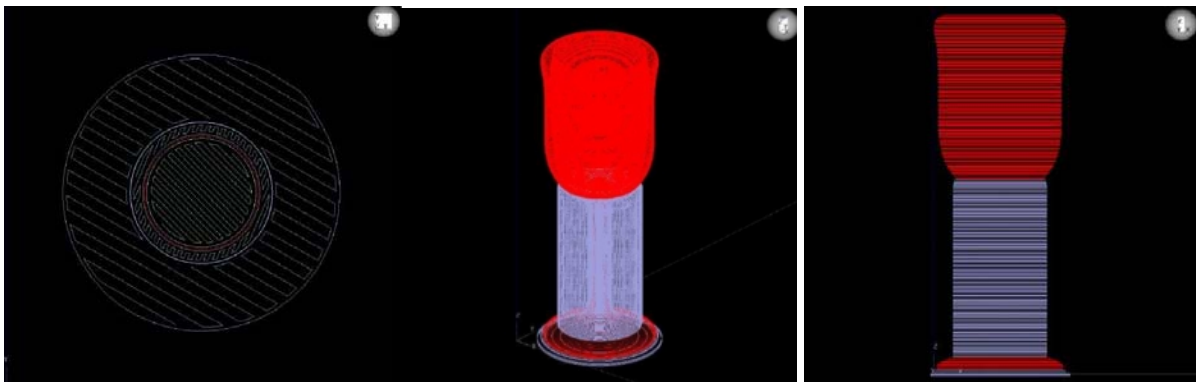
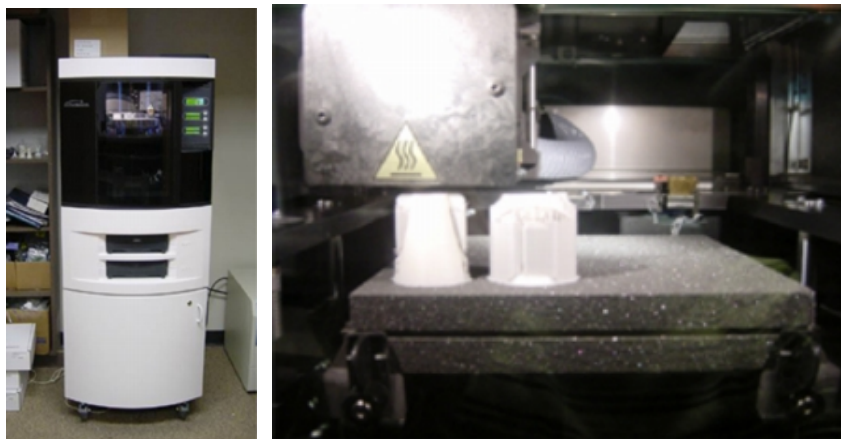


Figure II.9: Wine glass as seen in Catalyst as cross-section, from front, and in perspective view.

Slices are created horizontal to the x axis dividing the STL file into a stack of two-dimensional part boundary contours. Once the slices are compiled the support material is generated automatically. The design and location of the support material is dictated by the geometry of the model. After slicing and support generation boundary curves, or closed curves used to define a region in the xy plane, are completed. Two different types

of boundary curves are found in the analysis of a model: part boundary curves, which are a result of slicing, and support boundary curves which are a result of support generation. Finally tool paths, the data used to describe extrusion tip positioning is produced. The model is then shown in its sliced state with color coded representation of its supports and boundary curves. Models can be examined further, if need be, by stepping through each consecutive slice layer to determine if model and support material exist in the proper places. The model is then placed on a graphic representation of the build table and can be saved or sent to the machine for prototyping. If saved, the model can later be merged with other pending jobs to maximize platform use. If sent to the machine, via a network connection, an approximate build time is supplied. The status of the machine, material, and build time remaining can be monitored via a designated IP address as well as directly on the machine interface.

In the building process (Figures II.10), the FDM machine feeds a continuous thread of material through a heated nozzle, approximately 138°C, where it melts almost to the point of liquefaction. The heated thread extrudes according to the tool paths created in the CMB file. Once the material is extruded from the nozzle it immediately hardens in its temperature-controlled environment and adheres to the layer beneath it. This additive process occurs for each slice layer until the entire part has been deposited. Part build time varies according to geometry size but falls roughly at 5.5 minutes per cubic centimeter.



Figures II.10 Dimension FDM machine and view of build in progress

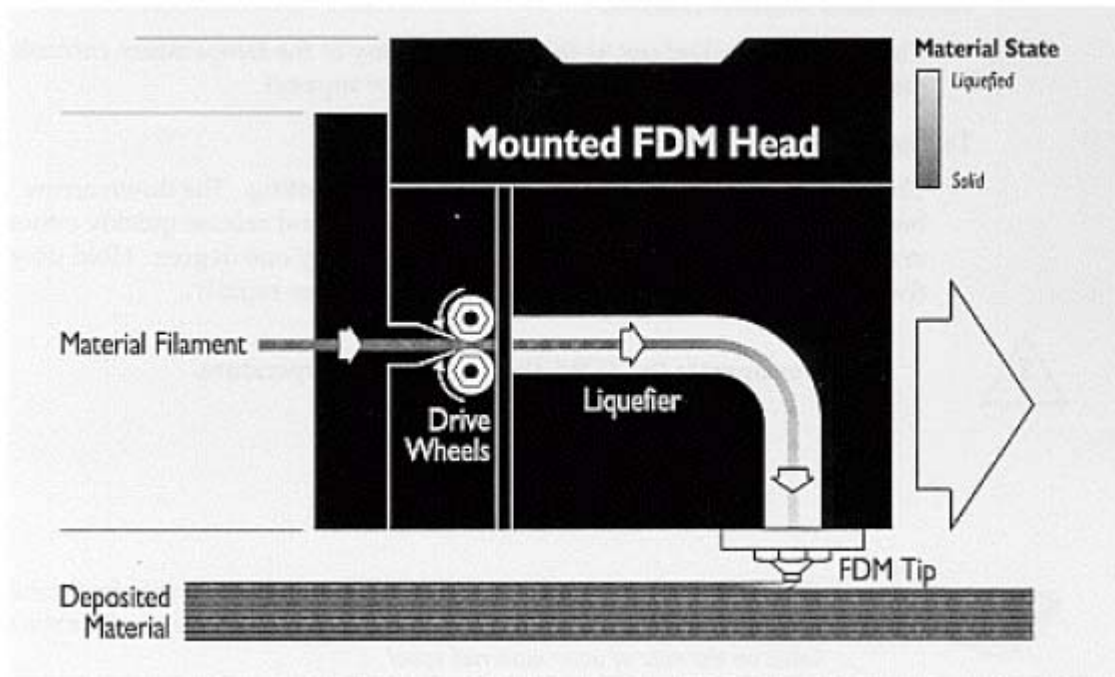


Figure II.11 FDM Machine

Once the building cycle is complete the part can be removed from the machine immediately. The part is released from the build platform and all supports are either broken away or dissolved in an ultrasonic tank depending on the type of support material used. There is no further post-processing needed. Many of the model materials in FDM are suitable for sanding, priming, painting, and machining.

II.4.1 Mechanical Properties of FDM ABS

The properties of FDM-deposited ABS differ from those of cast ABS because of the deposition process. [20] The FDM process lays down beads (or roads) or semi-molten plastic, so the material is, unlike cast ABS, anisotropic. The bead orientation (raster direction), bead width and the amount of spacing between adjacent beads (air gap) all affect the mechanical properties. The materials testing reported in Ahn was performed on FDM (Stratasys 1998 model) P400 ABS specimens with various raster orientations and two air gaps. Injection-molded ABS specimens had a tensile strength of about 26 MPa, while FDM ABS specimens with roads oriented in the direction of tensile stress had a tensile stress of about 20 MPa. If the load is applied with the beads alternating in layers at $+45^\circ$ and -45° , the tensile strength was reduced to about 12 MPa. The lowest

tensile strength occurred for beads oriented at 90° to the loading (the build plane perpendicular to the load direction). Tensile strength under this condition was about 3 MPa. Air gap affected tensile strength as well, with specimens constructed with a negative air gap (adjacent beads slightly overlapping) being stronger than specimens with the beads just touching (zero air gap). Compressive strength was found to be about 40 MPa for injection-molded ABS P400, about the same when the build layer plane was oriented in the load direction, and about 35 MPa when the build layer plane was perpendicular to the load. Bead width, color and model temperature had negligible effect on the tensile strength. Another paper reported tensile testing results for ABS deposited by a Stratasys 1650 RP machine. This paper indicated the highest ultimate and yield strengths (at 0° orientation) at 20.5 and 16.3 MPa respectively, and ultimate and yield strengths at $\pm 45^\circ$ orientation at 13.7 and 10.3 MPa. The weakest orientation was in this case the 45° orientation (no alternating bead angle in adjacent layers), with ultimate and yield strengths of only 7.0 and 6.6 MPa. For comparison, 6061-O wrought aluminum alloy has a tensile strength of 124 MPa. [20]

Useful guidelines for use of FDM ABS plastic in structural elements:

1. Build parts such that tensile loads will be carried axially along the fibers.
2. Be aware that stress concentrations occur at radiused corners. FDM roads exhibit discontinuities at such transitions.
3. Use a negative air gap to enhance strength and stiffness.
4. Consider the following issues on bead width:
 - Small bead width increases build time, but improves surface quality.
 - Wall thickness should be an integer multiple of bead width to avoid air gaps.
5. Consider the effect of build orientation on part accuracy.
 - Two-dimensional slices closely reproduce geometry.
 - Three-dimensional layer stacking creates linear approximations.
6. Be aware that tensile-loaded areas fail more easily than compression-loaded areas.

The manufacturer of the machine used at Penn State Altoona, Stratasys, lists the material properties (converted from USCS units; no indication was made of the bead orientation in which specimens were tested). [20]

Other material properties of ABS (injection molded, medium-impact grade) include specific gravity of 1.03-1.06 g/cc, hardness of Rockwell R102-115 (a fairly high hardness for a thermoplastic polymer), and a deflection temperature under flexural load of 455 kPa of 93.3-104.4°C (a fairly low heat deflection temperature). [21] FDM ABS is thus suitable as a structural element for low load, low-temperature applications, especially where weight savings and the ability to quickly fabricate complex, dimensionally-accurate parts are desirable qualities.

Table II. 8 Material Properties (Stratasys)

Material Type	Liquifier Temp (°C)	Build Speed (cm/sec)	Notched Izod Impact Strength Average (J/m)	Peak Flexural Stress (MPa)	Flexural Module Average (GPa)	Peak Tensile Stress Average (MPa)	Tensile Modulus Average (GPa)	Break Elongation Average (%)
ABS FDM	290	5.08	114.8	34.3	1.21	21.6	1.64	3.18
Polycarbonate FDM	340	5.08	100.4	76.3	1.46	52.6	1.96	3.6
ABS Injection Molded	-	-	133.4	62.1	2.21	30.3	1.86	50-95
Polycarbonate Injection Molded	-	-	640.5	93.1	2.31	65.5	2.48	120

II.4.2 Example Design Project Applications

The Electromechanical Engineering Technology design course, , requires students to design and construct a device that draws on both their electrical and mechanical backgrounds, and involves some form of computer control. The course is offered in the last semester, and typically involves teams of two, who develop a project proposal, plan and track the project using project management software, make several oral presentations on their progress, and submit regular status reports and interim and final reports.[22] The final week of the class includes oral presentations on the projects before an audience of faculty, students, advisory board members, family members and other guests from the community. The FDM has become a major element in the design and fabrication phases of the projects. Serving to illustrate how the FDM was used in capstone design projects are a load-lifting waterwheel system and radio-controlled, infrared-targeting paintball tanks. The projects were performed during the 2002-2003 and 2003-2004 academic years, respectively..

In a project to compete in the 2003 ASME Student Design Contest, and as part of their design project, a team of two designed and built a water wheel. The wheel was designed to have the water buckets arranged on a belt, suspended vertically between two pulleys. The water wheel lifted a cart filled with uncooked rice, simulating a water-powered mine ore lifting system. The water buckets had to be light and uniform, and shaped carefully to enable smooth flow and balance, including holes for attachment to the belt and an overflow notch. The FDM was used to fabricate buckets for the wheel (Figure 11, including a US half-dollar coin, diameter 30.6 mm, for scale), and to make the “ore” cart, which had to be lightweight and dimensionally accurate as well.

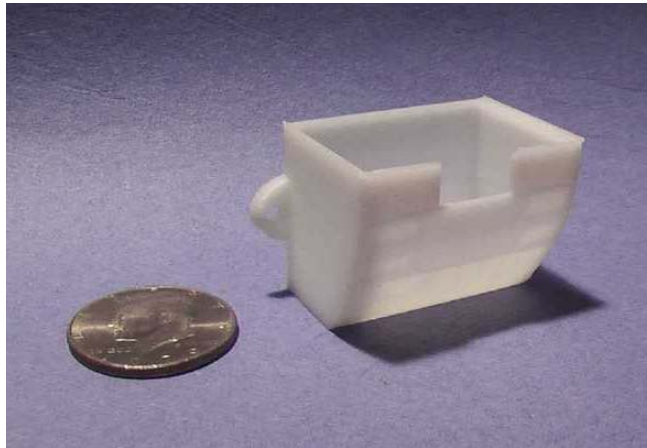


Figure II.12 : FDM Fabricated Water Wheel Bucket [21]

Two teams in 2003-2004 designed and built paintball-shooting tanks as part of their capstone design course. The tank chassis were remote controlled (radio frequency). A turret on each tank, carrying infrared emitters and detectors and the paintball gun, automatically aimed and fired on the opponent tank as the teams remotely maneuvered the chassis. Both teams agreed on the emitter specifications, and the rules of the actual competition. Both teams used the FDM to fabricate a housing (Figure 12, including a U.S. half-dollar coin for scale) for the infrared detectors. An array of five IR detectors are arranged in an arc, and the signal strength from the detector array is used to automatically control the turret azimuth and signal for the gun firing (when the side-shielded center detector is on) as the tank chassis is maneuvered. The application made good use of the FDM's ability to quickly produce a lightweight structure in a complex shape, where load requirements were low. The second team used the FDM to fabricate a brush holder for a slip ring to connect the turret electronics to the chassis.

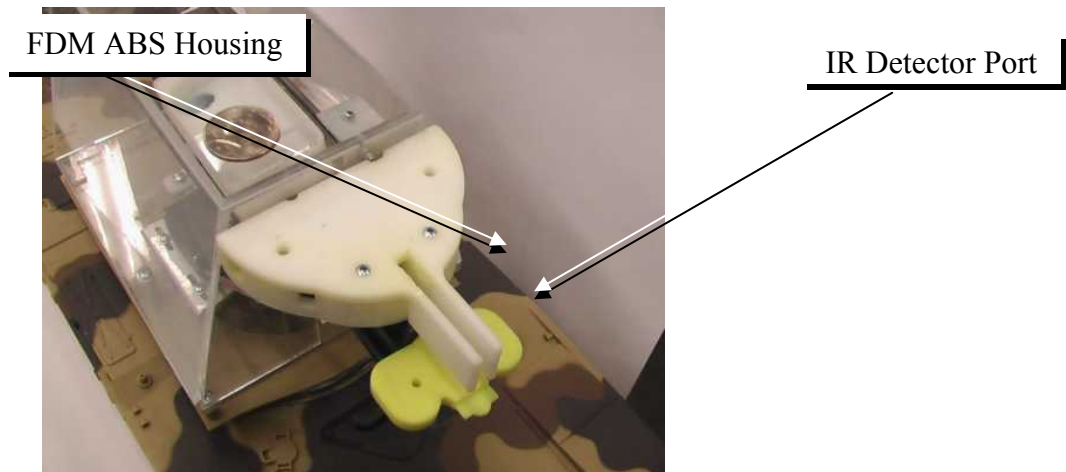


Figure II.13: FDM Using Paintball IR Tank [21]

II.5.EXTRUSION PROCESS:

Extrusion is a processing technique for converting thermoplastic materials in powdered or granular form into a continuous uniform melt, which is shaped into items of uniform cross-sectional area by forcing it through a die. Extrusion end products include pipes, profiles for construction, automobile, and appliance industries or raw material like in this thesis. Extrusion is perhaps the most important plastics processing method today.

A simplified sketch of the extrusion line is shown in Figure II.14. It consists of an extruder into which is poured the polymer as granules or pellets and where it is melted and pumped through the die of desired shape (in this thesis it is circular with 1.8 mm diameter). The molten polymer then enters a sizing and cooling trough or rolls where the correct size and shape are developed. From the trough, the product enters the motor-driven, rubber-covered rolls (puller), which essentially pull the molten resin from the die through the sizer into the cutter or coiler where final product handling takes place.

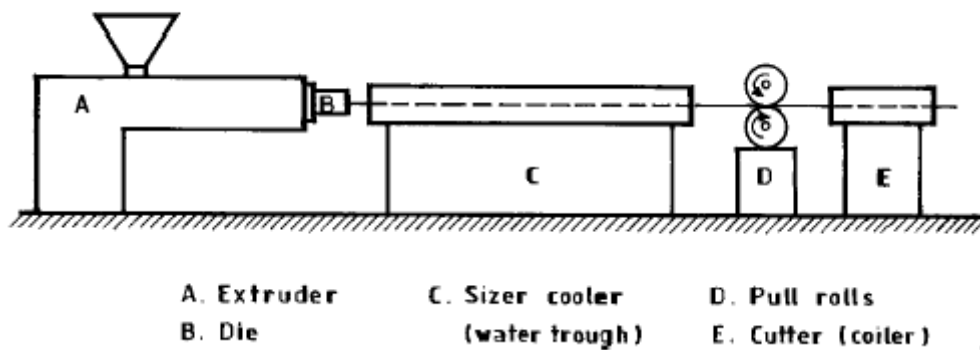


Figure II.14 Extrusion Machine [20]

II.5.1 Extruder

Figure II.15 is a schematic representation of the various parts of an extruder. It consists essentially of the barrel, which runs from the hopper (through which the polymer is fed into the barrel at the rear) to the die at the front end of the extruder. The screw, which is the moving part of the extruder is designed to pick up, mix, compress, and move the polymer as it changes from solid granules to a viscous melt.

The screw turns in the barrel with power supplied by a motor operating through a gear reducer. The heart of the extruder is the rotating screw (Figure 8). The thread of an extruder screw is called a flight, and the axial distance from the edge of one flight to the corresponding edge on the next flight is called the pitch. The pitch is a measure of the coarseness of the thread and is related to the helix.

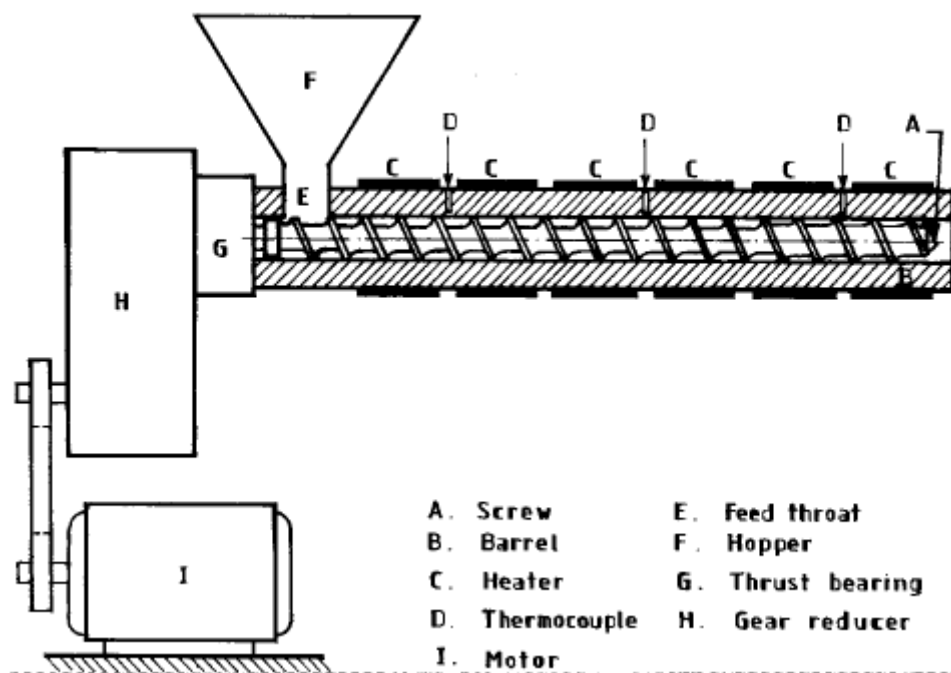


Figure II.15 Extrusion Machine [20]

We trying to reach filament of ABS with 1,8 mm diameter. It is very hard to obtain this dimension about long time. Electric current which come from city lines directly affect the speed and pressure of extruder.

We bought 7 different types of ABS plastic materials and we extrude them

into filament which have diameter 1,8mm. But because of hardness of process we can not reach regular diameters all of filament.

There are a lot of problems which we have to cope with. These problems are;

II.5.1.1. Obtaining the melting temperature right

This is the hardest part of extrusion process. We have to know the melting and extrusion temperature true.

All material has a Melt Temperature and Melt Temperature range. In general speaking, the melt temperature for easily-flow grades will be taken from the bottom of the range, or for more viscous grades, from the top of the range.

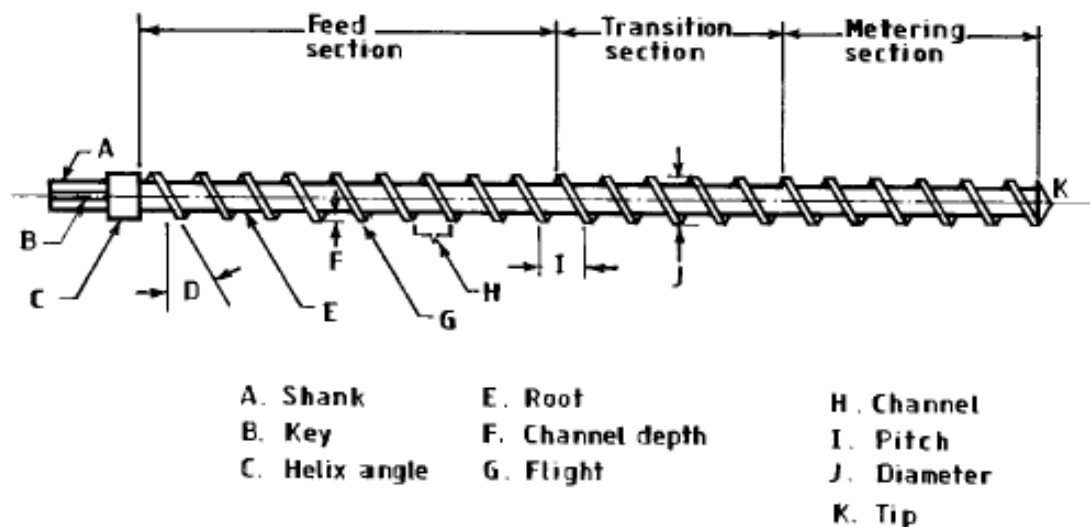


Figure II.16 Extrusion Screw Design [20]

II.5.1.2. Extrusion pressure and extrusion speed

This is another important part. We have to adjust the pressure and speed of the extrusion screw. In this subject, extrusion design is very important. Depend on that, it directly affects the extrusion process.

Extrusion pressure directly affects the quality of final part. The pressure should be high enough for extruding plastic without any undesirable cavity. The speed of screw affects directly the pressure at the extrusion point and quantity of extruded plastic per second. If we increased the pressure and speed more than desirable, we cannot reach the cylindrical profile.

III. PRODUCTION AND TESTING OF NEW MATERIAL

III.1 MATERIAL TESTS OF RAPID PROTOTYPING MACHINE ABS MATERIALS

Our aim is producing of supply materials for Rapid Prototyping machine and improving materials properties and its using. With the production of supply material in Turkey, which is exported, costs are decreased and escape from foreign dependence.

This studies processes to support the use of thermo plastics filament in rapid prototyping. First, we got different types of ABS material from domestic and international plastic producer.

In first part of study, we decide to make test on samples. We made first the Tensile Test, secondly Mold Flow Index test which is the most important properties of plastic for FDM process and at the end Hardness Test.

On the other hand, smooth surfaces of strings are critical. Rough surfaces prevent ejection of the injection molded part and play a role in the overall quality of the final part. And also affect the FDM process, it cause problems in rapid prototyping machine.

III.1.1 Using Materials in Rapid Prototyping Process for Studies

ABS: All systems in the FDM line-up offer ABS as a material option, and nearly 90% of all FDM prototypes are produced in this material. Users report that the ABS prototypes demonstrate 60-80% of the strength of injection molded ABS. Other properties, such as thermal and chemical resistance, also approach or equal those of injection molded parts. This makes ABS a widely used material for functional applications.

Polycarbonate: Use of a new RP material available for FDM — polycarbonate is growing rapidly. The additional strength of polycarbonate produces a prototype that can withstand greater forces and loads than the ABS material. Some users believe that this material produces a prototype that demonstrates the strength characteristics of injection molded ABS.

Other materials: While not as widely used as ABS, there are other specialty materials for

III.2. PLASTICS CHARACTERIZATION AND SELECTION BY TESTS

When we want to use plastic materials, we select plastic which is most useful for us. We have to think and select the most suitable material. There are some properties of plastic which help us in selection.

III.2.1 Strength Test of the Plastic

One of the most important properties of material is strength. Strength of material give us the bounds of using. Strength is a mechanical property that you should be able to relate to, but you might not know exactly what we mean by the word "strong" when we're talking about polymers. First, there is more than one kind of strength. There is *tensile* strength. A polymer has tensile strength if it is strong when one pulls on it.

Stress-strain behavior is another important property. The description of stress-strain behavior is similar to that of metals, but a very important consideration for polymers is that the mechanical properties depend on the strain rate, temperature, and environmental conditions.

Mechanical properties change dramatically with temperature, going from glass-like brittle behavior at low temperatures to a rubber-like behavior at high temperatures.

Tensile strength is important for a material that is going to be stretched or under tension. Fibers need good tensile strength. Then there is compressional strength. A polymer sample has compressional strength if it is strong when one tries to compress it.

The ability of a material to resist breaking under tensile stress is one of the most important and widely measured properties of materials used in structural applications. The force per unit area (MPa or psi) required to break a material in such a manner is the ultimate tensile strength. The rate at which a sample is pulled apart in the test can range from 0.5 to 50 cm per minute and will influence the results. T

III.2.2 Elongation Test

But there's more to understanding a polymer's mechanical properties than merely knowing how strong it is. All strength tells us is how much stress is needed to break something. It doesn't tell us anything about what happens to our sample while we're trying to break it. That's where it pays to study the elongation behavior of a polymer sample. Elongation is a type of deformation. Deformation is simply a change in shape that anything undergoes under stress. When we're talking about tensile stress, the sample deforms by stretching, becoming longer. We call this elongation, of course.

There are a number of things we measure related to elongation. Which is most important depends on the type of material one is studying. Two important things we measure are ultimate elongation and elastic elongation .

Ultimate elongation is important for any kind of material. It is nothing more than the amount you can stretch the sample before it breaks. Elastic elongation is the percent elongation you can reach without permanently deforming your sample. That is, how much can you stretch it, and still have the sample snap back to its original length once you release the stress on it.

The ultimate elongation of an engineering material is the percentage increase in length that occurs before it breaks under tension. Ultimate elongation values of several hundred percent are common for elastomers and film/packaging polyolefins. Rigid plastics, especially fiber reinforced ones, often exhibit values under 5%. The combination of high ultimate tensile strength and high elongation leads to materials of high toughness.

We made the extrusion process in private company. We made ABS raw material for RP machine which material is long filament. They have to be in diameter of 1.8-1.9mm and it is very hard to obtain. Thereupon, material selection and prepare to using is very hard. We use their thin filaments for tensile test.

III.2.3. Mold Flow Index Test of Samples

In Rapid Prototyping process, melting of ABS plastic is the most important process. Melt Flow Rate measures the rate of extrusion of thermoplastics through an orifice at a prescribed temperature and load. It provides a means of measuring flow of a melted material which can be used to differentiate grades as with polyethylene, or determine the extent of degradation of the plastic as a result of molding.



Figure III.1 MFI Machine

Common Melt Flow Rate Conditions by Material

	200°C/5.0kg
Acrylonitrile-butadiene-styrene	230 °C /3.8kg
	220 °C /10

We made test with ASTM D1238 standards under 5kg and 200°C in Technical Education Faculty in Marmara University.

Experiment is done on the following system.

1. We cut samples small pieces about 3mm long and up to 2mm diameter cylindrical pieces.
2. Then we put them in to machine and wait about 10 minutes to melt,
3. After than with the help of weight Abs plastic started melt down on the cap.
4. Every 10 minutes we took melted plastic
5. Measure their weights with a sensitive device.

III.2.4 Hardness Test

First, all samples of ABS material cut about 1cm pieces. Then, we melt them in oven which is in M.Ü. Material Science Engineering Laboratory. All of samples warm to 285°C which is melting degree, we prepared test sample. A measure of the indentation resistance of elastomeric or soft plastic materials based on the depth of penetration of a conical indenter. Hardness values range from 0 (for full penetration) to 100 (for no penetration). Full penetration is between 2.46 and 2.54 mm (0.097 and 0.100 in) depending on the equipment used.

Experiment Setup:

We used the Zwick Shore hardness test equipment with ASTM D2240 DIN 53505 standards.

Experiment is done on the following system.

1. We cut samples small pieces about 3mm long and up to 2mm diameter cylindrical pieces.
2. Then we put them cap and put them in to oven on melting temperature
3. After than we cut the top of melted material to reach true values in test.
4. And we took 10 hardness values of each sample under 15 kg weight.

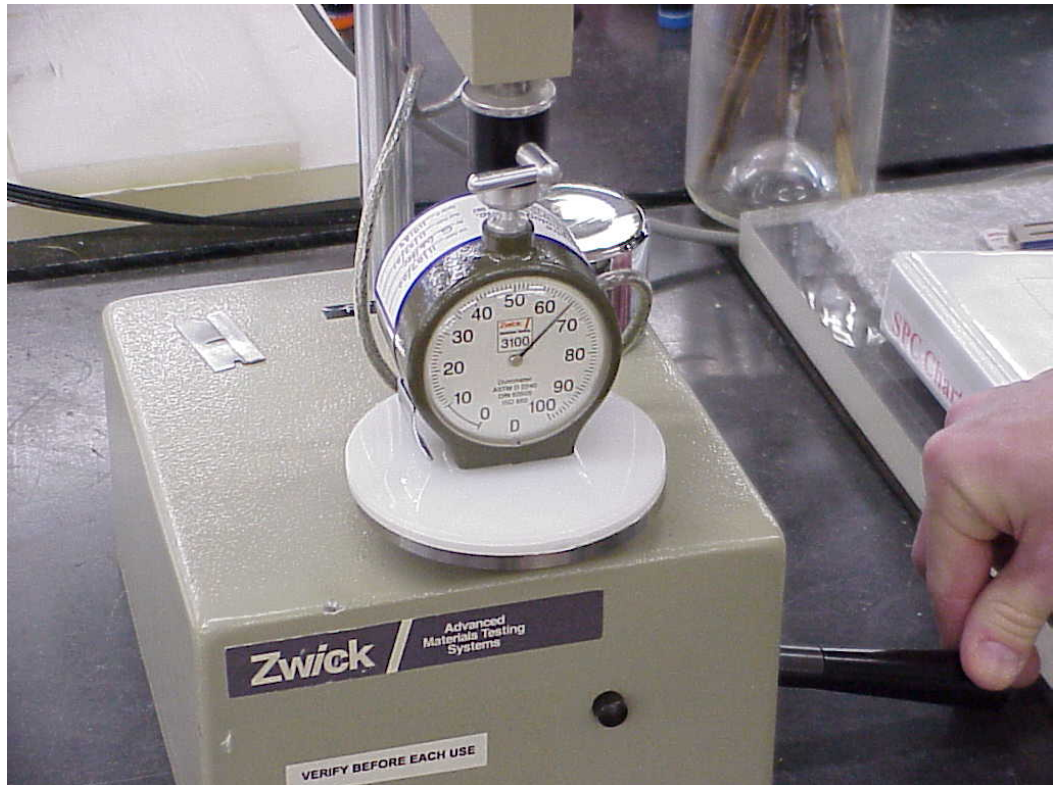


Figure III.2 Hardness Test Machine

III.2.5 SEM Scanning Electron Microscope Imaging

SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. This particular type of microscope is exceedingly useful.

The types of signals made by an SEM can include secondary electrons, back scattered electrons, characteristic x-rays and light (cathodoluminescence). These signals come from the beam of electrons striking the surface of the specimen and interacting with the sample at or near its surface. In its primary detection mode, secondary electron imaging, the SEM can produce very high-resolution images of a sample surface, revealing details about 1 to 5 nm in size. Due to the way these images are created, SEM micrographs have a very large depth of focus yielding a characteristic three-dimensional appearance useful for understanding the surface

structure of a sample. This great depth of field and the wide range of magnifications (commonly from about 25 times to 250,000 times) are available in the most common imaging mode for specimens in the SEM, secondary electron imaging, such as the micrograph taken of pollen shown to the right. Characteristic x-rays are the second most common imaging mode for an SEM. X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and give off energy. These characteristic x-rays are used to identify the elemental composition of the sample. Back-scattered electrons (BSE) that come from the sample may also be used to form an image. BSE images are often used in analytical SEM along with the spectra made from the characteristic x-rays as clues to the elemental composition of the sample.

We made two SEM on original materials. Two material seem very similar in SEM images in Appendix 2.

III.2.6 XRD X-ray Scattering Techniques

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an x-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy.

We made two XRD test for analyzing the percentage of polymers which compose ABS.

Result of XRD is %15 Acrylonitrile % 60 Butadiene % 25 Styrene in Appendix 3 and Appendix 4

III.3 PREPARATION OF ABS MATERIALS

We produced ABS strings for rapid prototyping machine. First, we purchase raw ABS materials from producers. Then, we made extrusion process with extrusion machine. Then we have to know the physical properties of material to using in machine. Prototyping process is very sensitive process which can be affected by many disturbances. When we know physical values of samples of ABS, we can realize the production is good or not.



Figure III.3 Extrusion Machine

III.4 FABRICATION OF NEW RAW MATERIAL

The filaments used in FDM process need to be of specific size, strength and properties. A single-screw extruder machine was used to produce such filaments. The single screw extruder is one of the most important types of extruders used in the polymer processing industry. Its key advantages include its relatively lower cost, simple design, ruggedness, reliability, and acceptable performance.

A single screw extruder was selected to fabricate the filaments from the ABS material. The ABS granule is fed into the feed hopper. The ABS material flows by gravity from the feed hopper down into the extruder barrel. As the material flows, it fills the annular space between the extruder screw and barrel. Since the barrel is stationary and the screw is rotating, the frictional forces will act on the material, both on the barrel as well as on the screw surface. As the material moves forward, it will heat up as result of frictional heat generated and conducted from the barrel heaters.

When the temperature of the ABS material exceeds the melting point, a thin film of ABS material, will form at the barrel surface. This is where the plasticising action starts. As the ABS material moves forward, the amount of solid material at each location will reduce as a result of melting. When the entire solid ABS has disappeared, and the end of the plasticising zone has been reached then the melt-conveying zone starts. In the melt-conveying zone, the ABS material is simply pumped to the die. Since the die exerts a resistance to flow, a pressure is required to force the material through the die. This is referred to as the die head pressure. The die head pressure is determined by the shape of the die, temperature of the ABS material melt, the flow rate through the die, and the rheological properties of the composite melt. The extruding filament exiting the die is then carried away by a conveyor belt, whose speed matches the output flow rate.

During extrusion, a phenomenon, sometimes referred to as die swell, occurs. Actually, it is not the die but the polymer that swells. The elastic behavior of the polymer melt is largely responsible for the swelling of the extrudate upon leaving the die. This is primarily due to the elastic recovery of the deformation of the metal–polymer composite in the die. A die with a short land length will cause a large

amount of swelling, while a die with long land length will reduce the amount of swelling. Therefore, the land length of die was increased from 5 to 10 mm, which leads to decrease the extrudate swelling. Because of swelling, the diameter of die used was taken to be smaller than the required diameter of the filament.

The die diameter was 1.65 mm and the resulting diameter of filament formed was in the range of 1.78–1.85 mm due to the extrudate swelling. Therefore, the geometry of exit flow channel is generally different from the required product geometry. Thus using the proper geometry of the die and appropriate volume of flow parameters, flexible winding filaments of desired diameter and tolerance were produced.

IV. TEST RESULT OF ABS WIRE SAMPLES

We made tests on ABS materials which is selected and used for FDM machine. In the first phase of our study, we made tests on 6 samples. Two of these samples are original raw materials which are using for FDM machine. We find 4 more samples from domestic and international suppliers according to properties which are given by original ABS supplier.

Table IV.1 Properties of original materials [2]

	Test Method	Units	FDM	
			ABS	Polycarbonate
Tensile Strength	ASTM D638	Mpa	45.7	62.5
Tensile Modulus	ASTM D638	Mpa	1641	1958
Tensile Elongation at Break	ASTM D638	%	10	10
Flexural Strength	ASTM D790	Mpa	73.5	94.2
Flexural Modulus	ASTM D790	Mpa	2.300	2.300
Hardness	DIN 53505/22 40	Shore D	78	78
Melting Temperature		(ft-lb)/in	280	280
Water Absorbion	D570-98	%	0.20-0.45	0.17
Deflection Temperature @ 455 Kpa	D648	C	90	125
Deflection Temperature @ 1820 Kpa	D648	C	90	125
Izod impact - notched	D256-A	J/m	160	710

Test Samples:

We have five different production and one support material which use in the machine. Then we give them number to realize and do test easily.

1-) Sample 1 have a very smooth surface after extrusion from domestic supplier.

2-) Sample 2 include ABS and some rubber material from Resinex-BYM. (See appendix for detail information)

3-) Sample 3 is the original material which came from Stratasys USA

4-) Sample 4 is newest one we bought from DOW (See appendix for detail information)

5-) Sample 5 is the ABS which have rough surface from Resinex-BYM with code: MAGNUM ABS 3904

6-) Sample 6 is the support material of machine which is made by different mixture of PC we made some test on it for future works.

IV.1 TENSILE STRENGTH TEST RESULTS OF SAMPLES

We made tensile strength test on 5 of these samples for determine and compare each other. Tests are made 10 times for each material and took average of values to get rid of errors. Sample 4 couldn't tested.

	Maximum Force	Maximum Strength	Elongation
Sample 1	156 N	49,5 MPa	%100
Sample 2	152 N	48,5 MPa	% 6
Sample 3 (Original)	158 N	50,1 MPa	% 70,8
Sample 5	161 N	51,5 MPa	% 34
Sample 6	154 N	48,5 MPa	%9

As a result we can see that second sample is not suitable for use.

During the test, sample 3 was deformed perfectly .Other samples deformed preparedly, after plastic deformation on some place usually other part of sample didn't being plastic deformation and usually breaks down with first deformed place.

On the other hand, elongation is the other point of material. After elastic deformation, plastic deformation started and especially first and third sample along more than others.

IV.2 MFI TEST RESULTS OF SAMPLES

TABLE IV.2 MFI TEST RESULTS

Experment No	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
1	0,942 g	1,380 g	1,630 g	3,320g	1,248g
2	0,861 g	1,433 g	1,578 g	3,355g	1,253g
3	0,811 g	1,417 g	1,578 g	3,365g	1,278g
4	0,784 g	1,380 g	1,530 g	3,475g	1,245g
5	0,750 g	1,370 g	1,516 g	3,600g	1,259g
6	0,720 g	1,375 g	1,525 g	3,505g	1,243g
7	0,700 g	1,379 g	1,560 g	3,452g	1,257g
8	0,689 g	1,335 g	1,510 g	3,338g	1,272g
9	0,710 g	1,350 g	1,530 g	3,290g	1,243g
10	0,730 g	1,332 g	1,520 g	3,315g	1,248g
Average	0,7697 g/10min	1,3891 g/10min	1,5477 g/10min	3,4015 g/10min	1,2546 g/10min

We can see the melted materials.



Sample 1



Sample 3

Figure IV.1 Sample1 and Sample 3 after MFI Test

On the other hand, we could see the materials how they melt. And we can see melted pieces they melt well or not. In first and third samples were melting is so good and there were little cavity in materials. But in fifth sample it wasn't melted so well, there were some cavities in melted material.



Figure IV.2 Sample 5 after MFI Test

IV.3 EXPERIMENT MEASUREMENTS OF HARDNESS TEST

1. Sample's average hardness value is 26
2. Sample's average hardness value is 27
3. Sample's average hardness value is 24
4. Sample's average hardness value is 24
5. Sample's average hardness value is 27
6. Sample's average hardness value is 28

Each value is average of 10 tests.

Results

In the experiment results, we see that hardness values of the materials are quite similar. In other words, Selected ABS materials' hardness values are so close to each other. In order to reach the true values of samples we made test 10 times and take the average values.

In first phase of the study, mechanical tests are done on 6 types of samples. Following results are taken:

IV.4 DISCUSSION

	Strength	MFI (Mold Flow Index)	Elongation	Hardness	Using in RP	Supplier
Sample 1	49,5 Mpa	0,78 gr/min	100%	26	Not applicable	Domestic Supplier
Sample 2	48,5 Mpa	1,81 gr/min	6	27	Good, Some Problems occurs in RP process	Resinex-BYM
Sample 3	50,1 Mpa	1,54 gr/min	70,8	24	Original ABS	Stratasys USA
Sample 4	----	3,40 gr/min	-----	24	Very soft flow for RP, not applicable	DOW
Sample 5	51,5 Mpa	1,25gr/min	34	27	Very hard flow in RP, not applicable	Resinex-BYM
Sample 6	48,5Mpa	----	9	28	Original PC	Stratasys USA

According these results, only sample 2 is applicable for using in RP machine. But when we use this sample in FDM machine, it creates problems in FDM process. We investigate the problem in process and we find out ,problem occurs because of the dimension of sample. ABS strings should have 1.8-1.9mm diameter. Because of the extrusion process it is very hard to get it. In some sample, this diameter can be more than 2mm and it cause blockage in the FDM machine.

We made die for this undesirable samples and process once more of ABS strings. We heat die to operation temperature for ABS and reduce the diameter to desirable values. But we couldn't reach the required results after this operation.

In the second phase of our study, we search new material which can be used in FDM without any problem. According to conversation and meeting with one international supplier, they suggested trying a new sample (Appendix 2).

We made strings for FDM machine with new ABS material and we used in FDM machine and we reached good results. We produced one sample prototype with new ABS material, and there is no problem about 2 hours operation. Final product which made by new ABS material is quite similar with original one.

V. CONCLUSION AND RECOMMENDATIONS

A new raw material for FDM machine has been successfully produced and tested for direct rapid tooling application using the FDM rapid prototyping process. Characterization of this material displays desirable mechanical properties, offering fabrication of flexible feedstock filaments for producing functional parts and tooling directly on the FDM system. This material has quite similar properties like strength, mold flow property and availability. These properties can help to establish the upper limits for the process ability of filament in terms of the particle size and the volume fraction of filler content.

Composites consisting of large as high tensile modulus as original raw material, tensile stress and elongation are quite enough for using, most important and the hard part is the extrusion process. When comparing new material with original raw material, main difference is color of the ABS. And it can be changed in extrusion process with adding colorant.

Application of this new raw material in rapid tooling using the FDM system has shown that good qualities parts and very clear process. The material is especially suitable for direct rapid tooling application.

In this work, we find out production of raw material for FDM machine in Turkey is available. With the production in Turkey, big money saves in Turkey and foreign dependence is finished.

For improve this thesis, optimization can be done in extrusion process and different type of ABS and PC material can produced and use in FDM machine.

REFERENCES

- [1] International Union of Pure and Applied Chemistry, et al. (2000) "IUPAC Gold Book" Retrieved on 11 May 2007 from "IUPAC Gold Book" on <http://goldbook.iupac.org/>
- [2] Clayden, J.: Greeves, N. et al. (2000), p1450-1466
- [3] [http://www.polymerchemistryhypertext.com/\(08.06.2008\)](http://www.polymerchemistryhypertext.com/(08.06.2008))
- [4] Masood SH. *Intelligent rapid prototyping with fused deposition* (2003).
modelling. Rapid Prototype (1996);2(1):24–32.
- [5] Meyers .: Chawla. *Mechanical Behavior of Materials*, Prentice Hall, Inc. 1999, pg. 41.
- [6] Brandrup, J.; Immergut, E.H.; Grulke, E.A.; eds *Polymer Handbook 4th Ed. New York: Wiley-Interscience, (1999)*.
- [7] CAS: *Index Guide*, Appendix IV (© 1998).
- [8] International Union of Pure and Applied Chemistry, et al. "IUPAC Gold Book" Retrieved on 11 May 2007 from "IUPAC Gold Book" on <http://goldbook.iupac.org/> (2005)
- [9] D. W. Van Krevelen, *Properties of Polymers*, 3rd ed., Elsevier, Amsterdam, the Netherlands,(1990).
- [10] D. V. Rosato, *Rosato's Plastics Encyclopedia and Dictionary*, Hanser, Munich, (1993).
- [11] W. V. Titow, *Technological Dictionary of Plastics Materials*, Elsevier Science Ltd., Kidlington, Oxford, (1998).
- [12] D. P. Bashford, *Thermoplastics Directory and Databook*, Chapman & Hall, New York, (1997).
- [13] C. P. MacDermott and A. V. Shenoy, *Selecting Thermoplastics for Engineering Applications*, 2nd ed., Marcel Dekker, Inc., New York, (1997).
- [14] J. Brandrup, E. H. Immergut, and E. A. Grubke, eds., *Polymer Handbook*, 4th ed., John Wiley & Sons, Inc., Chichester, (1999).
- [15] J. A. Brydson, *Plastics Materials*, 6th ed., Butterworth-Heinemann Ltd., Oxford, (1995).
- [16] D. G. Baird and D. I. Collias, *Polymer Processing*, John Wiley & Sons, Inc., Chichester, (1998).
- [17] J. M. Charrier, *Polymeric Materials and Processing*, Hanser, Munich, (1990).
- [18] World-Wide Web URL <http://cede.psu.edu/StudentGuide.>, (01.05.2008).
- [19] World-Wide Web URL <http://www.rhino3d.com.>, (01.10.2007).

[20] Ahn, Sung-Hoon, Michael Montero, Dan Odell, Shad Roundy and Paul K. Wright. *Anisotropic Material Properties of Fused Deposition Modeled ABS. Rapid Prototyping*, Vol. 8, No. 4, (2002), pp. 248-257.

[21] http://www.buildfdm.com/data/product_brief_matspecs.pdf, (05.07.2008).

[22] IDES, Inc. *IDES Prospector Pro*. <<http://ppro.ides.com>> (05.08.2008).

APPENDIX

APPENDIX 1

Technical Sheet of Sample 7



Lustran ABS E401

Extrusion grades / General purpose grades

ISO Shortname

Extrusion grade, very high impact resistance, high gloss surfaces

ISO 2580-ABS 1.EG,095-04-35-20

Property	Test Condition	Unit	Standard	Value
Rheological properties				
X C Melt volume-flow rate	220 °C; 10 kg	cm ³ /(10 min)	ISO 1133	5
C Molding shrinkage, parallel	60x60x2	%	ISO 294-4	0.5 - 0.8
C Molding shrinkage, normal	60x60x2	%	ISO 294-4	0.5 - 0.8
Mechanical properties (23 °C/50 % r.h.)				
X C Tensile modulus	1 mm/min	MPa	ISO 527-1,-2	1900
C Yield stress	50 mm/min	MPa	ISO 527-1,-2	40
C Yield strain	50 mm/min	%	ISO 527-1,-2	2.5
Strain at break	50 mm/min	%	acc. ISO 527-1,-2	> 15
C Charpy impact strength	23 °C	kJ/m ²	ISO 179-1eU	210
C Charpy impact strength	-30 °C	kJ/m ²	ISO 179-1eU	170
C Charpy notched impact strength	23 °C	kJ/m ²	ISO 179-1eA	30
C Charpy notched impact strength	-30 °C	kJ/m ²	ISO 179-1eA	16
X Izod notched impact strength	23 °C	kJ/m ²	ISO 180-1A	30
Izod notched impact strength	-30 °C	kJ/m ²	ISO 180-1A	19
Flexural modulus	2 mm/min	MPa	ISO 178	1900
Flexural strength	2 mm/min	MPa	ISO 178	60
X Ball indentation hardness		N/mm ²	ISO 2039-1	85
Thermal properties				
C Temperature of deflection under load	1.30 MPa	°C	ISO 75-1,-2	94
C Temperature of deflection under load	0.45 MPa	°C	ISO 75-1,-2	100
X C Vicat softening temperature	50 N; 50 °C/h	°C	ISO 308	99
C Coefficient of linear thermal expansion, parallel	23 to 55 °C	10 ⁻⁶ /K	ISO 11359-1,-2	0.9
C Burning behavior UL 94 (1.6 mm)	1.6 mm	Class	UL 94	HB
Burning rate (US-FMVSS)	2.0 mm	mm/min	ISO 3795	55
Glow wire test (GWFI)	2.0 mm	°C	IEC 60695-2-12	700
Electrical properties (23 °C/50 % r.h.)				
C Relative permittivity	100 Hz	-	IEC 60250	3.1
C Relative permittivity	1 MHz	-	IEC 60250	2.9
C Dissipation factor	100 Hz	10 ⁻⁴	IEC 60250	50
C Dissipation factor	1 MHz	10 ⁻⁴	IEC 60250	90
C Volume resistivity		Ohm·m	IEC 60093	1E14
C Surface resistivity		Ohm	IEC 60093	1E16
C Electric strength	1 mm	kV/mm	IEC 60243-1	35
C Comparative tracking index CTI	Solution A	Rating	IEC 60112	600
Other properties (23 °C)				
C Density		kg/m ³	ISO 1183	1040
Processing conditions for test specimens				
X C Injection molding-Melt temperature		°C	ISO 294	240
C Injection molding-Mold temperature		°C	ISO 294	70
C Injection molding-Injection velocity		mm/s	ISO 294	240

Firma ARISAN

Page 1 from 2 pages

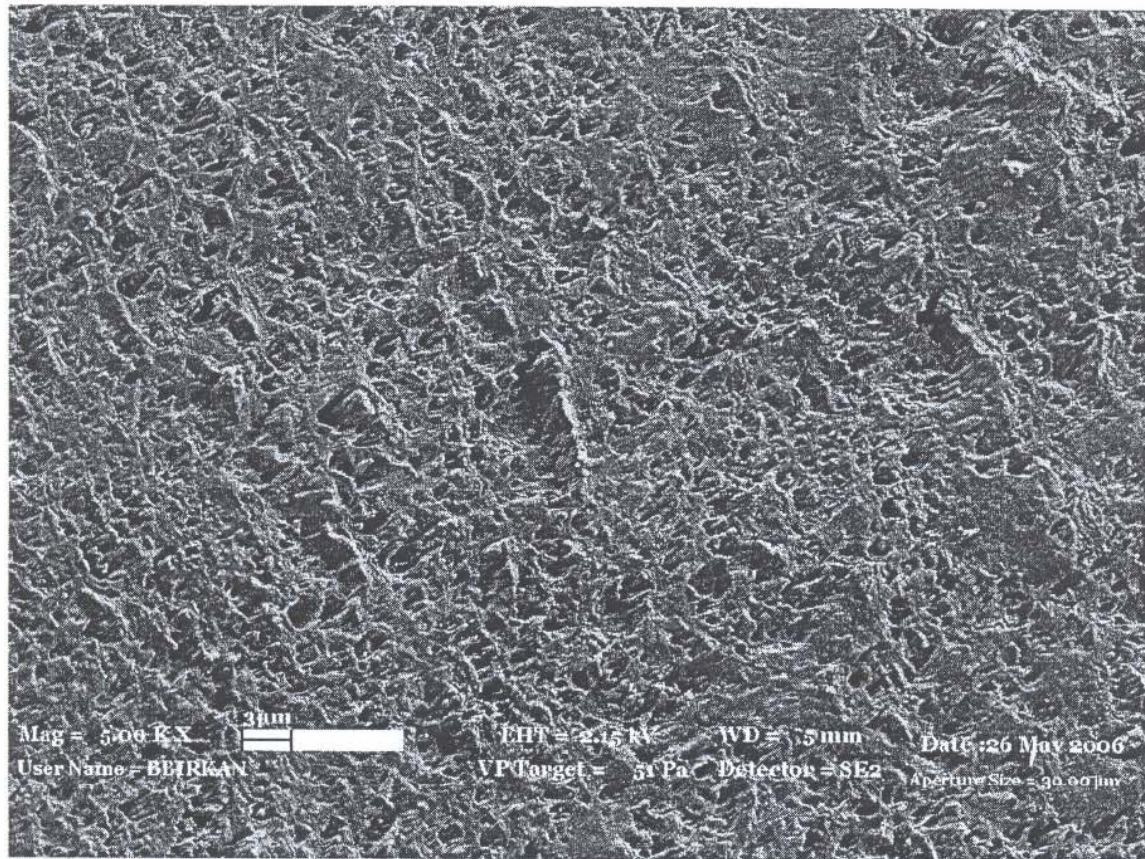
Lustran ABS /
Novodur®

Edition 16.09.2004

ISO Datasheet

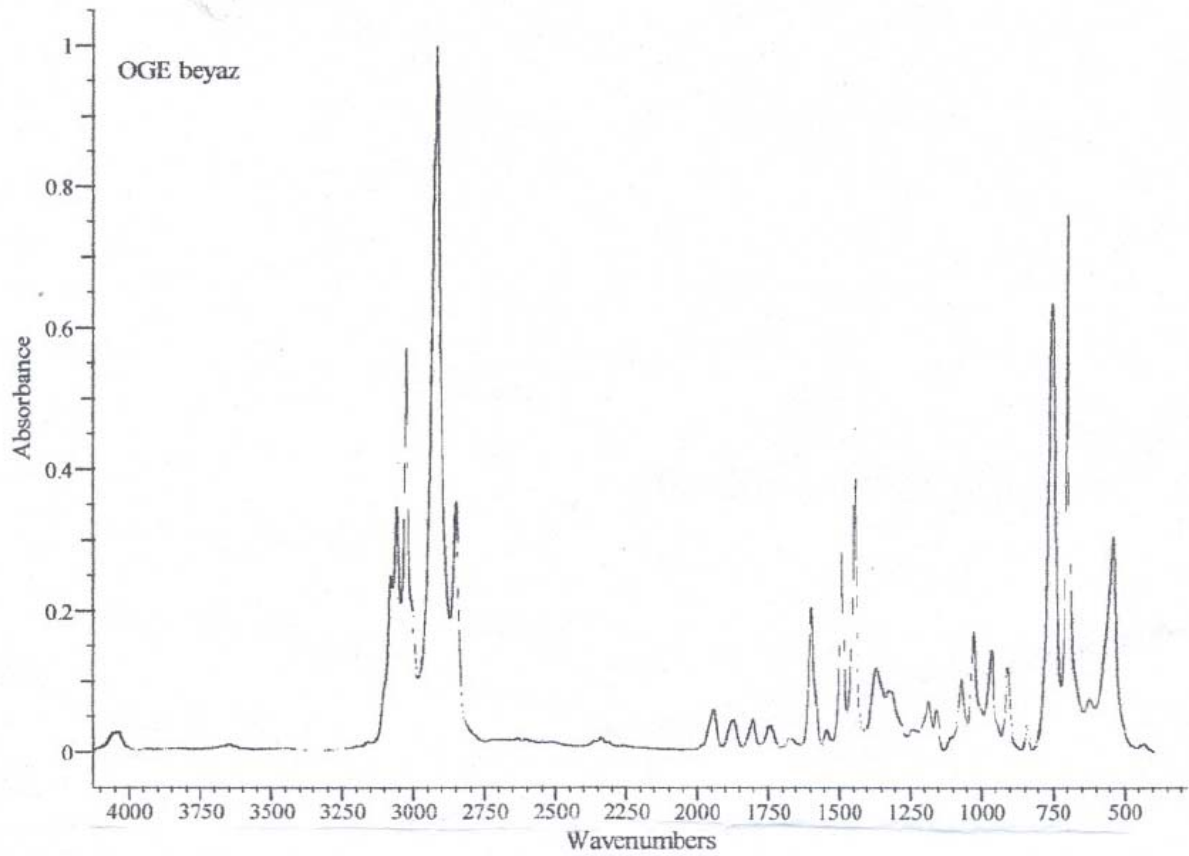
APPENDIX 2

Scanning Electron Microscope Imaging (Sample 3)



APPENDIX 3

XRD X-ray Scattering Techniques Results of Sample 3

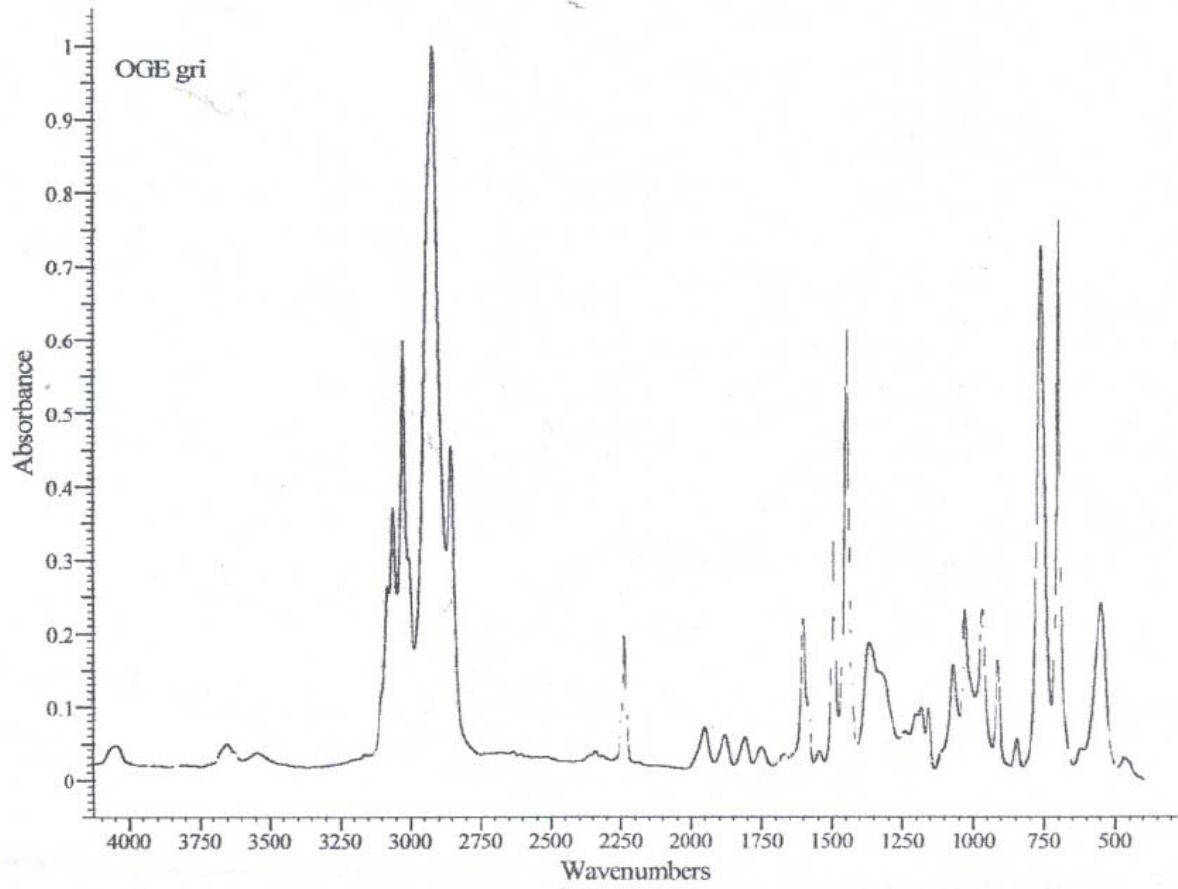


Name	Value
Title	STEREON 880A
Technique	FILM (CAST FROM CHLOROFORM)
Comments	Chemical Description= BUTADIENE-STYRENE COPOLYMER
Hardness	(SHORE D) 75
Source of Sample	FIRESTONE SYNTHETIC RUBBER AND LATEX COMPANY
Viscosity Data	Melt Index= (CONDITION G) 8.0 G/10 MIN.

Beyaz numune, nitril içermiyor.

APPENDIX 4

XRD X-ray Scattering Techniques Results of Sample 6



Name	Value
Title	ABSON 89110*ACRYLONITRILE/BUTADIENE/STYRENE COMPOUND
Technique	FILM
Classification	Polymers= ACRYLONITRILE-BUTADIENE-STYRENE RESINS
Source of Sample	GOODRICH, B.F., CHEMICAL COMPANY

Gri olan numune; nitril içeriyor. Standart ABS gradeler olabilir

APPENDIX 5

Technical Sheet of Sample 6

Applications

- Information technology equipment
- Electrical parts
- Other structural/internal parts



Physical Properties ⁽¹⁾	Test Method	English Units	SI Units
Specific Gravity	ASTM D 792	1.33	1.33
Melt Flow Rate, 300°C/1.2kg	ASTM D 1238	5 g/10 min	5 g/10 min
Mold Shrinkage, Linear Flow	ASTM D 955	0.002-0.004 in/in	0.002-0.004 mm/mm
Mechanical Properties ⁽²⁾			
Tensile Strength at Break	ASTM D 638	14,500 psi	100 MPa
Tensile Elongation at Break	ASTM D 638	4.0 %	4.0 %
Tensile Modulus	ASTM D 638	870,000 psi	6,000 MPa
Flexural Strength	ASTM D 790	24,650 psi	170 MPa
Flexural Modulus	ASTM D 790	797,500 psi	5,500 MPa
Thermal Properties			
Deflection Temperature Under Load	ASTM D 648		
264 psi (1.8 MPa), annealed		289°F	143°C
66 psi (0.45 MPa), unannealed		293°F	145°C
264 psi (1.8 MPa), unannealed		284°F	140°C
Vicat Softening Point	ASTM D 1525		
50°C/hr, 50N		302°F	150°C
120°C/hr, 10N		320°F	160°C
Ball Indentation Temperature	IEC 60335-1	>275°F	>135°C
CLTE, flow, -40 to 80°C	ASTM D 696	14x10 ⁻⁶ in/in/°F	25x10 ⁻⁶ mm/mm/°C
CLTE, cross flow, -40 to 80°C	ASTM D 696	29x10 ⁻⁶ in/in/°F	51x10 ⁻⁶ mm/mm/°C
Electrical Properties			
Dielectric Strength, 1.6mm thickness	ASTM D 149	>692 V/mil	>28 kV/mm
Dielectric Constant, 1.6mm, 10Hz to 1 MHz	ASTM D 150	3.1	3.1
Dissipation Factor, 10 Hz	ASTM D 150	50x10 ⁻⁴	50x10 ⁻⁴
100 Hz		25x10 ⁻⁴	25x10 ⁻⁴
1MHz		160x10 ⁻⁴	160x10 ⁻⁴
Volume Resistivity, 1.8mm thickness	ASTM D 257	1x10 ¹⁶ ohm-cm	1x10 ¹⁶ ohm-cm
Surface Resistivity	ASTM D 257	3x10 ¹⁴ ohm	3x10 ¹⁴ ohm
Comparative Tracking Index	IEC 60112		
At 3mm thickness		175 V	175 V
Flammability ⁽³⁾			
UL94 Classification at			
1.5 mm	UL94	V-0	V-0
Limiting Oxygen Index	ASTM D 2863	35 %	35 %
Glow Wire Temperature, 1.0-3.0 mm thickness	IEC 60695-2-10	1,760°F	960°C
Processing Conditions			
Drying Temperature, 3 to 4 hours		250°F	120°C
Melt Temperature		555 to 600°F	290 to 315°C
Mold Temperature		175 to 240°F	80 to 115°C

CV

ÖZGÜR KIRELLİ

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PERSONAL INFORMATION

Birth Place : Eskişehir
Birth Date : 26.11.1980
Marital Status : Single
Citizenship : T.C
Military Obligation : Finished (May 2006)

EDUCATION

2004 - : Marmara University , İstanbul
Mechanical Engineering (English) Graduation Program

1998 - 2004 : Marmara University , İstanbul
Mechanical Engineering (English) Undergraduation
Program

1995-1998 : Cumhuriyet High School, Eskişehir

1994-1995 : Orhan Oğuz High School (English Preparation),
Eskişehir

1992-1994 : Cumhuriyet High School , Eskişehir

1987-1992 : Millizafer Primary School

WORK EXPERIENCE AND INTERNSHIPS

01.02.2007 - : Siemens A.Ş. Energy (R&D specialist)

01.10.2004 -30.05.2004 : Lecturer Laboratory Assistance, Introduction to
Computer Systems and Computer Programming (FORTRAN)

01.09.2003 -12.09.2003 : Aygaz A.Ş. Genel Müdürlüğü

18.07.2003 - 28.08.2003 : Arçelik A.Ş Eskişehir Refrigerator Factory

05.07.2002-13.08.2002 : Ford-Otosan İnönü Engine Factory

03.07.2001 - 02.08.2001 : Marmara University, Mechanical Engineering Department

FOREIGN LANGUAGES

Good command of English
German (Beginner)

COMPUTER

I-deas 8,9,10 , Autocad R14, Autocad 2000, Mechanical Desktop 5.0/6.0, Fortran 90-95, MS Office 2000 , Windows 98/NT/2000/XP, Matlab,Lingo,Solidworks(beginner).

LICENSES AND CERTIFICATES

- * GRID Management Systems 1999
- * Class-B driving license
- * Festo Pneumatics, Electropneumatics and Hydraulic Certificates (3 Days)

INTERESTS

- * Cinema , Classical Music, Guitar
- * Football, Swimming , Basketball
- * Racing , Engine and Design Technologies

SOCIAL ACTIVITIES

- * Marmara University Mechanical Engineering Club Management Board President, 2004
- * Marmara University Mechanical Engineering Club Management Board Vice-President, 2003
- *Marmara University Mechanical Engineering Club Management Board Member 1999-2002
- * ASME International (American Society of Mechanical Engineers) Marmara University Student Section Management Board Member, 2003
- * Marmara University Cariyer Step Organization Committe 1999-2003

REFERENCES

Çetin ARBATLI, Porsuk Ticaret A.Ş., Manager (Retired) ,Eskişehir
Mehmet COŞAR ,Siemens A.Ş. Energy, Group Manager, İstanbul