

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES

EFFECTS OF MOISTURE AFTER INJECTION
ON THE MECHANICAL PROPERTIES OF PA 6
AND PA 66 MATERIALS

by
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March, 2013
İZMİR

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**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Master of Science in Mechanical
Engineering, Mechanics Program**

**by
Hilmi Burak MORALIOĞLU**

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İZMİR**

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “EFFECTS OF MOISTURE AFTER INJECTION ON THE MECHANICAL PROPERTIES OF PA 6 AND PA 66 MATERIALS” completed by HİLMİ BURAK MORALIOĞLU under supervision of ASSOC.PROF. DR. EMİNE ÇINAR YENİ and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.



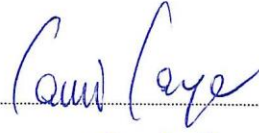
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EFFECTS OF MOISTURE AFTER INJECTION ON THE MECHANICAL PROPERTIES OF PA 6 AND PA 66 MATERIALS

ABSTRACT

Polyamides are among the first engineering plastics which have a wide variety of usage in industrial applications. These materials are very sensitive to moisture which acts as a plasticiser. With the increasing of absorbed moisture, strength and stiffness reduces but toughness and elongation increases. Higher moisture levels improve the impact absorbtion ability and ductility. In this thesis, the effects of moisture absorbtion on mechanical properties of PA 6 and PA 66 materials were investigated using tensile test specimens which had the dimensions in accordance with ASTM D 618, which were prepared by using the injection molding method. The tensile test specimens were conditioned in 80 celcius degrees water with three different time periods. 10, 20 and 30 hours immersions were applied. After conditioning, specimens were isolated from the environment by the help of HDPE bags and tensile tests were conducted for every specimen at certain time periods. Stress – strain curves were drawn for 10, 20, 30 hours test specimens and the results were compared with each other. It has been observed that after conditioning of PA 6 and PA 66 materials, the yielding and ultimate strength decreased; toughness, impact absorbtion ability and strain rates increased. The importance of production conditions of polyamide materials were realised with the help of tensile tests which consisted of same conditioned test specimens.

Keywords: Polyamide, moisture content, mechanical properties

PA 6 VE PA 66 MALZEMELERİNDE ENJEKSİYON SONRASI NEMİN MEKANİK ÖZELLİKLERE ETKİSİ

ÖZ

Endüstriyel uygulamalarda geniş bir kullanım alanı olan polyamidler, ilk mühendislik plastikleridir. Bu malzemeler neme çok duyarlıdır ve nem plastikleştirici olarak etki gösterir. Alınan nem miktarının artması ile malzemelerin dayanımı azalırken, süneklik ve uzama miktarları artmaktadır. Malzeme içerisindeki yüksek nem miktarı, malzemenin darbe dayanımını ve tokluk değerlerini iyileştirmektedir. Bu tezde enjeksiyon metodu ile, PA 6 ve PA 66 malzemelerin ASTM D 618 standardına uygun olarak imal edilmiş olan çekme numunelerinin nem almasının mekanik özelliklere etkisi incelenmiştir. Çekme numuneleri 80 santigrat derece su içerisinde 3 farklı zaman periyodunda şartlandırılmışlardır. 10, 20 ve 30 saat şartlandırmaları numunelere uygulanmıştır. Şartlandırma sonrası numuneler çevre etkilerinden korunmaları için yüksek yoğunluklu polietilen torbalar içerisinde saklanmışlar ve belirli zaman periyotlarında numunelere çekme testi uygulanmıştır. 10, 20, 30 saat test numunelerinin gerilim - şekil değişimi eğrileri çizilmiş ve sonuçları değerlendirilmiştir. Gözlemler sonucunda PA 6 ve PA 66 malzemelerinin nem alma sonrasında akma ve kopma mukavemetlerinin azaldığı; süneklik, darbe dayanımı ve yüzde uzama değerlerinin arttığı görülmüştür. Poliamid malzemesinin imalat şartlarının, elde edilen ürüne nedenli büyük bir etkisi olduğu, aynı şartlandırmaya maruz kalmış test numuneleri ile yapılan deneylerde görülmüştür.

Anahtar sözcükler : Poliamid, nem miktarı, mekanik özellikler

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CHAPTER ONE

INTRODUCTION

This chapter deals with the fundamentals of polymer technology and their specifications. Polymers can be classified into three groups, namely thermoplastics, thermosettings and elastomers. These materials have an important role on industrial production and daily usage.

Thermoplastic materials have a wide range of usage in plastic technology. They can be repeatedly reproduced by melting them and then returning them to room temperature (Groover, 2002).

Thermosetting plastics can not be reproduced. They are cured and their bonds between mers are generated by using heat, activators or catalysts. Thereafter, any attempt to reheat them for forming causes them to degrade.

Elastomers have great elastic deformation capability when force is applied. Many of them can be streched by a factor of 10 and afterwards return to their original length and shape (Groover, 2002). They can be classified into two main groups. First one is natural elatomers which was firstly discovered by Charles Goodyear in the year 1839 with vulcanization of rubber. The second group is synthetic elastomers.

Plastics are used at automative, aerospace and aeronatics industries, in the production of cans, boxes, containers, cable and wire technologies, household appliances, etc. They can be seen almost in every application in this century. Their widely usage is due to their some attractive properties for indstry. These include,

- Low thermal conductivity
- High corrosion resistance
- Good electrical resistance
- Low density
- Formabiliyty (casting, molding, extrusion, etc.)

- Resistance to acidic and basic environments
- Good optical properties
- Low energy consumptions

Plastics also have some negative properties. Among them are

- Compared with metals they have low strength
- Low moduli of elasticity
- Low melting or degrading temperatures
- Sensitivity for ultraviolet radiation, moisture and some other environments

1.1 Polymerization

Polymers consist of small molecules that join with each other to produce macromolecules. Polymer molecules have many repeating units that are named as monomers or briefly mers. These molecules are generally unsaturated and they have strong covalent bonds (Tlustý, 2000). Polymerization process consists of two different methods; the first method is additional polymerization and the other one is step polymerization.

1.1.1 Additional Polymerization

In this polymerization method, some chemical catalysers are used for opening double bonds between atoms so that they join each other as monomer molecules. In order to produce the macromolecule, each mer joins with each other and as a result, macromolecule chains are formed. Because of this, this process is known as chain polymerization (Degarmo, Black, & Kohser, 1997)

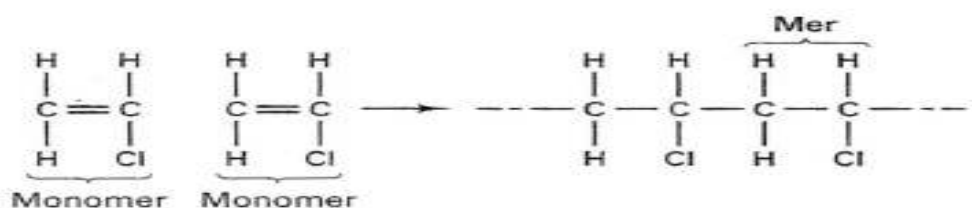


Figure 1.1 Polymerization by addition, in this case, producing a polyethylene macromolecule

1.1.2 Step Polymerization

In this type of polymerization, two or more different monomers are joined with each other for creating a new type of molecule. This process is slower than additional polymerization and generally water is condensed during polymerization, hence the term “condensation polymerization” is used for this processes. Heat, pressure and catalysers are generally needed to carry out this process (Groover, 2002).

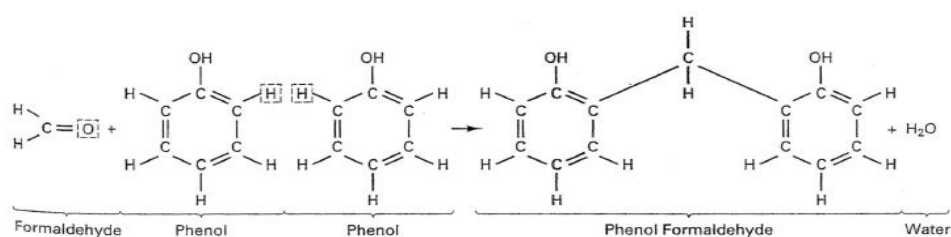


Figure 1.2 Step polymerization of phenol formaldehyde (bakelite)

Both thermoplastics and thermosets use this method for polymerization such as nylon 6, 66, polycarbonate, phenol formaldehyde, urea formaldehyde and silicones. Groover, (2002) is expressed, the meaning of polymerization is producing macromolecules. Macromolecules consist of “n” repeating mers, therefore “n” is called the degree of polymerization. The degree of polymerization affects the properties of polymers. The higher the degree of polymerization, the higher the mechanical strength (Degarmo, Black, & Kohser, 1997).

1.2 Polymer Structures and Copolymers

Polymer structures can be identified into three groups. These are stereoregularity, branching and copolymers.

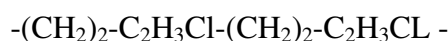
1.2.1 Stereoregularity

Stereoregularity is a special arrangement of atoms in mers of a polymer. In the chain location of a polymer the H atoms change their position with another atom.

These three types of structures give the polymers different properties. Generally linear or branched structures are seen on thermoplastic polymers. Thermosetting plastics and elastomers have cross-linked structures. If linear and branched structures are compared, it is seen that branched structures are more rigid and have higher melting degrees. Cross-linking gives the polymer an irreversible situation when thermosets and elastomers start to occur by polymerization (generally condensation polymerization), the crosslinks cause the polymer to become chemically set (Tlusty, 2000). If thermosets or elastomers are reheated for melting or reforming, the polymer does not melt, it degrades or is burnt. Thermosets consist of a high degree of cross-linked structures then elastomers. So thermosets are stiff, hard and brittle, whereas elastomers are more elastic (Tlusty, 2000).

1.2.3 Copolymers

A special kind of polymer, which is named as copolymer, has two different types of monomers which are combined into the same macromolecule (Degarmo, Black, & Kohser, 1997). For example, ethylene-vinylchloride copolymer is as



Copolymers can be found in different structural forms. These are (a) alternating, (b) random, (c) block and (d) graft.

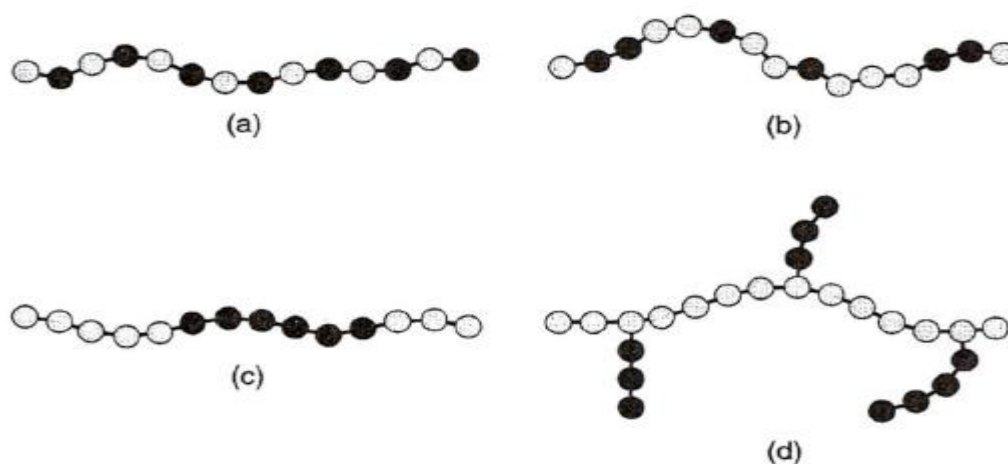


Figure 1.5 (a) alternating, (b) random, (c) block, (d) graft structural type of copolymers

We can mention terpolymers in this stage. Terpolymers are certain kinds of polymers which consist of three different types of mers like ABS (acrylonitrile – butadiene – styrene) (Tlustý, 2000).

1.3 Crystallinity

In polymer technology none of the polymers can be totally consisted of crystalline forms like metals or ceramics. We can mention the degree of crystallinity for polymers. The crystalline structures give the polymer stiffness, strength, density, higher modulus of elasticity and higher temperature for processing (Groover, 2002).

Crystallinity can be seen only in simple structures like linear polymers. Branched, cross-linked, copolymers (random and graft type) can not crystallize. In linear polymers, isotactic polymers always crystallize, syndiotactic polymers sometimes crystallize and atactic ones never crystallize (Groover, 2002). Another important factor is the cooling speed. Slow cooling speeds increase crystallinity.

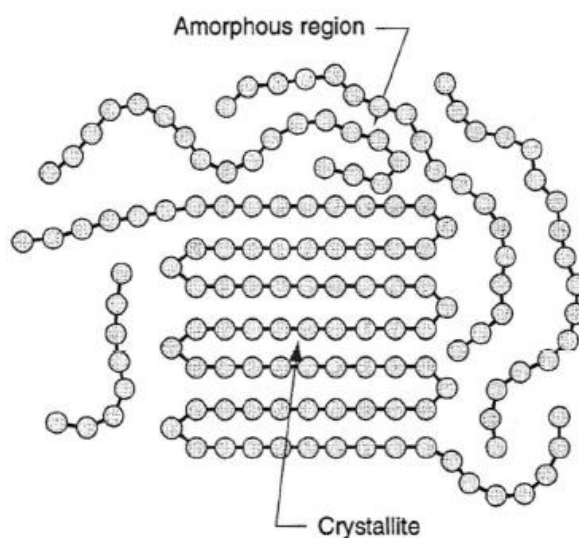


Figure 1.6 Crystal structure of a polymer

As can be seen in Figure 1.6, a linear amorphous polymer structure has a partially crystallized region.

1.4 Additives

Additives which are added to the polymer structure may change many properties of polymers. Additives can be listed as (1) fillers, (2) flame retardants, (3) plasticizers, (4) colorants, (5) uv light absorbers, (6) lubricants etc...

1.4.1 Fillers

Fillers are generally added in a polymer structure for reducing the cost. Fillers improve the mechanical, thermal and electrical properties of polymers. Calcium carbonate, clay, asbestos, powders of silica, fibers of glass and carbon are the examples of fillers (Tlustý, 2000).

1.4.2 Flame Retardants

Polymer structures are generally sensitive to heat. They can easily burn and release toxic gasses to the environment. Flame retardants added to polymer structures for reducing flammability increase the combustion temperature and generate incombustible gasses.

1.4.3 Plasticizers

Plasticizers are added into polymer structures for reducing the glass transition temperature (T_g). Addition of plasticizers convert the polymers to a more flexible state for forming (Tlustý, 2000).

1.4.4 Colorants

Colorants are added into polymer structures to gain the structure color. Colorants can be dyes (liquid form) or pigments (powder form) (Tlustý, 2000).

1.4.5 U.V. Light Absorbers

U.V. lights cause a destructive effect on crosslinks of polymers. Loosing of bonds cause decrease the stiffness and mechanical properties. U.V. light absorbers prevent the polymers from the effects of radiation.

1.4.6 Lubricants

During the molding process, it is important to fill the mold completely with the molded material. Lubricants reduce the friction and change the flow ability of the material. So, the material easily fills the mold and the lubricant helps releasing the part out of the mold (Tlusty, 2000).

1.4.7 Cross-linking Agents

Cross-linking agents help producing polymer structures which have cross-links. They act like a catalyst. Vulcanization of natural elastomer is a good example of this issue. Sulphur has a great role on vulcanization (Groover, 2002).

1.5 Thermoplastic Polymers

Thermoplastic polymers have macromolecules consisting of linear or branched type structures rather than cross-linked structures. This linear or branched type structures molecules can be modeled like a cotton ball (Tlusty, 2000). Individual molecules have strong covalent bonds but this molecular structures are bonded with adjacent molecules by weaker Vander Waals forces (Tlusty, 2000). This secondary Vander Waals forces are very sensitive to changes in heat. In the elevated temperatures, these polymers become much softer and viscoelastic, when cooled they become stiffer and harder. This property variations depend on glass transition temperatures of polymers (Tlusty, 2000). The mechanical and physical properties of polymers may vary above or under the glass transition temperature (T_g). If the temperature reaches the melting point (T_m), the polymers return to liquid phase.

Between the temperatures of ($T_g - T_m$) the hard and brittle polymer becomes soft and viscoelastic (Groover, 2002). Below the temperature (T_g), the polymers return to their hard and brittle structure (Groover, 2002). This property gives the thermoplastic polymers a significant role in manufacturing. They can be repeatedly heated from solid to liquid and after forming recooled to the solid state. Thermoplastic polymers are used in a great variety of applications in industry. Acetals, acrylics, acrylonitrile-butadiene-styrene, cellulose, fluoropolymers, polyamides, polycarbonates, polyesters, polyethylenes, polypropylenes, polystyrenes and polyvinylchlorides are the best known commercial thermoplastics polymers.

1.6 Thermosetting Polymers

The opposite of thermoplastics, thermosetting polymers have cross-linked structures. These cross-linked structures can be produced by activation of temperature, activation of catalysts or activation of mixing two chemicals (Groover, 2002). Thermosets have no glass transition temperatures, if the temperature is elevated, thermosets can not melt, they degrade or burn (Groover, 2002). Because of this, thermosets can not be reproduced like thermoplastics. They have great advantages over thermoplastics. They are more rigid, more strong, less soluble and have higher service temperatures (Groover, 2002). But they are brittle, have lower ductility and poorer impact properties than thermoplastics (Groover, 2002). Amino resins, epoxies, phenolics, polyesters, polyurethanes and silicones are the best known thermosetting polymers.

1.7 Elastomers

Elastomers are polymers that have cross-linked structures in their molecules. These structures are not very heavy like thermosets. Because of this, they are not stiff and hard as thermosets. But they are elastic and have high impact resistances. They are amorphous and their glass transition temperature is well below the room temperature (approximately $-50\text{ }^{\circ}\text{C}$ to $-60\text{ }^{\circ}\text{C}$) (Groover, 2002). They are brittle and hard under this temperature and above this temperature, they are elastic and rubbery

(Groover, 2002). Elastomers are divided into two main groups, the first one is natural rubbers and the second one is synthetic rubbers.

1.7.1 Natural Rubber

Polyisoprene is the main constitute of natural rubber. It was first invented by Charles Goodyear at the year of 1839. Goodyear used sulphur with heat for producing cross-linking structures. This process is called the vulcanization of rubber and it makes the material hard and resilient (Groover, 2002). This rubber is used mainly in automotive industry for tires, pipe gasgets, bushing, seals and shock absorbers etc...

1.7.2 Synthetic Rubber

Styrene – butadiene rubber, ethylene – propylene – diene rubber, chloroprene rubber, isoprene rubber, polyurethanes, silicones are the most known synthetic rubbers. These rubbers are much cheaper than natural rubbers. Belts, hoses, tires, tanks, gasgets etc... are made of synthetic rubbers.

1.8 Polyamides

Polyamides are a kind of thermoplastic polymers which have amide groups in their linear chain structures. These type of polymers were first developed by Wallace H. Carother and his colleagues who firstly synthesised polyamide 66 in 1935 (Brydson, 2006).

Deopura, Alagirusamy, Joshi, & Gupta, (2008) are represented the polyamides in two main groups. One is nylon XY and the other one is nylon Z. In group nylon XY (for example nylon 66), X represents the carbon atoms in diamine monomer and Y represents the number of carbon atoms in diacid monomer. In group nylon Z (for example nylon 6), Z represents the number of carbon atoms in the monomer.

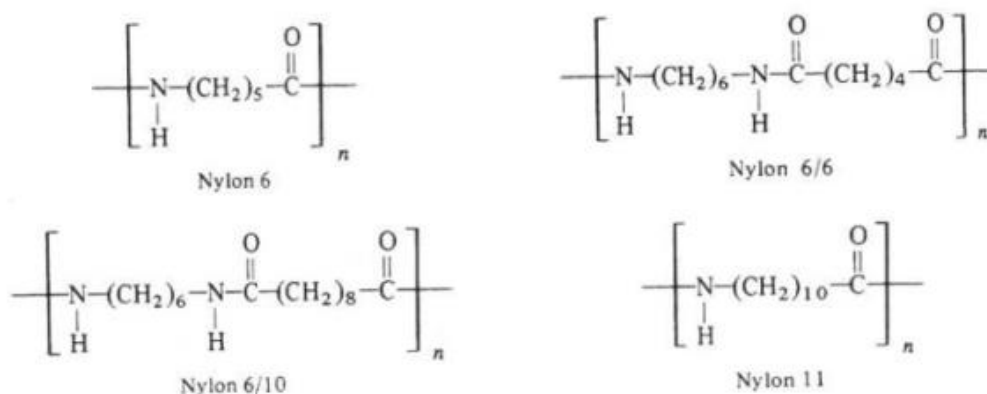
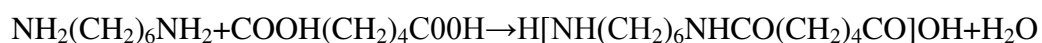


Figure 1.7 Molecular structures of nylons

Polyamides can be produced in using many methods. The most known and commonly used methods are 1) reaction of diamines with dicarboxylic acid (producing nylon salts) 2) self – condensation of a ω -amino acid 3) opening of a lactam ring 4) reaction of diamines with diacid chlorides 5) reaction of diisocyanates with dicarboxylic acids (Brydson, 2006).

Polyamides can have aliphatic or aromatic chain backbones. Aliphatic polyamides consist of some chemical materials reactions. These chemicals are 1) adipic acid 2) hexamethylenediamine 3) sebacic acid and azelaic acid 4) caprolactam 5) ω -aminoundecanoic acid 6) ω -aminoenanthic acid and 7) dodeconelactam (Brydson, 2006).

For example nylon 66 is produced with reaction of diacid and diamine (the first production method). Hexamethylene diamine and adipic acid reaction gives a chemical salt. Polymerization of this salt produces nylon 66.



Nylon 6 use the second method for polymerization. Caprolactam is used for this process.



For polyamides, the higher the amide groups [-CONH-], the higher a) the density b) tensile strength, rigidity, hardness, resistance to creep c) T_m temperature d) resistance to hydrocarbons and e) water absorption (Brydson, 2006).

The degree of crystallinity affects the properties of polyamides. The higher the degree of crystallinity, the less water absorption, the higher abrasion resistance, the higher electrical and mechanical properties. Nylon 6 has the lowest degree of crystallinity in polyamide family and because of this, nylon 6 has the highest machinability rating among all other polyamides (Akkurt, 2007).

Polyamides (especially nylon 6 and nylon 66) are the first engineering plastics and they have a wide variety of usage in industrial applications. Deaning (1972) gives the polyamides applications that, polyamides are used for producing gears, cams, bearings, housings, tire cords, gaskets, valve seats, pulleys, coatings etc... and using textile applications, blends with wool, rayon, cotton for dresses, stockings, undergarments, carpeting etc...

1.8.1 General Properties of Polyamides

The mechanical properties of polyamides are given in Table 1.1. These properties are dependent on temperature, moisture content, testing rate, additives and structure of polyamides (Brydson, 2006).

Polyamides have good resistance to environments like hydrocarbons and alkalis. Mineral acids can attack polyamides but the rate of effect depends on type of acid and the concentration (nitric acid is generally active at all concentrations) resistance to all chemicals is limited at elevated temperatures (Brydson, 2006).

Table 1.1 Mechanical properties of typical polyamides

Property	Unit	46	66	6	610	612	11	12	66/610 (35:65)
Yield Strength	MPa	100	80	76	55	60	38	45	38
Tensile Strength	MPa	80	94.5	81	-	60	52	54	-
Elongation at Break	%	30	80 - 100	100 - 200	100 - 150	100 - 250	30 - 300	200	> 200
Modulus of Elasticity	MPa	3000	3000	2800	2100	-	1400	1400	1400
Impact Strength	J/m	-	53 - 110	53 - 160	50 - 120	53 - 80	96	110 - 290	-
Rockwell Hardness	RV	R123	R118	R112	R111	R114	R108	R107	-
Specific Gravity	g/cm ³	1.18	1.14	1.13	1.09	1.07	1.04	1.02	1.09

Thermal properties of polyamides are given in Table 1.2.

Table 1.2 Thermal properties of selected polyamides

Property	Units	46 (dry)	66	6	610	612	11	12	66/610/6 (40:30:30)
Melting Point	°C	295	264	215	215	210	185	175	160
Deflection Temperature (1.82 MPa) (0,45 MPa)	°C	160 —	75 200	60 155	55 160	65 160	55 150	51 140	30 —
Coefficient of Linear Expansion	10 ⁻⁵ /cm°C	9.2	10	9.5	15	9	15	12	—

Polyamides have good electrical insulation properties under conditions of low humidity and temperature (Brydson, 2006). Variations in humidity and temperature affect negatively or positively the electrical properties of polyamides. The relation between volume resistivity and absorbed water for nylon 66 is shown in Figure 1.8 and the electrical properties of some selected polyamides are presented in Table 1.3.

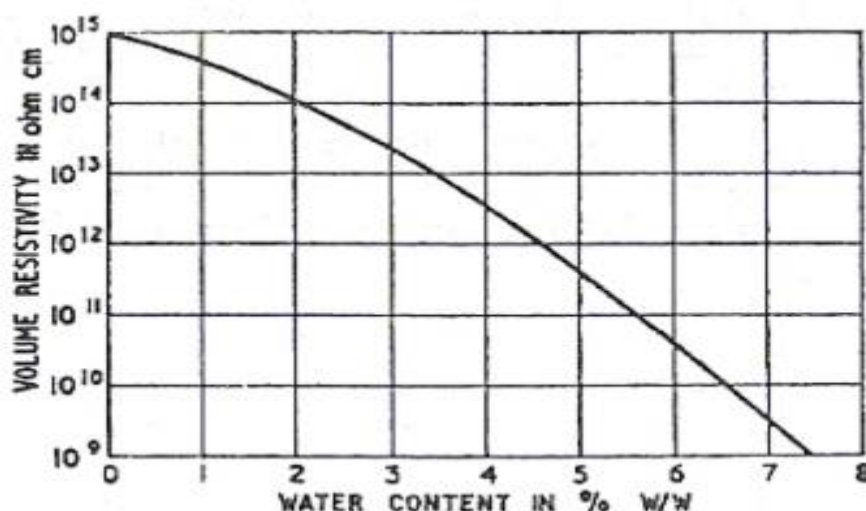


Figure 1.8 Effects of moisture content on the volume of resistivity of nylon 66

Polyamides are hygroscopic polymers because of hydrogen bonding character at amide groups. Water absorption affects electrical, thermal and mechanical properties of polyamides. Humidity has a plasticising effect on polyamides. This causes reduction of tensile strength and modulus of elasticity, but increases ductility and impact absorption ability (Brydson, 2006). Variation in absorbed water in a specimen causes variation in the electrical properties as mentioned above. Water absorption decreases with reducing amide group concentration in a polymer backbone. For example, nylon 66 absorbs 9% water during equilibrium at ambient temperature and 100% relative humidity, but nylon 11 absorbs 1.9% water under the same conditions (Fried, 2003). This issue will be discussed in more detail for PA 6 and PA 66.

Table 1.3 Electrical properties of some selected polyamides

Property	Units	Nylon 66	Nylon 6	Nylon 11	Nylon 610	Nylon 66/610/6 (40:30:40)	Nylon 66/610 (35:65)
Volume Resistivity	Ω m (dry)	$> 10^{17}$	$> 10^{17}$	$> 10^{17}$	$> 10^{17}$	—	—
	Ω m 50% RH	10^{15}	—	—	10^{16}	10^{15}	10^{15}
	Ω m 65% RH	10^{14}	—	10^{12} - 10^{14}	—	—	—
Dielectric Constant	10^3 Hz dry	3.6 – 6	3.6 – 6	—	3.7	—	—
	10^3 Hz 65%RH	—	—	3.7	—	—	—
	10^6 Hz 50% RH	3.4	—	—	—	—	—
Power Factor	10^3 Hz dry	0.04	0.04-	—	0.02	—	—
	10^6 Hz 65%RH	—	0.06 —	0.06	—	—	—
Dielectric Strength	kV/cm 50% RH 25 °C	> 100	> 100	—	> 100	—	—

CHAPTER TWO

PRODUCTION AND TESTING OF SPECIMENS

2.1 Injection Molding

Injection molding is a mass production method, which is especially suitable for thermoplastic polymers. According to Groover (2002), the principles of production are very simple. The polymer is heated to become sufficiently fluid to be forced to flow through a mold which has the net shape of the product. After injection, the material starts to solidify in the mold which has a special cooling system. With this method, small or big, complex or simple polymer parts can be produced (50 gr to 25 kg). Injection molding process is an economical production type only in a large number of productions. The complex and big molds are very expensive.

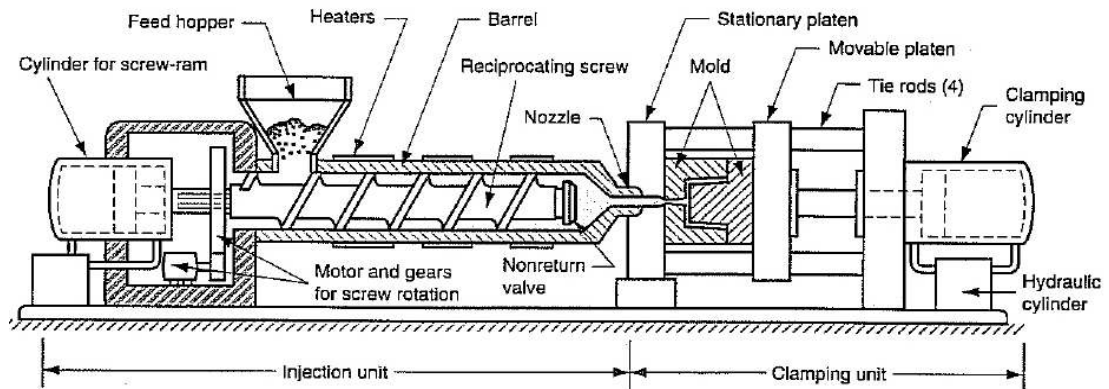


Figure 2.1 Diagram of the injection molding machine

In Figure 2.1, an injection molding machine diagram is shown. According to Gait & Hancock (1970), injection molding machines have two main parts. One is the injection unit. This unit works like an extruder. Polymer returns from the solid state to liquid state and is injected into the mold. The second part is the clamping unit. This unit is responsible for holding and locking of the mold.

If we mention about the cycle of injection process, we can divide it into four main parts. According to Groover (2002), the cycle is (1) Mold is closed by the clamping unit and locked for injection. (2) The screw rotates and it injects the melt into the

mold with a high pressure. (3) Screw rotates back, the nonreturn valve opens and the fresh polymer starts to fill into the barrel for the next injection. During this process, material which is in the mold continues its solidification. (4) The mold is opened and the part is falled down by ejectors.

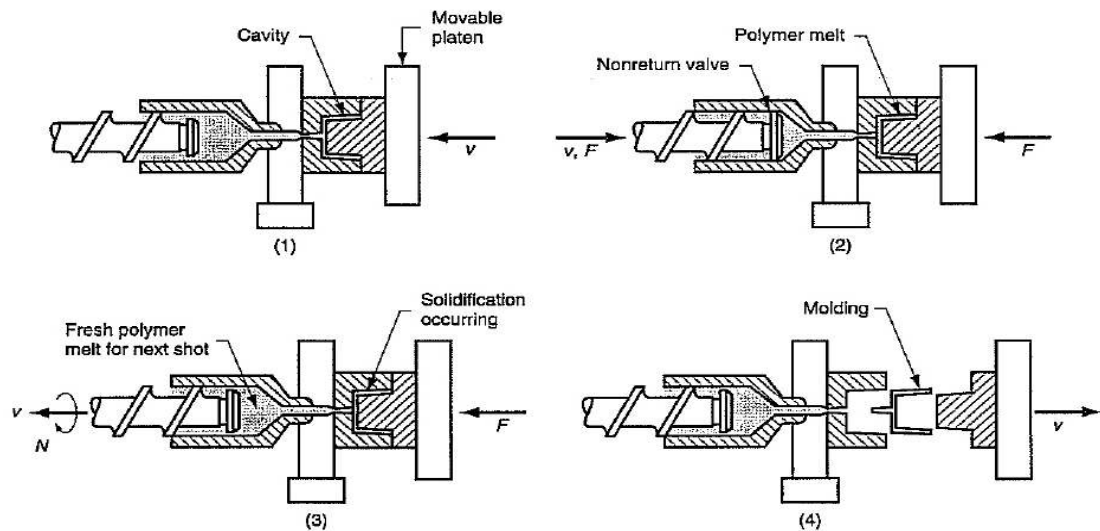


Figure 2.2 Typical molding cycle

Clamping units have two plates, one is fixed and the other is movable. This unit is responsible for holding two parts of the mold by applying an appropriate clamping force. These units can be designed by using three different arrangements. These are toggle, hydraulic and hydromechanical. The samples are shown below.

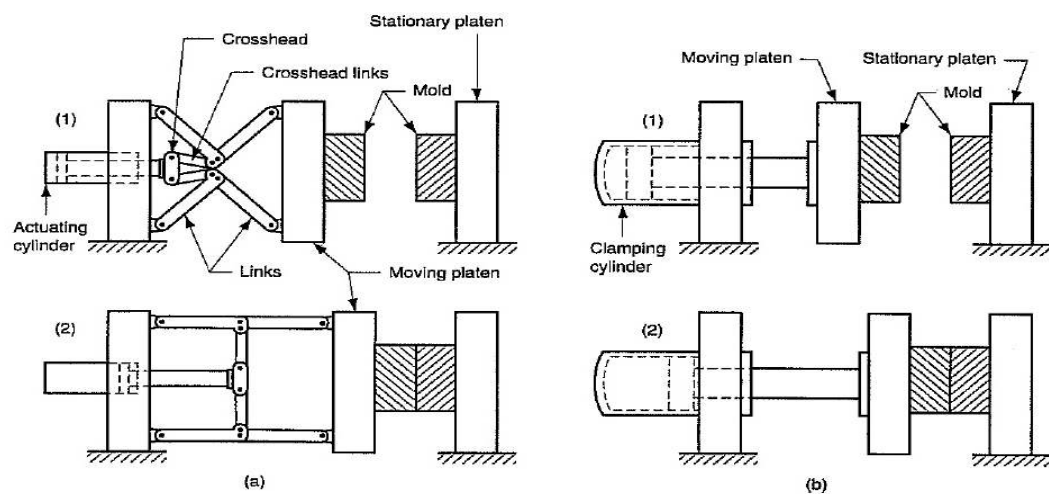


Figure 2.3 Two clamp designs 1) toggle clamp design a) open b) closed 2) hydraulic clamping a) open b) closed.

Toggle clamps use toggles for moving the mold into the open or closed position. The toggles can be activated by hydraulic or by a ball screw. This system is generally used with low tonnage machines (Groover, 2002).

Hydraulic clamps are suitable for high tonnages, they are much more flexible than toggle clamps. Hydraumechanical clamps are suitable for high tonnage usage like hydrolic clamps. Hydraulically opened – closed system are added with mechanical locking mechanisms.

Injection units can be classified into two main groups. The first one is the reciprocating screw machine (Figure 2.1). These kinds of machines have a barrel which is fed with pellets from the hopper and contain a screw which is rotated for mixing, heating and injecting the polymer into the mold (Gait & Hancock, 1970). A nonreturn valve is located near the screw for preventing the melt flow from reverse direction of flow.

The second type of injection units are screw plasticizer machines. These machine have two stages. The first stage is similar to the reciprocating screw machine. Pellets melt in this section with the help of the screw. This section feeds the other section. The other section is responsible for injection. A plunger is used for injecting melt into the mold. This type of injection unit can produce up to 4% more than reciprocating screw machines (Groover, 2002). However this system is more expensive and complex.

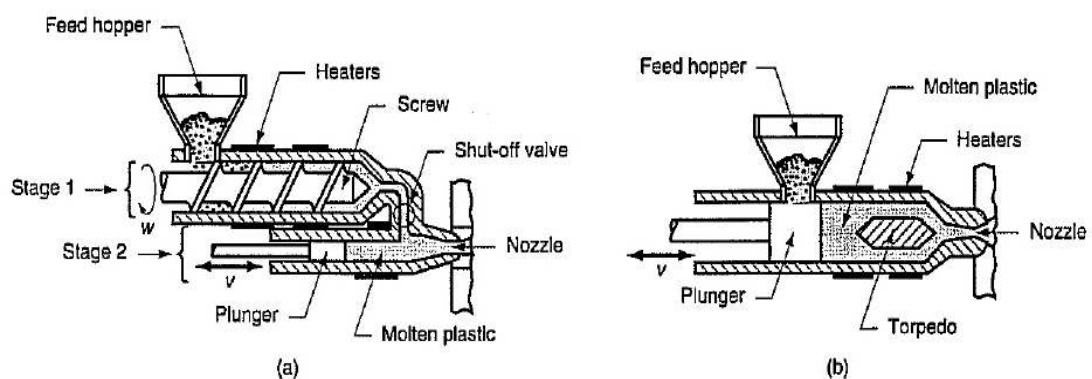


Figure 2.4 Two stage machine

In injection molding process every part has their own special molds. The molds can be classified into two groups. The first one is two plate mold, the second one is the three plate mold. Even if the mold is two or three plates, they have common components like sprue, runners, gates, cavity, ejector pins and the cooling system.

Sprue, runners and gates are located along the material's path from barrel to the cavity of mold. The distribution channels enable flow of molded material into cavity.

The cavity is specially designed for each injected part. The figure can be composed single or multiple parts. So one or more parts can be injected in a single injection cycle. The molds generally possess two halves and one part of figure is one side of the mold and the other part cavity is on the other part of the mold.

Ejector pins are needed to eject the injected part from the mold to the outside. Generally ejector pins are located into the movable part of the mold.

The cooling system has an important task in the injection process. Plastic must be cooled in the mold before it is ejected. Because of this, water channels are machined during the construction of the mold and high pressure water pumps are located on the injection molding machines.

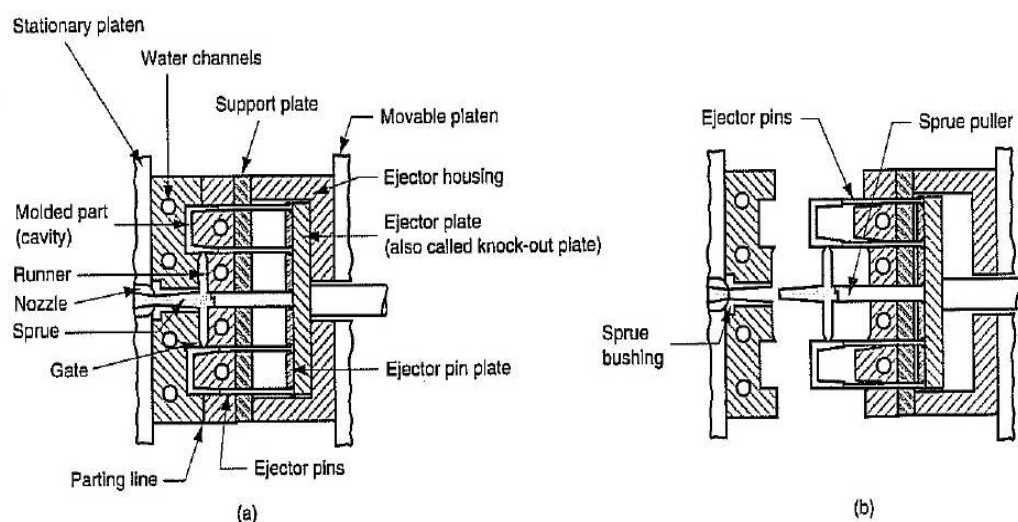


Figure 2.5 Details of two plate mold

Groover (2002), explains the second type of molds, are three plate molds. These type of molds are suitable for automatic injection machines. Molds have two movable parts and after injection, the sprue, runners and gates are ejected to one side and the injected part is ejected to the other side. These type of molds give the designer more flexibility. Distribution of the molten plastic can be much more suitable in comparison to two plate molds.

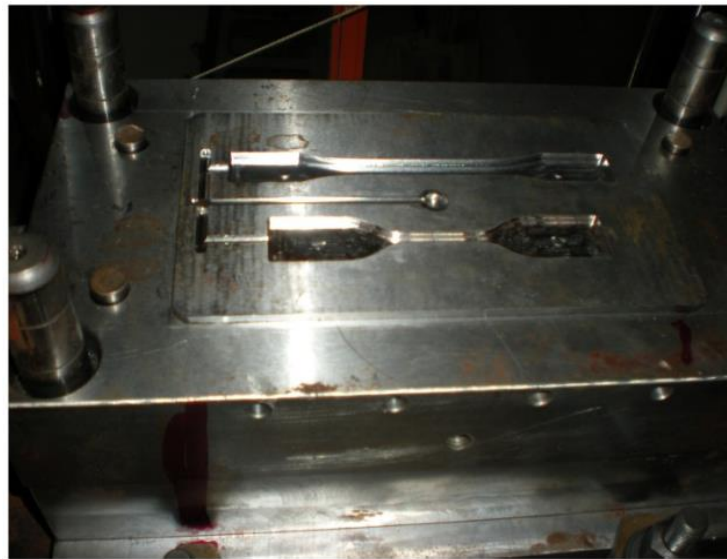


Figure 2.6 Injection mold of the test specimens

In Figure 2.6 the tensile test specimens injection mold can be seen. The kind of mold is the two plate mold and its cavity possesses two different types of tensile test specimens figure. The long one was our test specimen figure (type 1 test specimen) and the details of this figure are explained in section 2.2.1 Test Specimens part. The cooling channels, ejector pin houses, cavity of specimens sprue, runners and gates can be seen in Figure 2.6.

In Figure 2.7 the molded parts can be seen. In this figure, the sprue, runners and gates of mold can be easily seen.

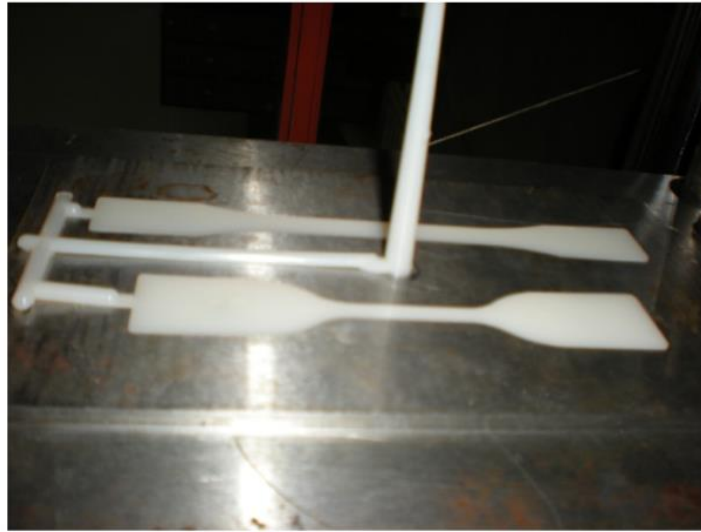


Figure 2.7 Production of a specimen

2.2 Tensile Test

Standard tensile test is the most common and simplest test for determining the tensile properties of materials. Tensile test speed, preparation of specimens and testing environment affect the tensile properties. The test specimen is fixed with grippers on the test machine. One of the grippers is fixed and the other one is movable. When load is applied to the material, movable gripper starts to stretch the specimen. The load, the extension of specimen or decrease in cross sectional area (diameter) are recorded. After all values are recorded during testing, stress – strain curves can be constructed.

In Figure 2.8 a stress – strain graph can be seen for a thermoplastic polymer. Applied force produce strains on specimens. Between the starting point and point B the material obeys the Hook's law. If the load is removed before reaching point B the specimen returns to its original length and diameter. This region is called the elastic zone and within this region the material has elastic strains. Point B is called the elastic limit or the yield point. If we apply forces beyond B (for example B^1), the material starts to deform in a plastic manner. After this point if we remove the load, the material can not return to its original length and diameter. It removes the elastic strains (ϵ^e) but the plastic deformations (ϵ^p) stay permanently on the material. Finally, point C is reached, where the applied force is maximum and rupture occurs.

The point C represents the the maximum load or the point of instability. Therefore, it is called the tensile strength or the ultimate strength. The material's total strain can be determined by adding the elastic and the plastic strains. This value is the ultimate strain of material and can be found by $\varepsilon = \varepsilon^e + \varepsilon^p$.

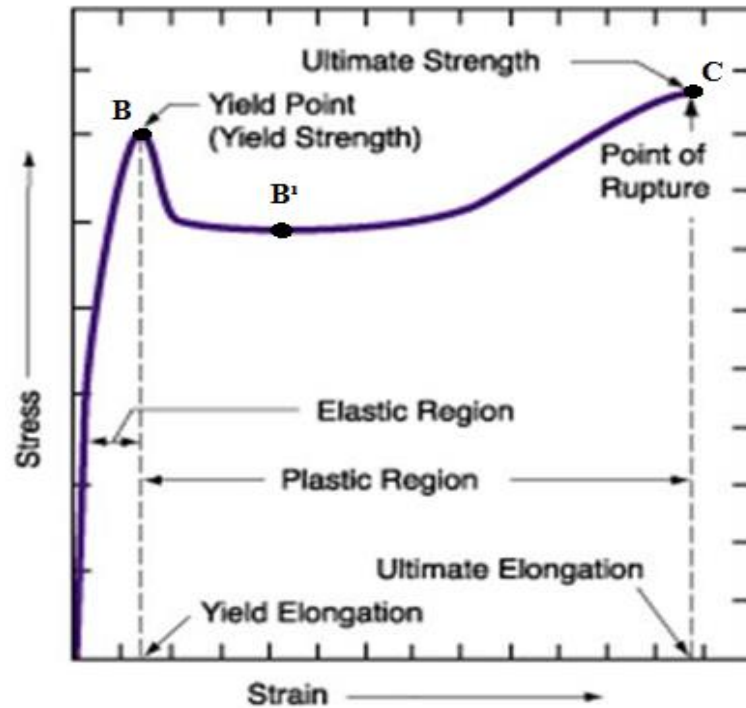


Figure 2.8 Typical stress – strain curve for a thermoplastic polymer

The stress – strain curve can be used for classifying plastics. Different plastic types have different stress – strain curve types. In Figure 2.9, different categories of plastic materials' stress – strain curves can be seen. A soft and weak material, like PTFE, has a curve like the first graph type in Figure 2.9. This means, this material has a low modulus of elasticity, low yield strength, and moderate elongation at break. Soft and tough materials, like polyethylene, have high elongation at break but has low yield strengths and moduli of elasticity. Hard and strong materials, like polyacetal, have high yield strengths and ultimate strengths and moduli of elasticity but low elongation. A hard and tough material, polycarbonate, has high modulus of elasticity, high yield and ultimate strengths and high elongation at break. A hard and brittle material, like phenolic, possess high modulus of elasticity but low elongation at break.

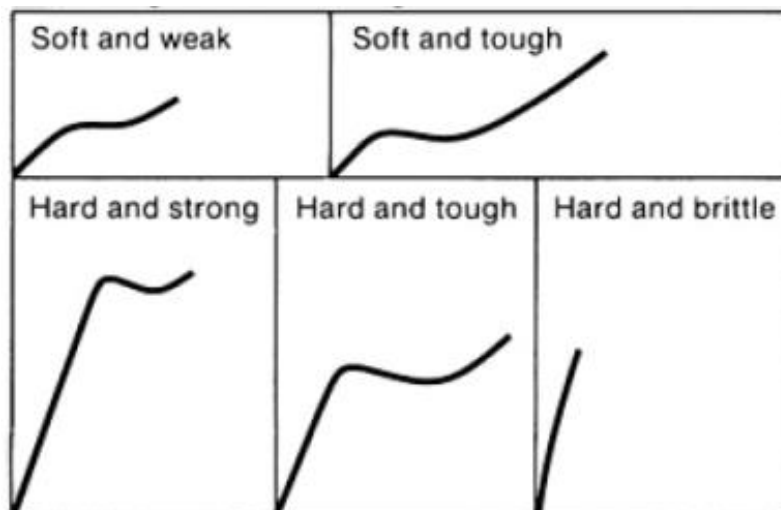


Figure 2.9 Tensile stress – strain curves of several categories of plastics

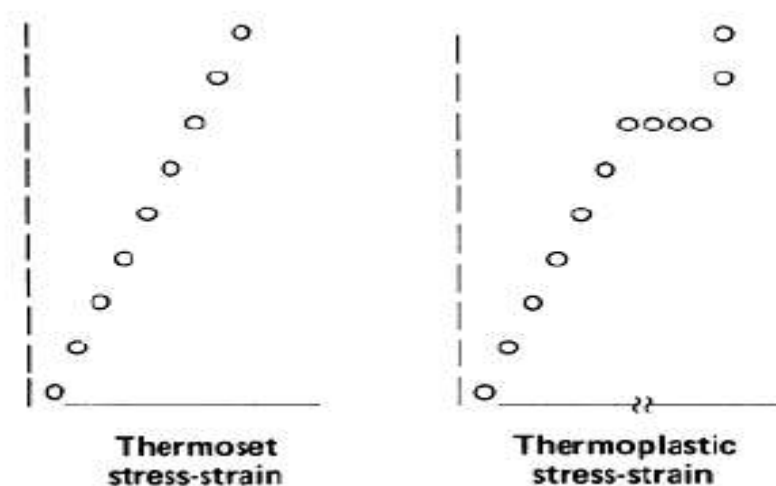


Figure 2.10 Stress – strain behaviors of thermosets versus thermoplastics.

If we consider the difference between the stress – strain curves of thermoplastics and thermosetting materials, it will approximately be similar to Figure 2.10. In thermoplastics, the area under the stress – strain curve is much larger than that for thermosetting materials. The stress - strain curve of thermoplastic materials possess a plateau region after the yielding point. The giant molecules regain their resistance after this point (strain hardening) and before failure, the stress – strain curve of the material increases. Thermosetting materials have more rigid networks and there is no break in their curves.

The strain rate is very important in a tensile test. Lower strain rates give the material much more time for deformation. Different strain rates give us different stress – strain curves, lower or higher tensile strength for same materials. In Figure 2.11, the effects of different strain rates can be seen for polycarbonate.

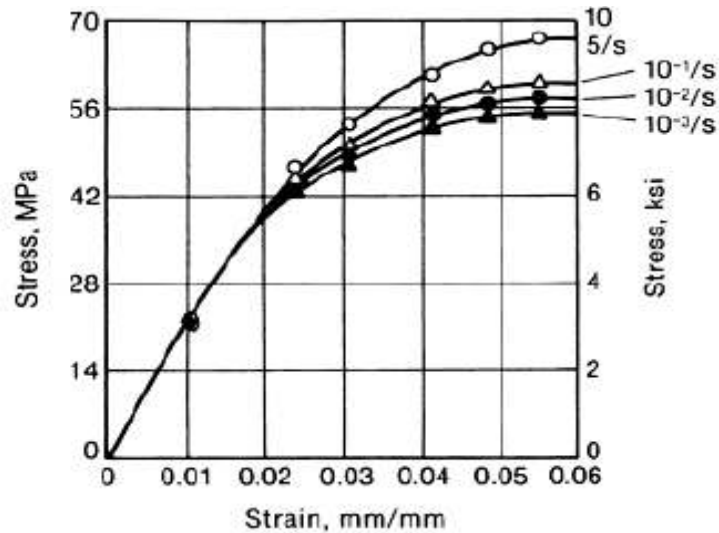


Figure 2.11 Stress – strain curve for rubber modified polycarbonate at room temperature as a function of strain rate.

According to ASTM D 618, it's recommended that the testing rate, for short term tensile properties, can be taken as 0.5 cm/min and the rupture occurs between 0.5 to 5 min. In our tensile test procedure, the testing rate was taken as 2 cm/min.

In Figure 2.12, the Shimadzu tensile testing machine, where the tests in this study are conducted, can be seen. It is located in the composite laboratory of Dokuz Eylül University. The capacity of the machine is max 10 kN.

In Figure 2.13 a specimen during testing is shown. After preparation of PA 6 and PA 66 specimens by injection molding, before the tensile testing is carried out, they were conditioned in 80 °C water for three different time periods of 10 hours, 20 hours and 30 hours. After that, tensile testing was done over a time period of about two weeks.



Figure 2.12 Tebsile test machine

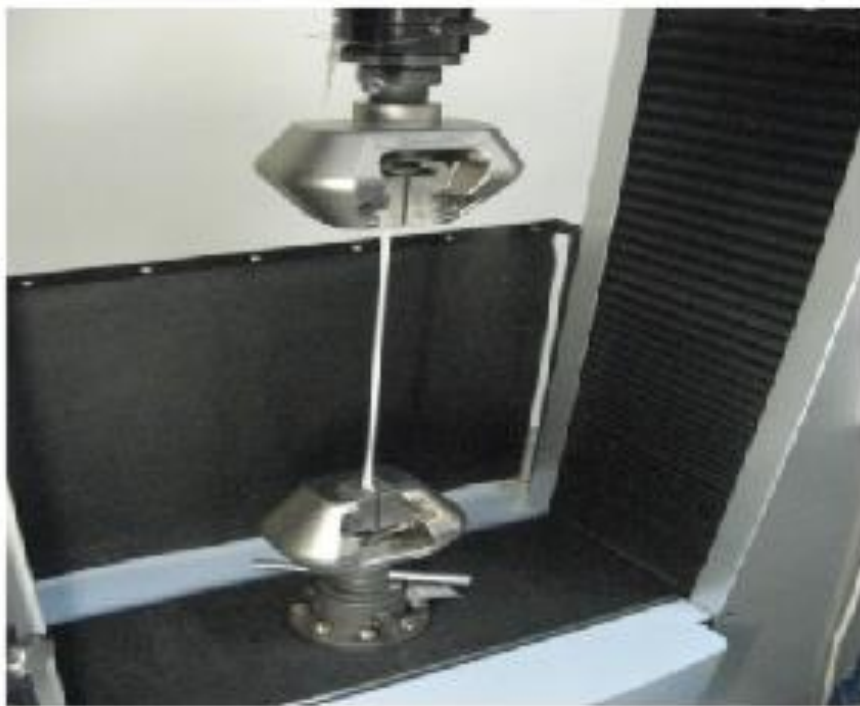


Figure 2.13 Testing of a specimen

2.2.1 Test Specimens

Test specimens can be prepared in different forms and dimensions. According to ASTM D 638 – 03 (standard test method for tensile properties of plastics) test specimens can be prepared as standard tensile specimens, rigid tubes or rigid rods. For sheets, plates and molded plastics, test specimens can be classified into 3 sub groups. These are rigid and semirigid plastics, non rigid plastics and reinforced composites. For sheets, plates and molded plastics, five different types of standard tensile test specimens are advised as indicated below. Type 1 and 2 can be used the materials which have a thickness of 7 mm or less. Generally type 1 is chosen but if the material does not break in the narrow section, type 2 specimens can be used. Type 4 specimens should be used if direct comparison are required between materials in different rigidity cases. Type 3 specimens must be used for all materials if the thickness is greater than 7 mm and max 14 mm. Type 5 specimens shall be used when only limited material having a thickness less of 4 mm.

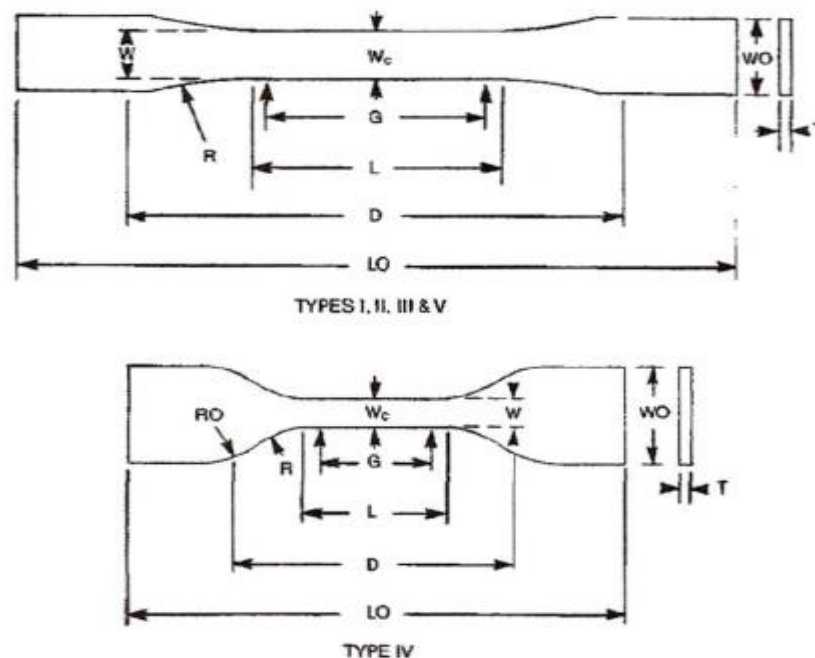


Figure 2.14 Types of test specimens

In Figure 2.14 the types of test specimens for sheets, plates and molded plastics can be seen.

Table 2.1 Dimensions of test specimens for various thicknesses

Thickness of Specimen [mm]						
7 or under			Over 7 to 14	4 or under		
Dimensions [mm]	Type 1	Type 2	Type 3	Type 4	Type 5	Tolerances
W	13	6	19	5	3.18	± 0.5
L	57	57	57	33	9.53	± 0.5
W0	19	19	29	19	-	+6.4
W0	-	-	-	-	9.53	+3.18
L0	165	183	246	115	63.5	no max
G	50	50	50	-	7.62	± 0.25
G	-	-	-	25	-	± 0.13
D	115	135	115	65	25.4	± 5
R	76	76	76	14	12.5	± 1
R0	-	-	-	25	-	± 1

In Table 2.1 the dimensions of test specimens for various thickness can be seen. The thickness of all molded specimen types can be taken 3.2 ± 0.4 mm.

For testing of PA 6 and PA 66 test specimens Type 1 was selected. This specimen is suitable for rigid and semi rigid plastics. The thickness is taken as 3.2 mm.

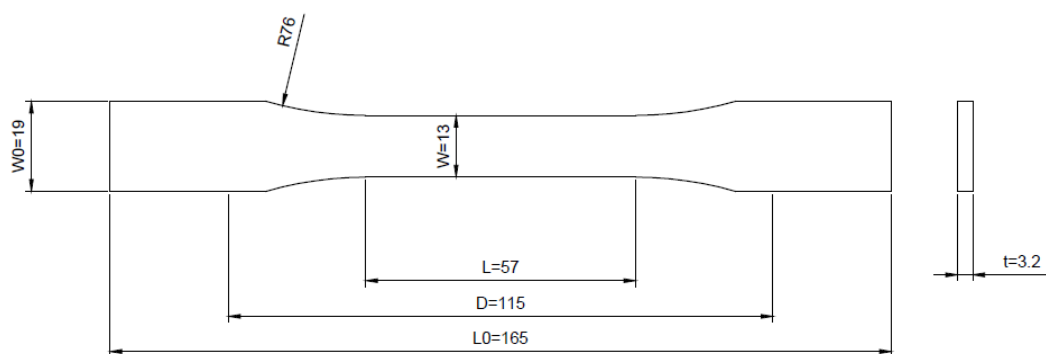


Figure 2.15 Type 1 tensile test specimen dimensions

2.3 Conditioning of Specimens

The prepared test specimens, after injection process, were immersed in 80 °C water at three different time periods. The first group of specimens have absorbed moisture at a time period of 10 hours. The second group absorbed moisture at a time period of 20 hours and the third group absorbed moisture at a time period of 30 hours. All groups of specimens after the completion of the immersion time were taken immediately from the water and were wiped with paper. The wiped specimens were put into HDPE bags for protection from the outside environment. Each specimen group was subjected to tensile testing over a time period of about two weeks. Groups were divided into 10 to 12 different small groups which consisted 4 tensile test specimens. The first of these small groups of specimens were pulled immediately after absorption and then every day one specimen group was subjected to tensile testing. So at the end of each test period, between 11 to 13 different tensile test datas were obtained for only one material and one condition. This testing process was applied for both PA 6 and PA 66 materials which were conditioned into different small groups.

2.4 Effects of Moisture Absorption on Polymers

The moisture content affects many properties of plastics like mechanical strength, dimensions, electrical insulation resistance, dielectric losses, appearance etc... The effects of moisture content depend on exposure (by immersion in water or by exposure to high humidity), shape of part (thickness), structural properties of polymer (homogeneous or nonhomogeneous material), time of immersion or exposure and temperature (Hellerich, Harch, & Haenle, 1992).

The higher the temperature, the higher the humidity, the diffusion time and thinner part thickness. Also, homogeneous structures have higher moisture absorption (Hellerich, Harch, & Haenle, 1992). In Figure 2.16, saturation via part thickness graph is shown for the material nylon 6.

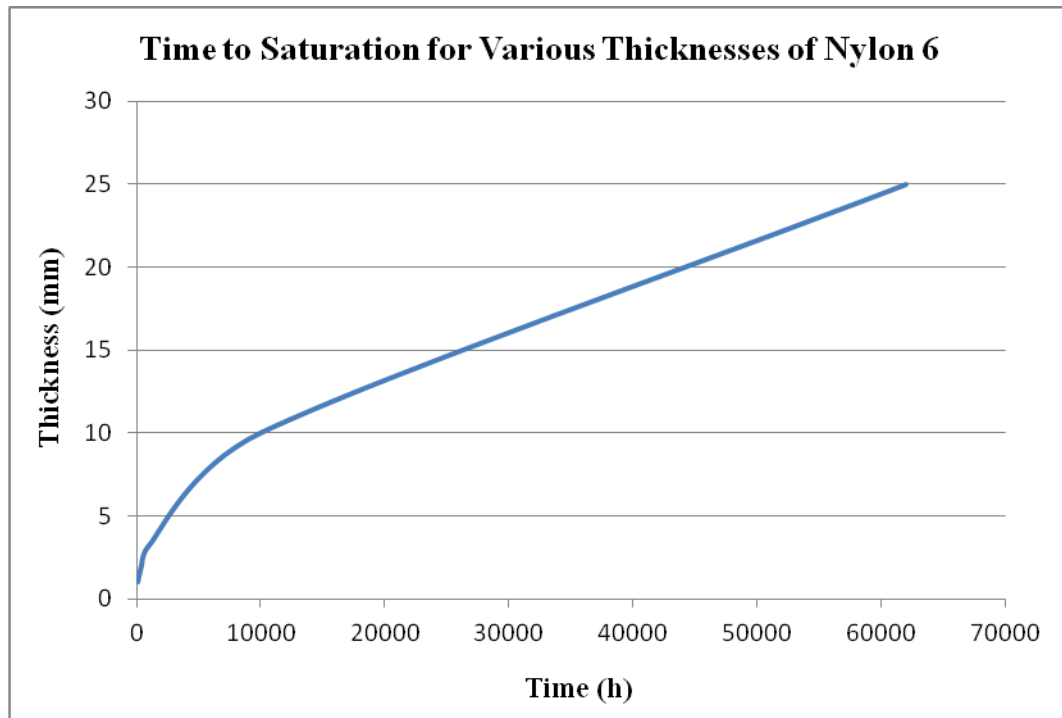


Figure 2.16 Time to saturation for various thicknesses of nylon 6

Moisture acts as a plasticizer in nylon (PA 6 and PA 66). Strength and stiffness reduces but toughness and elongation increases when the moisture content of polymer increase. Higher moisture levels improve the impact absorbtion ability and ductility.

If we exhibit the water absorbtion situation as a function of time for PA 6 and Pa 66 in atmospheric conditions of 23 °C and 50% relative humidity, we can get a graph like the one shown in Figure 2.17

In first 50 – 60 days the rate of moisture absorbtion is very high. On molded parts, firstly the surface starts to become saturate and it continuous with inner surfaces during which all body becomes saturated. After this point moisture content remains constant (Hellerich, Harch, & Haenle, 1992).

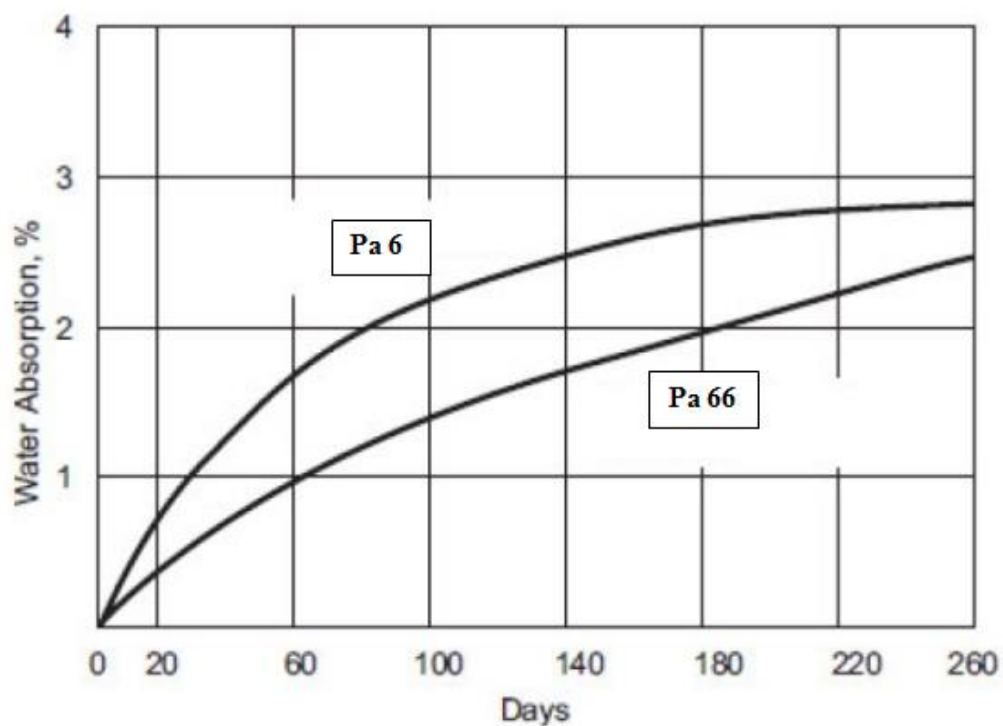


Figure 2.17 Water absorption of unreinforced PA 6 and PA 66 as a function of time

Absorbing moisture cause dimensional differences on PA 6 and PA 66. In Figure 2.18, the graph of linear expansion of unreinforced PA 6 and PA 66 as a function of water content at 23 °C are shown.

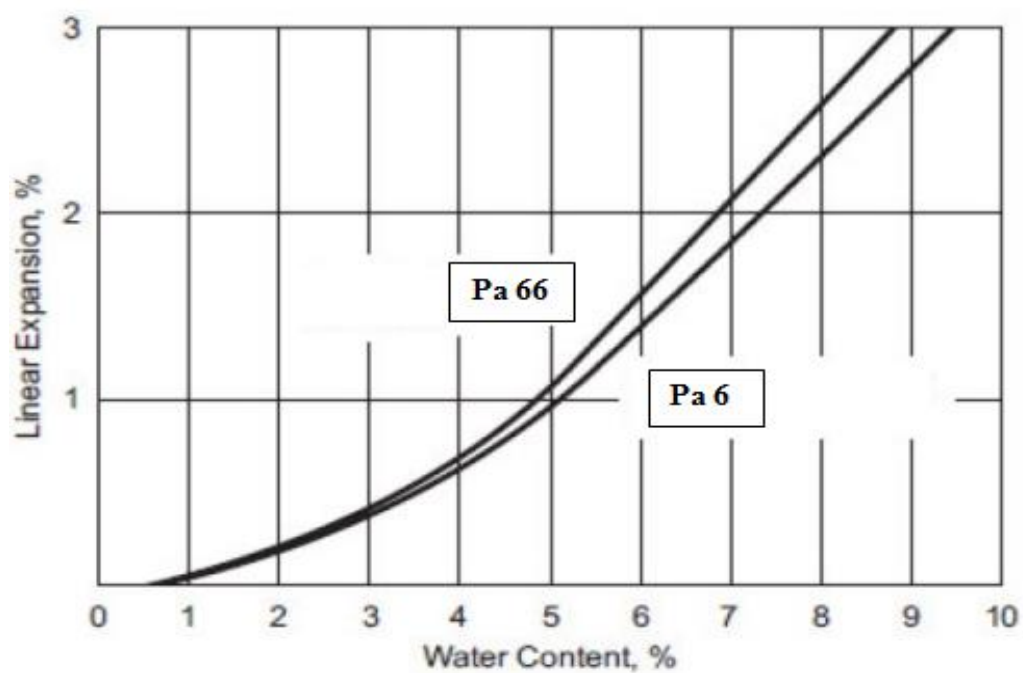


Figure 2.18 Linear expansion of unreinforced PA 6 and PA 66 as a function of water content

Moisture absorption depends on the structure of the polymer. Crystallinity decreases moisture absorption, therefore it decreases linear expansion and swelling.

The moisture content of a part can be measured by the calculation of weight gain. According to ASTM D 570, weight gains can be determined as

$$\text{increase in weight, \%} = \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100$$

When a part is produced, its weight is measured initially. The weight of the part is recorded for its dry state. After exposure to certain environment (immersion or exposure at water or air) the part is remeasured to determine the weight of the moistured body. The difference between the two values gives us the increase in weight. These kinds of tests give the designer an idea for product and the selected polymers reactions.

CHAPTER THREE

RESULTS

In this chapter the results of tensile tests are given. After testing procedure, the stress – strain graphs were drawn for evaluating the tensile behavior of PA 6 and PA 66 materials at different moisture levels. Each graph consist of one dried specimen and specimens at different moisture levels. Firstly, for both PA 6 and PA 66 materials, 10, 20 and 30 hours immersed specimens were compared within their own groups. And then for 1, 4, 7 and 10 days, the specimens were compared with each other for 10, 20 and 30 hours tests. The evaluation starts with the PA 6 materials as shown below.

3.1 Results of Pa 6 Specimens

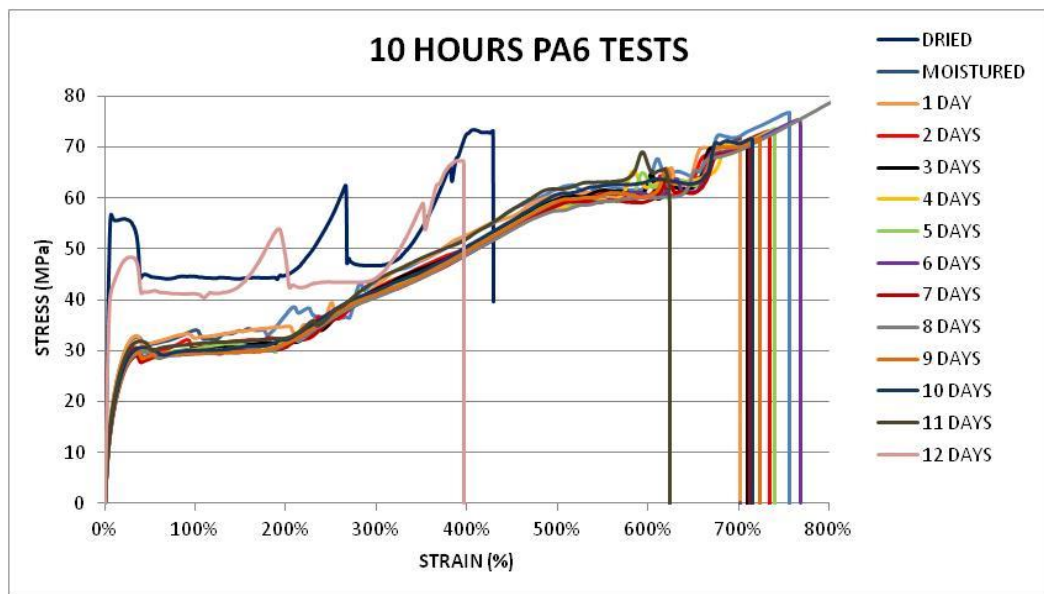


Figure 3.1 10 hours Pa 6 tests

The results of 10 hours immersion tests can be seen in Figure 3.1. For comparison the dried specimen graph was also added. This test procedure was ended 12 days after immersion, therefore 13 different test groups were handled for graphs. Each test group consists of four test specimens and one representative specimen which was the average of it's group was taken for these comparison graphs.

If we evaluate the results, firstly we can see that all specimens showed the same tendency. Their yield and ultimate strengths, as well as elongation rates changed with their testing time after immersion in water.

The dried sample's maximum elongation rate at break was between 400% to 450%. After moisturazing this value increased to a value between 700% to 800%. This situation has changed after about 10 days of moisturazing. The specimen groups 11 and 12 showed that the elongation rate at break dropped rapidly when comparison with the specimen groups before 11 days and the strain values started to approach the dried sample.

Same issue exists for yielding strengths. The dried sample showed a yield strength of about 55 – 60 MPa. After moisturazing this has decreased to a value between 27 to 33 MPa. After 10 days of moisturazing the yield strength started to approached to that of the dried sample. So if we continued the tests after 12 days, it's certain that the graph of samples would started to approach the dried sample and at the end when moisture levels decrease, the graph will be the same as the dried one.

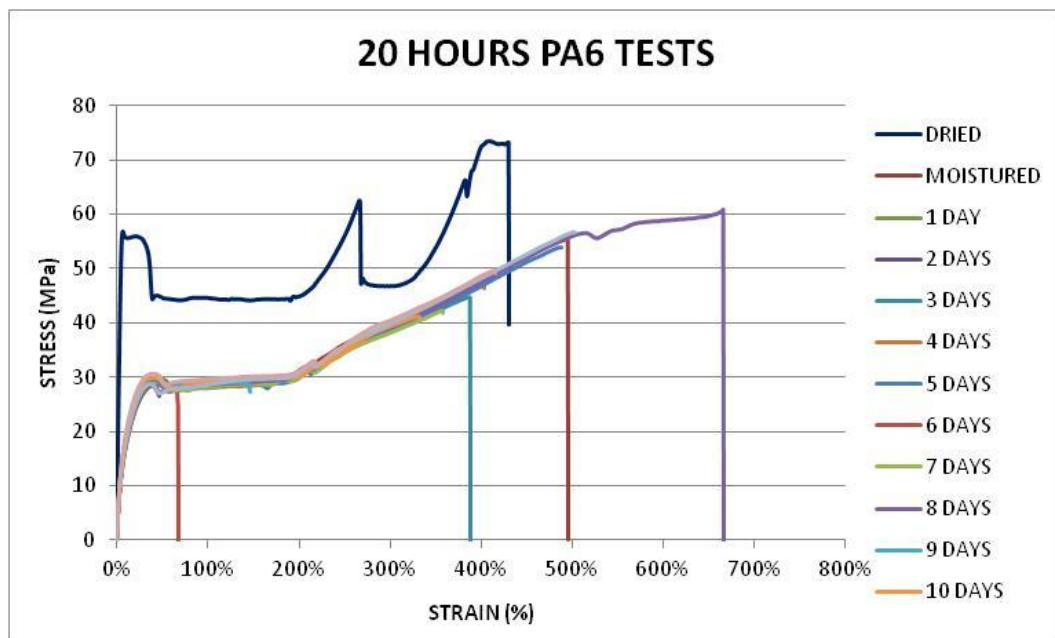


Figure 3.2 20 hours Pa 6 tests

If we seek 20 hours Pa 6 the graph will be like given in Figure 3.2. The same distribution exists for these tests as the 10 hours tests. Yield strengths of the specimens were between 27 to 31 MPa and tensile strengths had a maximum value of about 60 MPa. These values were less than the 10 hour specimen tests. The maximum strains at break were in the range from 400% to 680%. Similar to 10 hours tests, after 9 days of moisturizing, the specimens started to return their dried state. The approach of stress – strain properties can be seen in the figure.

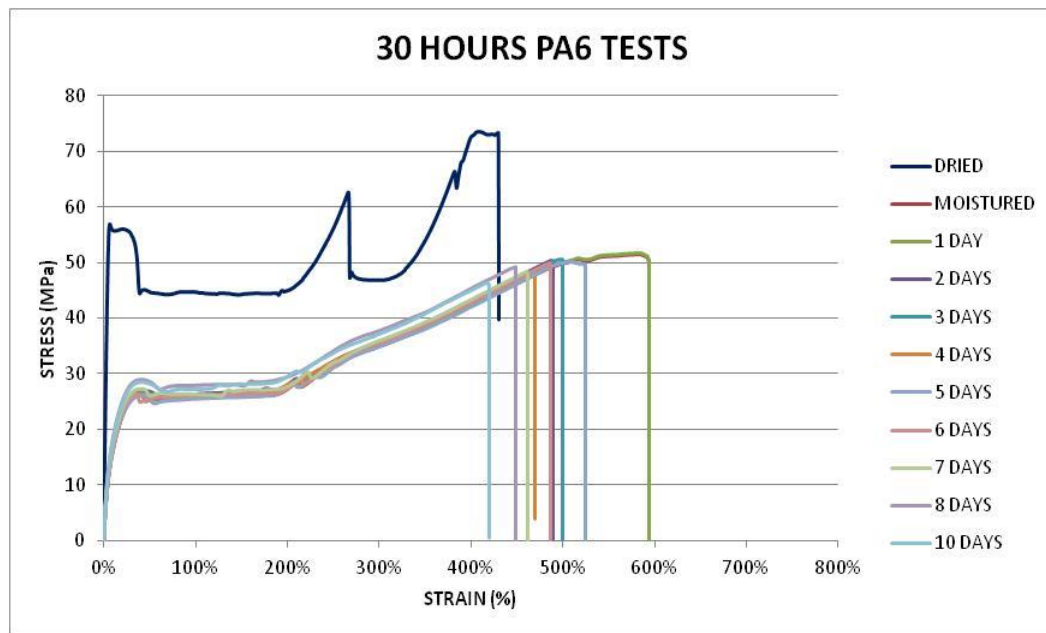


Figure 3.3 30 hours Pa 6 tests

After 30 hours PA 6 test graphs can be seen in Figure 3.3. In this test group 11 different specimen groups existed. The yield and tensile strength values were in their lowest levels when comparison with 10 and 20 hour test specimens. The yielding point ranged from 25 to 28 MPa and tensile strengths were about 50 MPa. The maximum strain at break ranged from 450% to 600%. Similar to other groups' tests, all specimens approximately follow the same path and maximum strain at break decreased with the decreasing of moisture level, in contrast to this situation the maximum stress at break and yield strength increased with the decreasing of moisture level.

We compared the moistured specimens and dried specimen stress – strain properties in their own conditioned status. The graphs of 1, 4, 7 and 10 day specimens which have both 10, 20 and 30 hours test condition status are compared with the dried specimens as shown below.

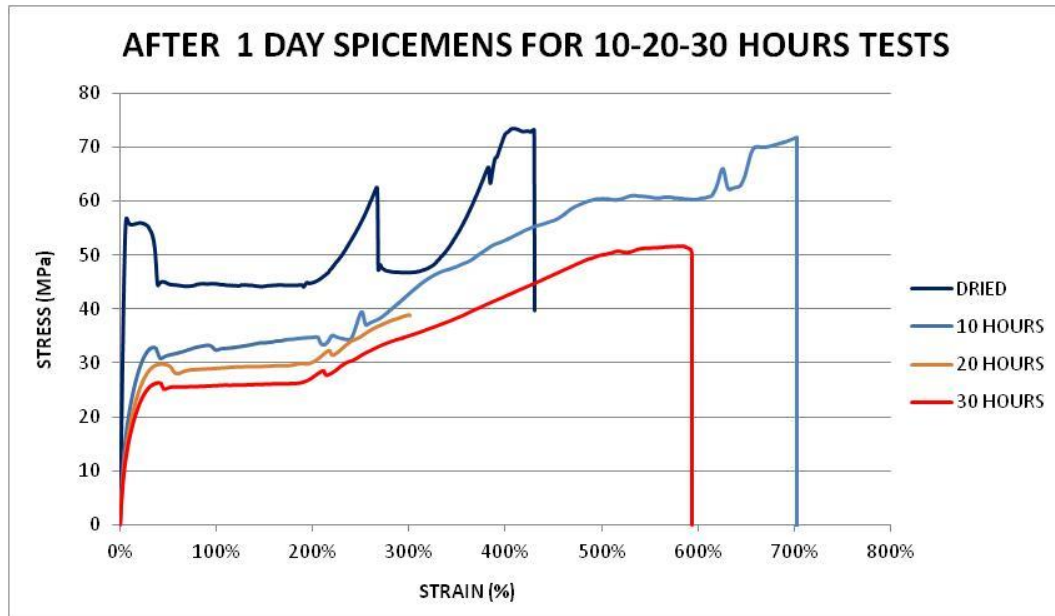


Figure 3.4 After 1 day specimens for 10 – 20 – 30 hours tests for Pa 6

The 1 day specimens for 10, 20 and 30 hours test graph are given in Figure 3.4. The strength of material decreased with increasing of moisture content. The dried sample had the maximum yield and tensile strength levels but minimum strain level.

The 4 days specimens for 10, 20 and 30 hours test graphs are seen in Figure 3.5. The same approach existed with 1 day specimen tests in this test group. The difference is, these test specimens were waited for 3 days more and this affected the graphs. The strain rates of 1 day specimens are higher than 4 days specimens and small differences can be seen at stress levels of specimens which are at the same conditions.

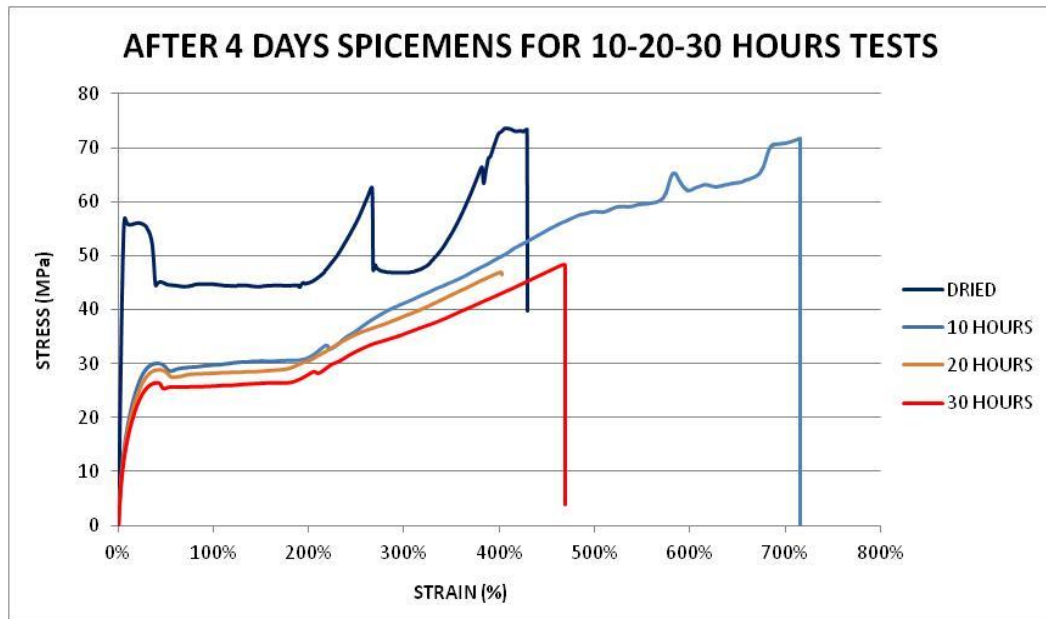


Figure 3.5 After 4 days specimens for 10 – 20 – 30 hours tests for Pa 6

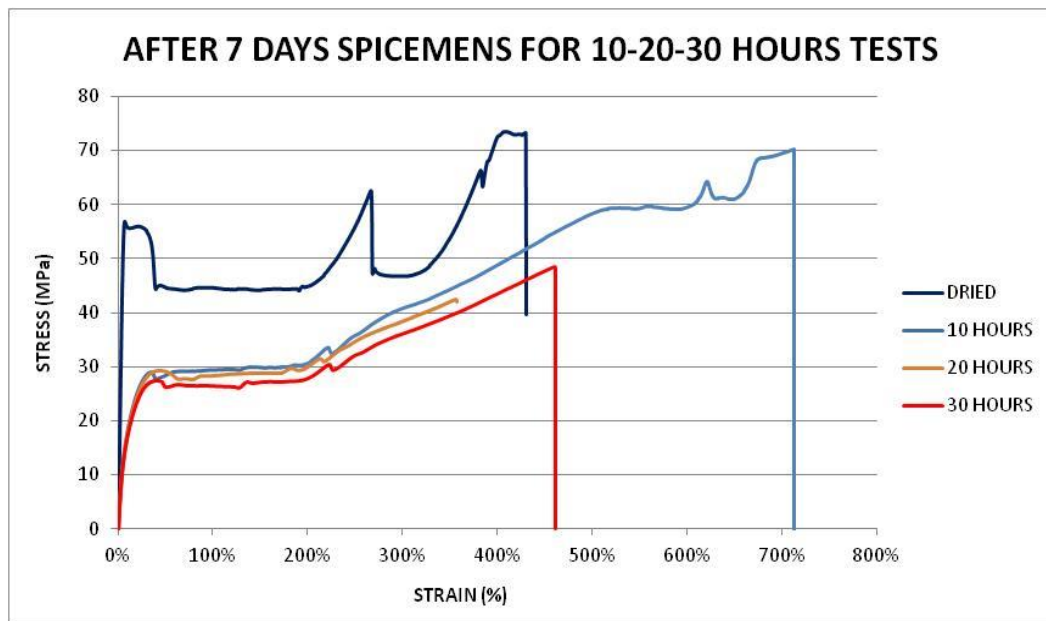


Figure 3.6 After 7 days specimens for 10 – 20 – 30 hours tests for Pa 6

The 7 days specimens for 10, 20 and 30 hours test graph are given in Figure 3.6. The yield strengths of specimens had a small increase in comparison with 4 day specimens and strain rates continued to reduce.

The results of Pa 66 materials are shown below, Figure 3.8. In this test procedure the same testing process like pa 6 test is applied. Three different conditioned material groups were subjected to tensile tests and stress – strain graphs were drawn.

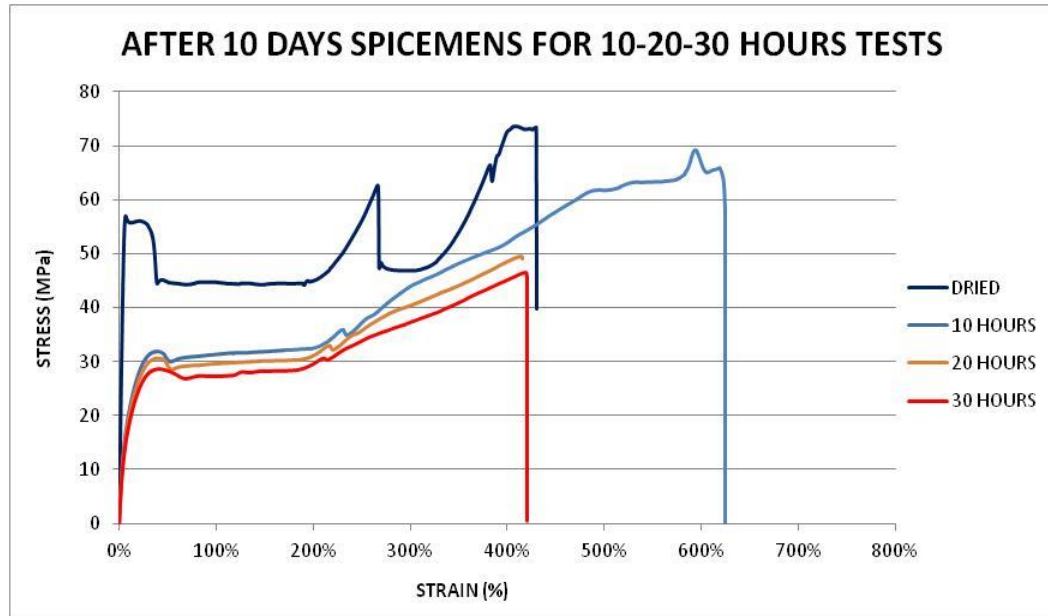


Figure 3.7 After 10 days specimens for 10 – 20 – 30 hours tests for Pa 6

3.2 Results of Pa 66 Specimens

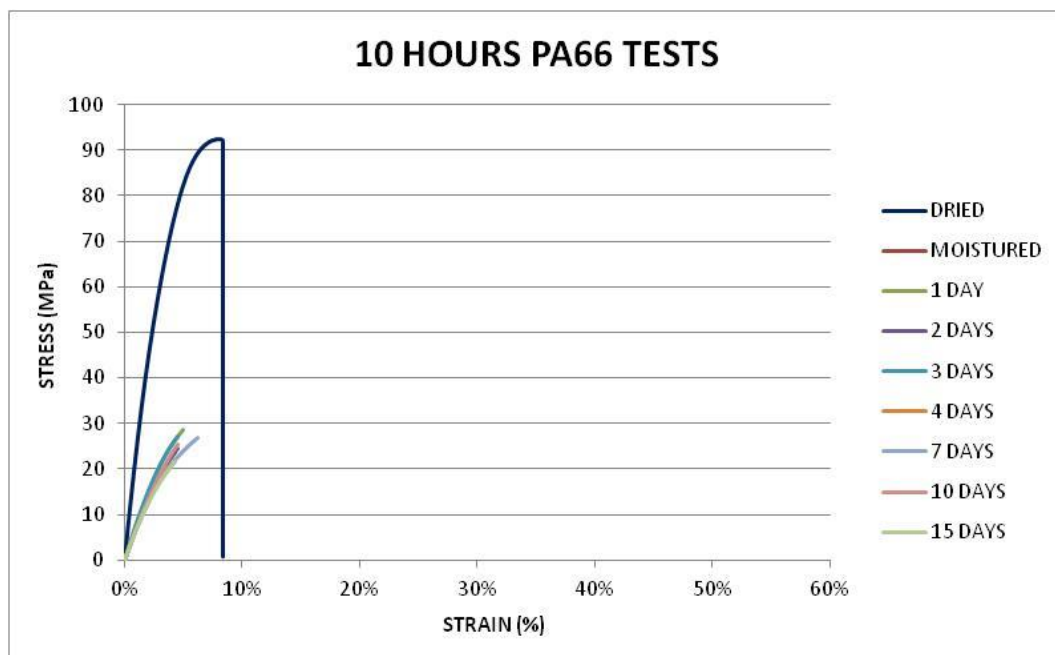


Figure 3.8 10 hours Pa 66 tests

The first test group, 10 hours Pa 66 tests, is seen in Figure 3.8. The values of dried and moistured samples were much different as seen. The difference in yield strengths were large and strain relations were inappropriate for comparison.

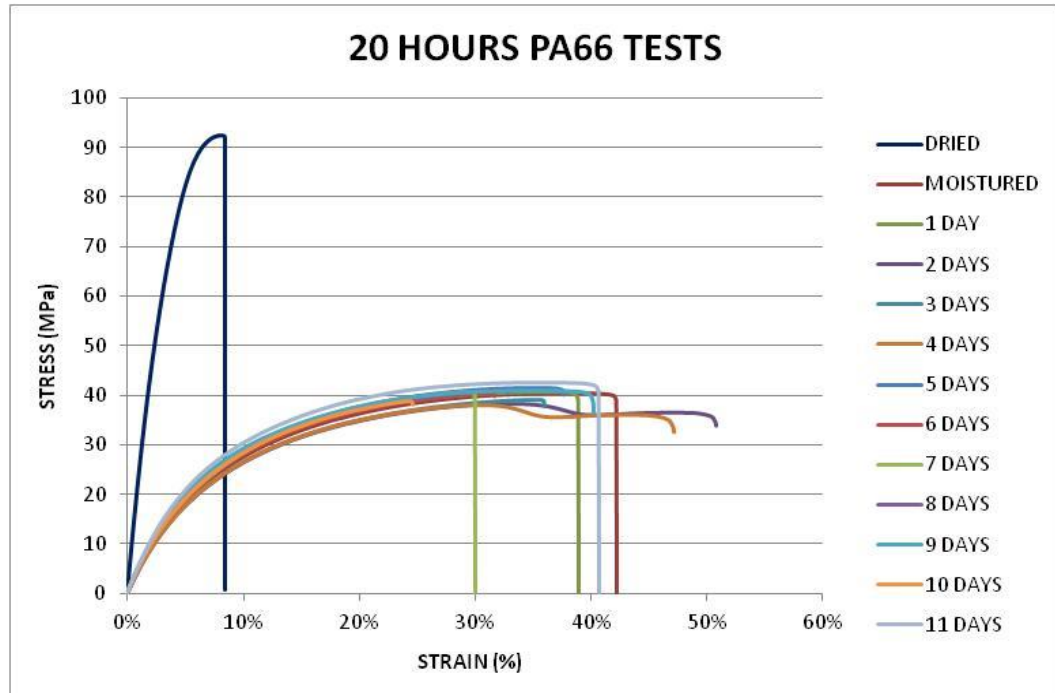


Figure 3.9 20 hours Pa 66 tests

20 hours PA 66 tests can be seen in Figure 3.9. In this test procedure, the strain rates were inappropriate with those of general tensile properties of PA 66 material. In general at the saturation state a strain rate of approximately 9% should be obtained. But in this test we found this value for moistured samples between 30% to 43%.

30 hours PA 66 tests are shown in Figure 3.10. In this test section, the strain rates were in agreement with those for Pa 66. After moisturizing, the strength of the material decreased and the strain rates were increased. At the end of testing time (day 8 and day 10) the specimens' stress – strain curves started to approach that of the dried sample. The strain rates started to reduce and the strength of the material started to increase.

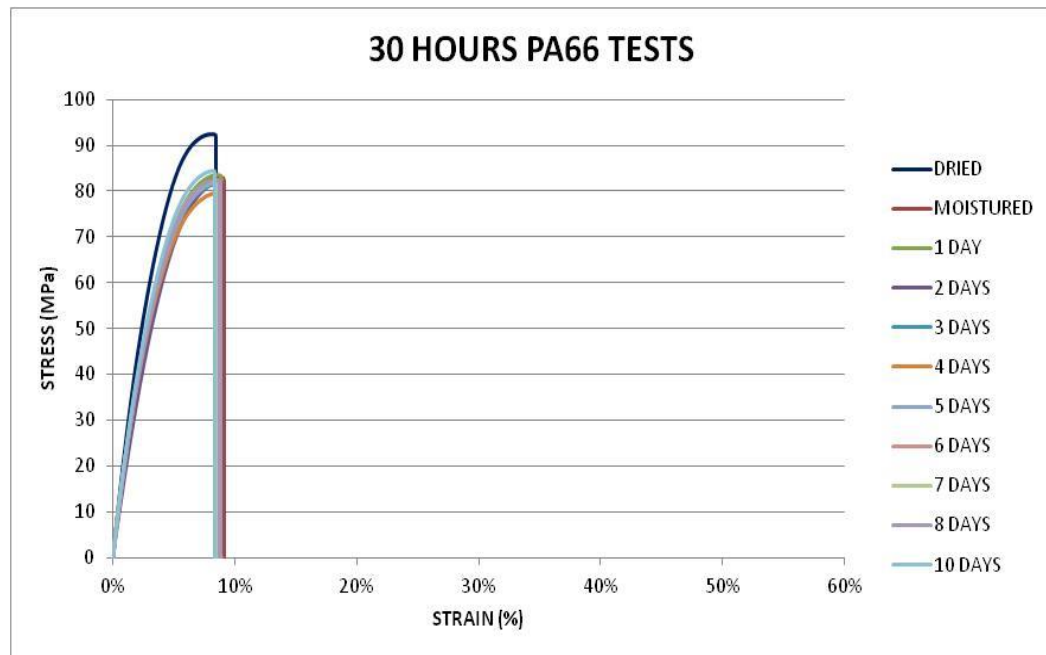


Figure 3.10 30 hours Pa 66 tests

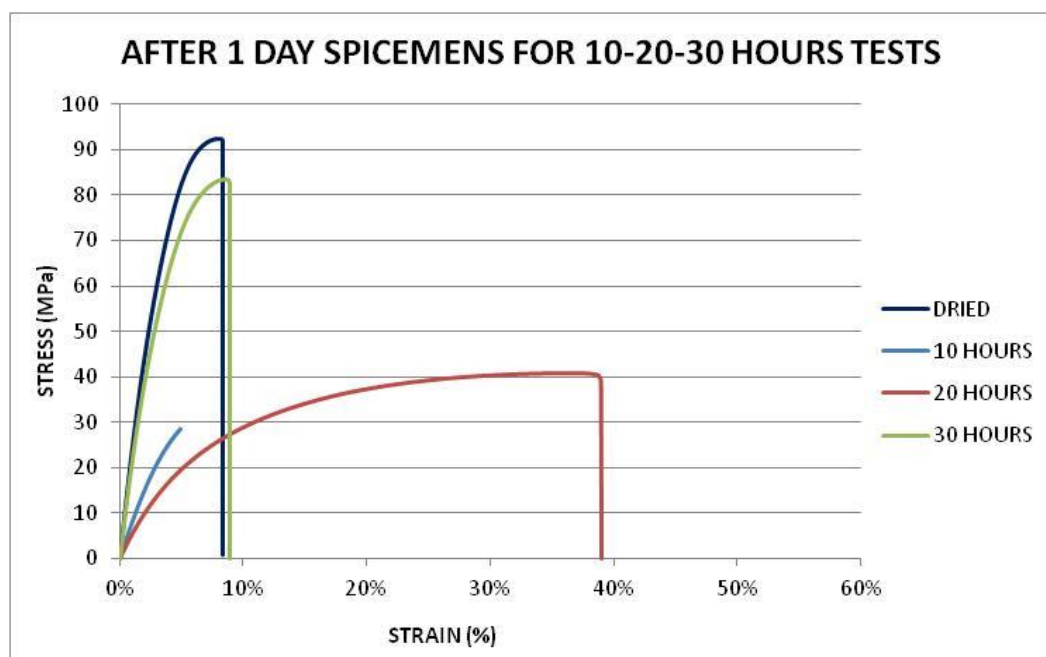


Figure 3.11 After 1 day specimens for 10 – 20 – 30 hours tests for Pa 66

After 1 day specimen tests, a comparison can be made as given in Figure 3.11. The great differences between 10, 20 and 30 hours test specimens can be seen easily by the help of this graph. Only the 30 hours test specimen curve was similar to the

dried sample. This great conflict might be caused by the differences between the manufacturing conditions of the test specimens.

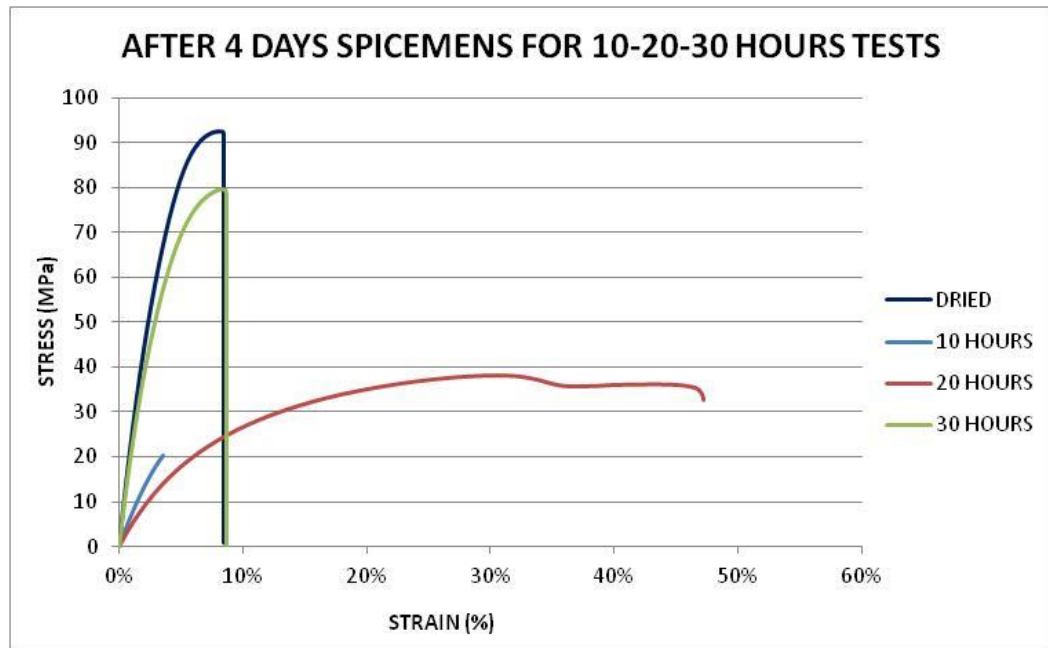


Figure 3.12 After 4 days specimens for 10 – 20 – 30 hours tests for Pa 66

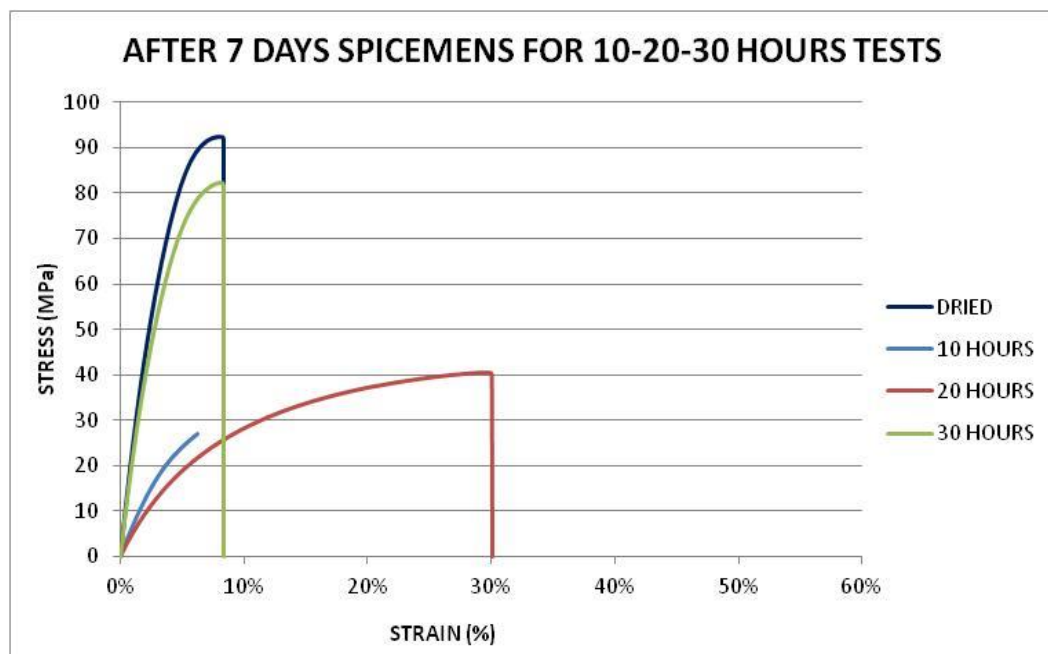


Figure 3.13 After 7 days specimens for 10 – 20 – 30 hours tests for Pa 66

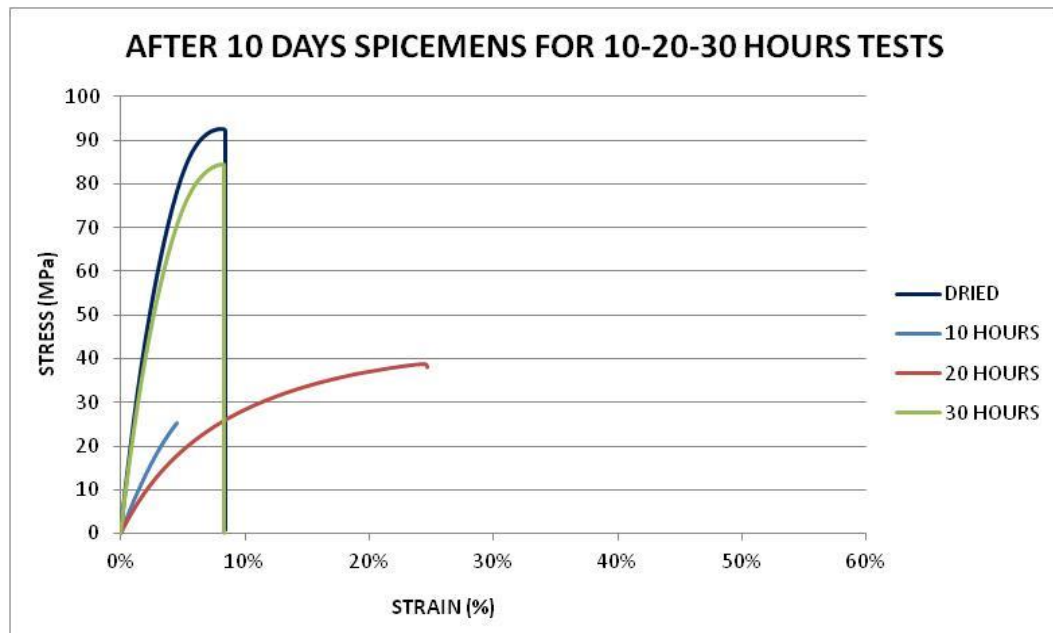


Figure 3.14 After 10 days specimens for 10 – 20 – 30 hours tests for Pa 66

In these tests great differences can be seen between test specimens which have different conditions. The reason of this difference might be differences production conditions. The samples of were produced in two different laboratories. One was Mazhar Zorlu Endüstri Meslek Lisesi and the other one a private plastic factory. The condition differences of specimens gave us unappropriate results. All groups were in harmony if we only investigate the results of one group of specimens individually. But when we started to look in general and compare the groups, the results were unsuitable.

The results of both PA 6 and PA 66 materials showed us that polyamide based materials properties are deeply affected by the moisture content. The part designer must employ appropriate production methods, storage of materials and environmental working conditions of products, if he/she aims to use polyamide materials.

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