THE EFFECT OF ANNEALING TEMPERATURE AND TIME ON MECHANICAL PROPERTIES OF CROSSLINKED POLYETHYLENE FILM

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BANAT RAID M. I.

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Prof. Dr. Tayfur Öztürk
Director

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

Prof. Dr. Erdal Bayramlı
Head of Department

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

Teoman Tinçer

Prof. Dr. Teoman Tinçer
Supervisor

Examining Committee Members

Prof. Dr. Kemal Alyürük (Chairman)
Prof. Dr. Leyla Aras
Assoc. Prof. Dr. H. İbrahim Ünal — H. İ. Ünal
Prof. Dr. Ali Usanmaz
Prof. Dr. Teoman Tinçer — Teoman Tinçer

ABSTRACT

THE EFFECT OF ANNEALING TEMPERATURE AND TIME ON MECHANICAL PROPERTIES OF CROSSLINKED POLYETHYLENE FILM

Banat Raid M. I.
Master thesis, Department of Chemistry
Supervisor: Prof. Dr. Teoman Tınçer

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During the last two decades the use of polyolefin pipe in different hot-water systems has increased considerably. Floor heating is the largest field of application.

The aim of the work is to evaluate the effect of annealing process on the mechanical properties of the crosslinked polyethylene films.

Crosslinked polyethylene film was prepared by extrusion process at two screw speeds 30 rpm and 45 rpm, in extruder attachment of Brabender Plastic-Corder. The mechanical properties of crosslinked polyethylene films extruded at 30 rpm and annealed at 70, 80 and 90°C for several periods of time 4, 6, 8, 10, 12 and 30 hours along the travel direction of processing and in the transverse direction were discussed in terms of annealing temperature and annealing time. Films extruded at 30 rpm had better mechanical properties than those extruded at 45 rpm when annealed at 90°C. Ultimate tensile strength of the polymer film annealed at 80°C increased when compared with annealing at 70°C and 90°C, while elongation at break increased as the annealing time increased in all annealing temperatures.

Annealing time increased the modulus and the highest values were found at the longest annealing time, 30 hours. Yield stress increased with annealing time especially after 12 hours of annealing and annealing temperature did not alter significantly. It was found that the yield strain of the polymer film annealed at 90°C higher than those annealed at 70°C and almost the same with that annealed at 80°C, but yield strain decreased with annealing time due to increase in gel content.

We found the annealing temperature of 80°C and the annealing time of 8 hours yielded better mechanical properties compared with those annealed at 70°C and 90°C at all annealing time.

Keywords: Crosslinked polyethylene, annealing time, and temperature, mechanical properties.

ÖZ

TAVLAMA SICAKLIĞININ VE SÜRESİNİN ÇAPRAZBAĞLI POLİETİLEN FİLMİNİN MEKANİK ÖZELLİKLERİNE ETKİSİ

Banat, Raid M. I.
Yüksek Lisans Tezi, Kimya Anabilim Dalı
Tez Yöneticisi: Prof. Dr. Teoman Tınçer

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Son 20-30 yıl içerisinde poliolefin boruların değişik sıcak-su sistemlerinde kullanılması, önemli ölçüde artmıştır.

Bu çalışmanın amacı, tavlama işleminin çapraz bağlı polietilen filmlerinin mekanik özelliklerine etkisini değerlendirmektir. Çaprazbağlı polietilen film, Brabender Plastic-Corder Extruder'inde, 30 ve 45 rpm vida hızlarıyla, ekstrüzyon işlemiyle hazırlanmıştır. 30 rpm'de ekstrüzyon ve 70, 80, 90°C'lerde 4,6,8,10,12 ve 30 saat süre periyotlarında tavlanan çaprazbağlı polietilen filmlerin mekanik özellikleri, hem işlem yönünde, hem de işlem yönüne dik olarak, tavlama sıcaklık ve süresi yönünden incelenmiştir. 30 rpm'de ekstrüzyon yapılan filmlerin mekanik özellikleri 45 rpm'de yapılandan, 90°C'de tavlamada daha iyidir.

80°C'de tavlanan polimer filminin kopma kuvveti, 70°C ve 90°C'de tavlananlarla karşılaştırıldığında artmıştır, fakat aynı zamanda kopma uzaması bütün tavlama sıcaklıkları için, tavlama süresi artttıkça fazlalaşmıştır.

Tavlama süresi modülü arttırmıştır ve en yüksek değer en uzun tavlama süresi olan 30 saat için bulunmuştur. Akma gerilimi, tavlama süresiyle özellikle 12 saatte yüksektir ve tavlama sıcaklığı akma gerilimini fazla değiştirmemiştir. 90°C'de tavlanan polimer filminin akma uzaması ve ona yakın olan 80°C'de tavlanan polimer filminin akma uzaması, 70°C'de tavlanandan daha yüksek bulunmuştur; fakat akma uzaması jel içeriği arttığı için tavlama süresiyle azalmıştır.

80°C'de 8 saat tavlama süresi, 70 ve 90°C'deki bütün tavlama süreleriyle karşılaştırıldığında daha iyi mekanik özellikler verdiği gözlenmiştir.

Anahtar Kelimeler: Çaprazbağlı polietilen, tavlama süresi ve sıcaklığı, mekanik özellikler.

TO THE BELOVED MEMORY OF MY PARENTS

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CHAPTER 1

INTRODUCTION

The mechanical properties of the polymer are of interest in all applications where polymers are used as structural materials. However, the prime consideration in determining the general utility of a polymer is its mechanical behavior. Four important qualities characterize the stress-strain behavior of a macromolecular compound: modulus, ultimate strength or tensile strength, ultimate elongation and elastic elongation. Polymers vary widely in their mechanical behavior depending on the degree of crystallinity, the degree of crosslinking and molecular mass. High strength and low extensibility are obtained in polymers by having high degrees of crystallinity or crosslinking, high elasticity and low strength in polymers are synonymous with a low degree of crosslinking and low degree of crystallinity. The temperature limits of utility of a polymer are governed by its crystalline T_m or T_g for amorphous polymer. Stress-strain performance of high polymers varies widely with sample history, changes in temperature and speed of deformation. Quenching, annealing temperature and time of annealing of the polymer melt are important steps on production line which play an important role in performing high product quality [1].

1.1 Polyethylene Types

Polyethylene is the largest produced plastic in the world. A wide variety of types and grades of polyethylenes are available commercially which share characteristics, such as low price, chemical inertness, and easy processing. The crystalline melting T_m decreases from 130°C to 110°C as the degree of crystallinity drops and the branching increases. The very low glass transition ($T_g \approx -110°C$) is associated with a good retention of mechanical properties, including flexibility and impact resistance at low temperatures.

The first method of production of polyethylene involved very high pressures and led to a highly branched polymer, with a correspondingly low crystallinity and low density (0.910-0.925 g/cm^3), known as low density polyethylene (LDPE). Another method was subsequently developed which required much lower pressures with special catalysts and led to much less branched, that is, linear polyethylene with higher crystallinity and density (0.941-0.965 g/cm^3), known as high density polyethylene (HDPE).

A new line of linear low density polyethylene (LLDPE) is now increasingly popular in which the equivalent branching is obtained by copolymerizing ethylene at low pressures and in presence of catalysts with small amounts of so-called α-olefin comonomers (butene, hexene, octene), which play the role of uniform short branches along a nearly linear backbone.

The last method can be used to obtain any density and affords a better control on the molecular architecture and the resulting semicrystalline morphology. Linear low density polyethylene (LLDPE), when compared to conventional low density polyethylene (LDPE), has better impact, tear, or puncture properties. It is possible to produce polyethylene of extremely (ultra) high molecular weight at least 10 times that of regular polyethylene, (3×10^6 - 6×10^6). The polymerization process lead to so-called linear molecules associated with high density (high crystallinity) polyethylene, although reported densities (0.93-0.94 g/cm^3) correspond to the usual medium crystallinity range. The molecular weight results in a high degree of physical entanglements that, above the melting point ($T_m \approx 130°C$), the material behaves in a rubber-like rather than fluid-like manner, the longer the chain the more opportunities there are for more entanglements, leading to higher strength. But the entanglement persist when the material is melted, and the higher viscosity makes it more difficult to shape the melt [2], causing considerable processing difficulties. Ultra high molecular weight polyethylene has a certain outstanding properties that probably qualify it as an engineering plastic, its chemical inertness is almost unmatched, and abrasion resistance, impact resistance (toughness) and fatigue resistance are important to mention [3].

1.1.1 High Density Polyethylene

The mechanical properties of high density polyethylene (HDPE) due to its high crystallinity and linearity permit its use as both a plastic and fiber. From structural viewpoint, this polymeric hydrocarbon like all other polyethylenes appears to be the least complex of all polymers, because of its structural regularity and lack of pendant groups. HDPE has fewer than 7 ethyl groups per 1000 carbon atoms. It has a relatively high specific gravity, around 0.96 g/cm^3. The specific gravity of a perfect single crystal of HDPE is assumed to be 1.0 g/cm^3.

Commercial HDPE is soluble in hot xylene, but this highly crystalline polymer is insoluble in most solvents at room temperature. The index of refraction of amorphous HDPE is 1.49, but that of high crystalline HDPE is greater than 1.52.

Although low-molecular-weight HDPE is apparently brittle, but increasing the molecular weight, polymer becomes ductile and at extremely high molecular weights HDPE gains an outstanding resistance to impact and abrasion. Since the intermolecular forces present in the nonpolar polyethylene molecules are weak dispersion (London) forces, the modulus and tensile strength of HDPE are relatively low [4, 5]. However, upon uniaxial orientation of HDPE one can obtain high modulus and high strength fiber and films, such as solution drawn ultra high molecular weight polyethylene (UHMWPE) has modulus of around 100-200 GPa.

1.2 Crosslinking

Thermosets owe their high tensile modulus, tensile strength and creep resistance to their fixed three dimensional structure caused by chemical crosslinking. Thermosets are polymers as shaped into the final product undergo a second chemical reaction in the presence of proper chemicals in which a continuation of heat and pressure causes strong chemical bonds to link the polymer molecules. Once these crosslinks have formed the material will not flow again.

Apart from crosslinking by the application of heat and pressure, radiation induced crosslinking by gamma radiation or electron beam irradiation has become more popular [6].

1.2.1 Crosslinked Polyethylene

The linear structure of thermoplastic polyethylenes of low density, linear low density and high density polyethylene (LDPE, LLDPE and HDPE) can be altered by three dimensional network upon crosslinking. Creep strength, low temperature impact strength and resistance to stress cracking are raised considerably. Crosslinked polyethylene does not melt but softens like an elastomer. It can, therefore, undergo heavily thermal stressed (90°C) for long periods (50 years) and very heavily (110°C) for a short time (2-years) [23].

Crosslinking in polyethylene can be achieved in several ways. The most important method, in practice, is by using peroxides (e.g. dicumyl peroxide: $[\ C_6H_5C(CH_3)_2\ ]_2\ O_2$). Peroxide is decomposed at elevated temperatures and oxy radicals are formed. The oxy radicals abstract hydrogen from polymer molecules and the polymer radicals combine to form a molecular network. Some side reactions are possible: e.g. disproportionations leading to molecular scission and the formation of the molecular branches [7, 8].

Crosslinking can also be carried out using a down stream source of high energy radiation (electron accelerator or isotopes, i.e. beta or gamma rays). Irradiation of polyethylene (PE) can also cause both oxidative degradation and chain scission together and crosslinking, the kinetics of the first process were controlled by diffusion of atmospheric oxygen into the bulk of the material. Another important parameter in these processes is the temperature, which can affect the diffusion coefficients of gases and the mobility of free radicals produced by gamma radiation [9, 10, 11, 12]. Degradation phenomena are significantly affected by atmospheric oxygen diffusion which increasing degradation on decreasing dose rate at the same temperature e.g. 25°C and 50°C, due to oxygen diffusion into the bulk of the material and oxidative degradation become more significant. At high dose rates the oxidation is limited to the external layers of the samples whereas in the bulk the prevailing effect is crosslinking [9, 13, 14]. Physical crosslinking remains less important than peroxide cross-linking because of high plant and operational costs.

Silane offers a third method of crosslinking. Polyethylene silanated by grafting forms (Si-O) crosslinkages on subsequent treatment in water bath. A two-step process for the crosslinking of polyethylene (PE) using an organic silane compound was introduced by Dow Corning in 1967. Vinyl silane is initially grafted onto the polyethylene chains. The actual crosslinking occurs at relatively low temperatures, lower than 100°C, and requires the presence of water and a tin catalyst. The silane groups are hydrolyzed in the presence of water. Crosslinking occurs by a condensation reaction of the hydroxysilane groups [5, 6, 15].

1.3 Mechanical Properties

Mechanical properties are the measure of the response of materials to external mechanical influences manifested in the ability of the bodies to develop reversible and irreversible deformations and to resist failure. The basic characteristics of mechanical properties of solids are usually determined by tests resulting in various deformations upon stress dependencies, such as stress-strain diagrams [2, 16].

When a polymer is used as a structural material, it is important that it is capable of withstanding applied stress and resultant strains over its useful service life. Polymers are viscoelastic materials, having the properties of solids and viscous liquids. These properties are time and temperature dependent. Thus, the effects of the rate of application of stress and the ambient temperature must be recognized when polymers are used as structural materials.

Numerous factors effect various mechanical properties of polymers, including molecular weight, processing, extent and distribution of crystallinity, composition of polymer, and use temperature. Most thermoplastic material have high molecular weights, so moderate changes in molecular weight do not appreciably influence mechanical properties such as yield stress, or modulus. Even so rupture properties such as ultimate elongation, impact strength, and ultimate strength are effected by high molecular weight increase, since longer chains are more likely to act as connectors between crystalline areas, allowing greater toughness. The modulus or stiffness of a polymer is also a function of intermolecular forces, however, modulus increases as the crosslink density of network polymer is increased. Crosslinking connects the chains, thus preventing slippage of the polymer molecules over each other, therefore crosslinked polyethylene (XLPE) display a much higher time to failure than the non-crosslinked one [17].

In general, the degree of crosslinking determines also the solubility, extent of swelling, free volume, and mechanical stability of the polymer. Tensile strength of crosslinked polymers is greater than those of uncrosslinked polymers, the enhancement in tensile strength is most likely due to higher level of mixing [18]. Crystalline and filled polymers resemble polymers with low crosslink density at temperature below the melting temperature T_m [5].

Tensile properties are most widely used for defining both the quality of production lots of polymeric materials and their design and engineering behavior. Tensile properties may also be used indirectly to measure other properties of a material for which a correlation exists. For example, a plastic film having high tensile strength and elongation in all directions will probably also have high impact strength, and measurement of tensile properties will correlate well with measurement of impact strength on such an item.

Tensile properties may be used to monitor or follow the progress of chemical or physical changes taking place in the polymer. For example, polymer exposed to high heat or ultraviolet light may undergo depolymerization and oxidation reactions which will be reflected in changes in tensile properties. In a similar manner, when polymers are exposed to an aggressive chemical environment, they may become either more brittle or less brittle, and the changes can be conveniently followed through measurement of tensile properties [19].

1.4 Pipe Properties

Among the properties of polyethylene that make it an excellent pipe material are flexibility, high strength-to-weight ratio, and chemical inertness. As a result, polyethylene pipe is light weight, coilable and quite resistant to corrosive environment. Its excellent low-temperature properties and toughness make it resistant to rupture from mechanical shock and from abrupt changes in operating pressures [20]. Polyethylene pipe can generally be used for continuos service at temperatures between (- 40°C) and (+ 120°C) depending on the type and grade [21].

During the last several decades the use of polyolefin pipes in different hot-water system has increased considerably. Originally, floor heating was the largest field of application, but today, polyolefin pipes are also utilized for district heating and tap water plumbing. However, the demands on acceptable long term durability are extensive. The current requirement for service life of a hot-water polyolefin pipe is 50 years [22]. The use of crosslinked polyethylene has experienced a growth in a variety of applications, e.g. in insulation in medium and high voltage cables and in pipes for domestic low temperature heat-distribution systems [23].

The variation of mechanical properties with percentage thickness reduction of flow-formed polyethylene pipe has been studied [24].The stress-strain behavior of the pipe exhibited more tensile strength as percentage reduction increased, due to structural changes from the spherulitic to fibrillar structure. Using extrusion aid recently, a common organic lubricant, will insure uniformity of mechanical properties, such as flexibility in different sections of the pipe [25]. The limited lifetime of polyolefins in hot-water applications is an important problem that has been studied empirically for many years [26, 27, 28].

It is well recognized that physical migration and chemical consumption of antioxidant determine the ability of antioxidant systems to protect polymers effectively against thermal oxidation. Once the antioxidant has been depleted oxidation becomes autocatalytic, and the material lifetime is severely limited [29]. Several studies have also been performed concerning antioxidant loss from hot water pipes [22]. Pipes exposed to an external environment of water are less affected by oxidation process than pipes surrounded by air [30]. In both crosslinked polyethylene (XLPE) and medium density polyethylene (MDPE) the main oxidation processes occur near the inner wall surface in contact with water. Gedde and Ifwarson [22] suggested that the oxidation process is greatly accelerated by antioxidant extraction into the water phase, and is also dependent on the rate of oxygen diffusion in the pipe wall [30].

Internally pressurized crosslinked polyethylene pipes fail according to chemical degradation, shows highly degraded brown spots (oxidation spots). The puncture fracture occurred in one of these spots, oxidative degradation of the amorphous chain segments including scission of entangled chains and interlamellar tie chains. The latter is the main reason for the major reduction in strength of the aged pipe leading to the pipe failure [22, 23, 30].

1.5 The Aim of The Study

Polyethylene heating pipes crosslinked chemically or radiolytically are used for many applications, mainly home heating and transport of hot water. In this study, we aimed to study the variation of mechanical properties (measured along the processing direction and in transverse direction) and thermal properties (melting point) with respect to crosslinked density and annealing temperatures and time in chemically crosslinked high density polyethylene. In addition to that we aimed to optimize mechanical properties at various production conditions.

CHAPTER 2

EXPERIMENTAL

2.1 Material Used

The granular high density polyethylene ready for crosslinking chemically under thermal process used as provided by supplier company (BOREALIS). The nature and type of crosslinking agent was kept under the License of the company. Therefore, all components are supplied as finished products.

2.2 Primarily Pipe Characterization

Original heating pipe samples as received from producing plant have the following dimensions: The outside diameter 16 mm, inside diameter 13.3 mm, thickness 2.7 mm.

Gel content of the inner and outer parts of the pipe was determined for the original heating pipe sample. Mechanical properties were carried out at different pipe sectors, along travel direction, transverse, circular, and 45° directions. Average value out of 6 test results was reported.

Heating pipe samples were annealed in both water and air at 95°C, for different periods of time: 24, 48, 72 and 96 hours. Melting points of the aged samples (5 mg) were carried out using (Perkin Elmer Model -4-DSC instrument).

2.3 Sample Preparation

Polymer films were prepared by using the Brabender Plastic-Corder, Model PLV 151, and extruder attachment, Model 8251 and 8266, type 25 D. The measuring extruder is attached to the Brabender Plastic-Corder by a shear pin coupling. Extrusion process was carried out at typical processing temperature in °C as in Table 2.1.

Table 2. 1. Extruder's zones of a typical processing temperatures of crosslinked polyethylene.

Zone	**Temperature (°C)**
Feed	160
Compression	170
Neck Metering	220
Die	250

Extrudate was passed through water bath to cool it. Screw rotation speeds in use were 30 rpm and 45 rpm.

2.4 Annealing Process

Long film obtained from extruder was cut off into one-meter-long films. These were annealed in water bath at 70°C, 80°C, and 90°C, separately. The following annealing periods were carried out; 4, 6, 8, 10 and 12 hours.

2.5 Mechanical Properties

The most common type of stress-strain measurement is made in tension, that is by stretching the material. A tensile stress is thus applied, defined for a section of uniform cross-section area, A_0 by the formula

$$\sigma_1 = F_1 / A_0$$

where σ_1 and F_1 are tensile stress and tensile force respectively.

If this tensile stress induces a stretch to length L_1, then the tensile strain ε_1 is defined as:

$$\varepsilon_1 = \frac{L_1 - L_0}{L_0}$$

Taking the stressing operation to the ultimate, that is increasing the force until the material breaks, tensile strength (ultimate tensile stress).

$$\sigma = F / A$$

where F and A are the force at failure and area of cross-section at failure respectively. As the material stretches so its dimensions orthogonal to the axis of applied force will decrease and thus the area of cross-section will decrease. However, for experimental convenience, most tensile strengths are based on the original cross-section (A_0) since this is easily measured, before the test is started. Ultimate elongation, or elongation at break, equals ($L-L_0$) where L is the length at failure. This is usually expressed as a percentage of the original length, i.e.

$$\frac{L - L_0}{L_0} \times 100\% \text{ [31, 32].}$$

Annealed films were cut off using standard dumb-bell shaped die for mechanical tests. The thickness of each specimen was measured by micrometer and recorded before mechanical tests. Annealed specimens were drawn at room temperature, by using Instron Tensile Testing Machine (Model TM 1102),with cross-head speed 5 cm/min., to determine ultimate properties. Initial gage length of specimens along travel direction of processing was 3.5 cm and for transverse direction of processing was 2.5 cm. For elastic modulus measurements, cross-head speed was adjusted at 0.65 cm/min. At least three test results were reported and the average of these tests were calculated.

2.6 Gel Content Determination

Crosslinked samples were extracted in hot xylene for (24 hr.) in soxhlet apparatus as described elsewhere [33]. Prepared samples were placed in perforated thin cylindrical glass tubes were closed with filter paper tightly to prevent escape of crosslinked high density polyethylene sample from tubes. After extraction samples dried to a constant weight and at least average of three tests was reported for the gel content.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1 Primary Characterization of The Heating Pipe

The mechanical properties of the crosslinked polyethylene heating pipe, as received from the producing company, were carried out in our laboratory and shown in Table 3. 1. These pipes were annealed at 95°C in air and hot water bath for 24, 48, 72 and 96 hours in our laboratory according to the prescription of polyethylene supplier company. The tensile strength and yield stress in hoop and in angular (45°) directions have larger values than those along travel direction of the pipe. Elongation at break along travel direction showed to have higher values than those in hoop and angular directions, thus the pipe exhibited acceptable performance even after testing over a long period of time.

The melting points of the heating pipe upon annealing at 95°C were shown in Table 3. 2. We observed slight changes in melting points with overall average around 129°C (This will be discussed later in terms of variation of gel content). Both low density polyethylene and high density polyethylene remain relatively stable until the temperature reaches their respective melting points, beyond that range, deformation resistance is greatly reduced with every marginal increase in temperature. Crosslinked polyethylene, on other hand, does not significantly deform even after the temperature exceeds the melting point of its base resin.

Table 3. 1. Mechanical properties of different pipe sectors as received without annealing.

Pipe sector description	Yield stress (MPa)	Elongation at yield (%)	Tensile stress (MPa)	Elongation at break (%)
Along processing direction	25.0 ± 0.9	9.0 ± 0.8	22.9 ± 0.5	209 ± 26
Circular section	44.8 ± 1.2	* 71.0 ± 4.4	39.0 ± 2.0	114 ± 16
Angular section 45°	47.0 ± 4.3	* 88.0 ± 2.8	35.0 ± 2.0	142 ± 13

*These values correspond to the specimen shape.

Table 3. 2. Melting points in °C, after annealing in oven (air) and water bath at 95°C.

Annealing Medium	Annealing time, hr.	Melting point, °C
Air, at 95°C	24	128.8
	48	130.8
	72	130.0
	96	128.0
Water, at 95°C	24	130.3
	48	128.4
	72	128.0
	96	129.0

3.2 Characterization of crosslinked polyethylene films with respect to annealing temperature and time of annealing.

3.2.1 Variation of Gel Content

The gel content of the annealed polymer films at 70, 80 and 90°C at several periods of time was given in Table 3. 3. We observed a general trend of increasing gel content with increasing annealing time due to increase probability of the free radicals to form more crosslinks. However, gel content with respect to annealing temperature decreased upon increasing annealing temperature at a given time period. The gel content almost remained the same for 70°C and 80°C but gel content was found to decrease at 90°C annealing possibly due to degradation which was assumed to be taken place at a certain extent at high annealing temperature, further more the high mobility of the polymer chains at high annealing temperature decreased the probability to form more crosslinks especially at low annealing time.

The crosslinked density of the polymer film and the heating pipe as received from the company without annealing was determined 78.0 ± 2.0 and 67.5 ± 0.4 respectively. We observed that the annealed samples had lower crosslinked density than the unannealed samples. The relaxation of the oriented polymer chains took place after extrusion upon annealing. During the initial annealing process, the relaxation of the stressed chains in the extruded samples might end with possible chain breakage hence decreasing the gel content. Further annealing, however, resulted in slow increase in crosslinking. This process should result in localized stress free material which could be used in service life. Otherwise, unannealed samples still having such stress concentrators may not reflect the final performance of the end product during the use life resulted from the increase of the crosslinked density.

Table 3. 3. Gel content of crosslinked polyethylene film annealed at 70, 80 and 90°C at several periods of time.

Annealing time, hr.	**70°C**	**80°C**	**90°C**
4	71.0 ± 0.9	73.0 ± 1.0	52.8 ± 1.2
6	72.3 ± 4.0	69.4 ± 3.1	57.0 ± 1.8
8	77.2 ± 3.0	68.6 ± 2.0	68.6 ± 2.1
10	70.0 ± 3.0	69.5 ± 3.5	61.6 ± 0.9
12	71.5 ± 1.0	65.2 ± 2.1	70.0 ± 0.5
30	71.1 ± 1.7	65.0 ± 1.1	71.0 ± 1.5

3.2.2 Mechanical properties of two screw speeds

The results of the mechanical properties of the polymer films extruded at two screw speeds at 30 rpm and 45 rpm were compared, the former observed to have higher mechanical properties as shown in Table 3. 4. and 3. 5. and Figures 1-5. Because of the high level of mixing and orientation of the polymer melt in metering zone in addition to orientation of the polymer film after leaving the die along the cool water bath.

The same trend could be seen at both screw speeds 30 rpm and 45 rpm in transverse direction, i.e. lower values of the mechanical properties at 45 rpm.

Figures 1-5 show the various mechanical properties: tensile strength, elongation at the break, modulus, yield stress and elongation at yield, of the polymer films annealed at 90°C, we observed a critical time of 6 hours to be the optimal time of annealing, i.e. the effects of physical aging diminish after a critical aging time which give indication for reaching the equilibrium state at this time of annealing.

Table 3. 4. Mechanical properties of crosslinked polyethylene films extruded at 30 rpm and 45 rpm, along and transverse direction of processing, and annealed at 90°C in water bath.

Sample description	Annealing time (hr.)	Tensile strength (MPa)	Elongation at break (%)	Modulus (GPa)
Along travel direction 30 rpm.	0	37.5 ± 0.6	659 ± 26	0.521 ± 0.002
	4	33.2 ± 0.0	625 ± 71	0.558 ± 0.002
	6	32.8 ± 1.2	865 ± 10	0.555 ± 0.001
	8	28.9 ± 1.2	536 ± 18	0.529 ± 0.008
	10	30.3 ± 1.8	609 ± 54	0.547 ± 0.009
Transverse direction 30 rpm.	0	25.8 ± 4.6	857 ± 60	0.394 ± 0.002
	4	26.6 ± 2.0	863 ± 40	0.460 ± 0.004
	6	20.4 ± 3.0	683 ± 10	0.417 ± 0.002
	8	27.6 ± 1.0	925 ± 31	0.446 ± 0.007
	10	23.0 ± 2.0	785 ± 49	0.468 ± 0.006
Along travel direction 45 rpm.	0	30.0 ± 2.6	415 ± 82	0.366 ± 0.005
	4	24.3 ± 2.5	276 ± 45	0.347 ± 0.003
	6	27.5 ± 5.1	302 ± 75	0.390 ± 0.001
	8	23.8 ± 4.7	254 ± 56	0.316 ± 0.003
	10	19.3 ± 1.7	238 ± 20	0.318 ± 0.001
Transverse direction 45 rpm.	0	23.3 ± 3.4	334 ± 55	0.441 ± 0.004
	4	16.8 ± 0.4	67 ± 30	0.362 ± 0.003
	6	17.6 ± 0.5	141 ± 16	0.345 ± 0.005
	8	17.0 ± 0.6	74 ± 56	0.342 ± 0.004
	10	17.4 ± 0.3	103 ± 33	0.304 ± 0.004

Table 3. 5. Yield stress and elongation at yield of crosslinked polyethylene films, extruded at 30 rpm and 45 rpm, along and transverse direction of travel, and annealed at 90°C in water bath.

Sample description Time (hours)	Yield stress MPa	Elongation at yield %
Along travel direction. 30 rpm.0	19.7 ± 1.0	9.5 ± 0.8
4	23.2 ± 1.6	10.2 ± 1.4
6	22.4 ± 0.3	11.0 ± 1.7
8	21.3 ± 0.4	10.5 ± 2.2
10	22.5 ± 0.5	8.6 ± 0.0
45 rpm. 0	21.4 ± 0.8	10.9 ± 1.6
4	20.8 ± 0.8	9.0 ± 0.8
6	21.8 ± 0.2	9.4 ± 1.4
8	22.4 ± 1.3	8.6 ± 0.0
10	19.6 ± 0.7	9.4 ± 1.4
Transverse direction. 30 rpm.0	19.4 ± 1.0	14.0 ± 1.7
4	17.4 ± 1.0	7.0 ± 0.0
6	17.8 ± 0.5	5.4 ± 0.0
8	16.7 ± 0.5	5.9 ± 0.9
10	17.5 ± 1.2	6.0 ± 0.9
45 rpm. 0	20.6 ± 0.8	13.0 ± 0.0
4	15.4 ± 1.2	7.9 ± 1.0
6	15.8 ± 1.1	6.0 ± 1.0
8	15.5 ± 0.3	4.8 ± 1.0
10	15.3 ± 0.5	5.4 ± 0.0

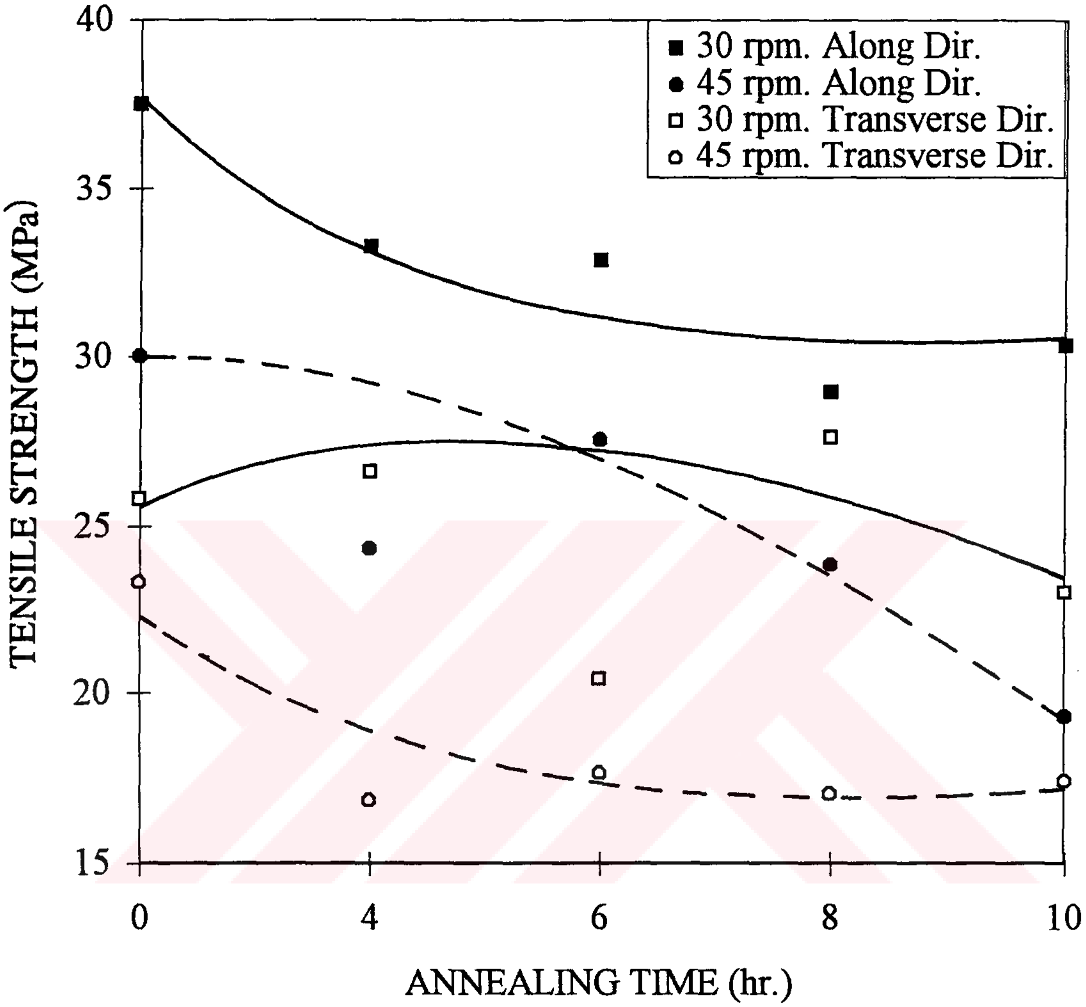


Figure 1. Tensile strength of two screw speeds versus annealing time at 90°C.

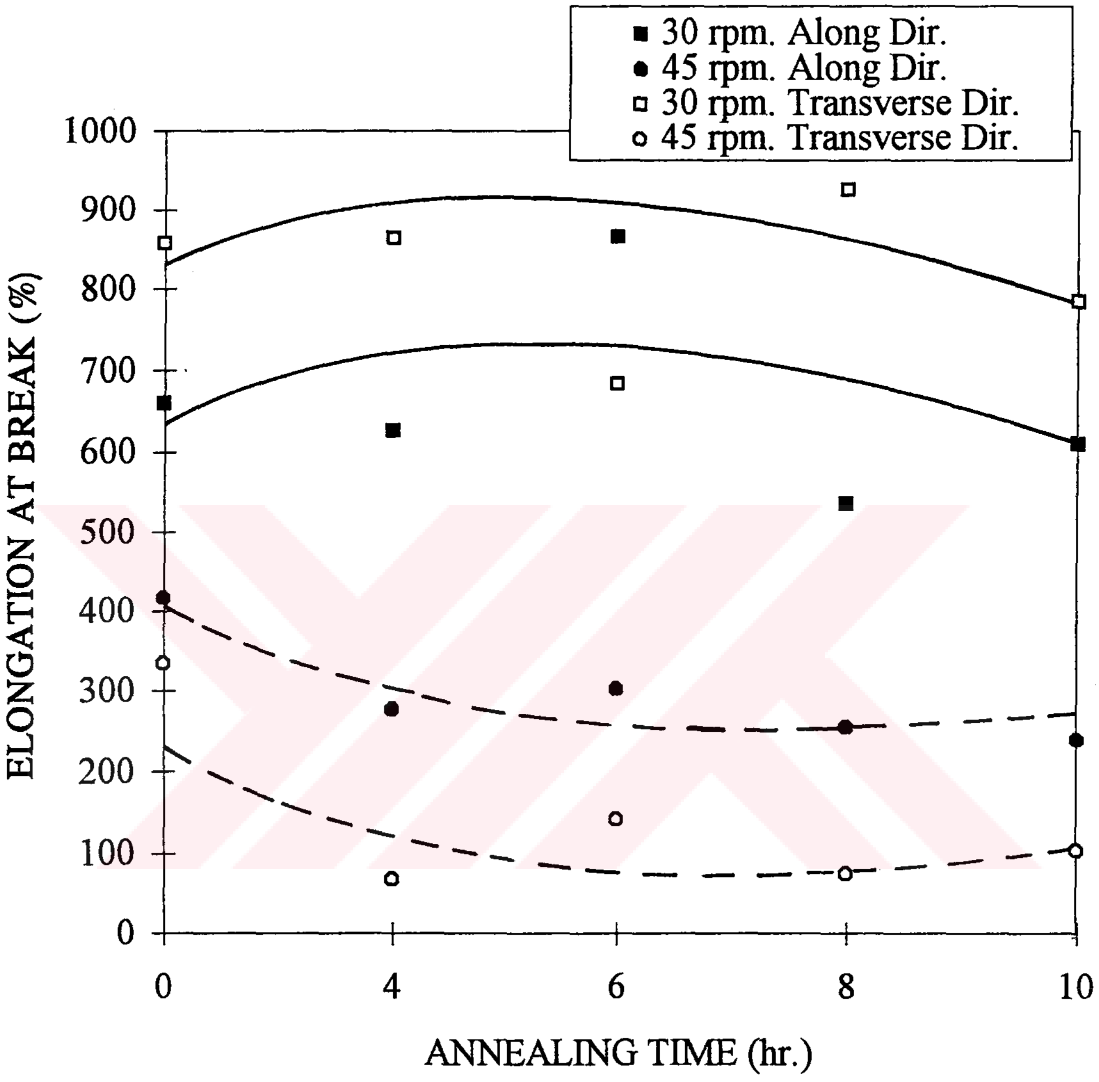


Figure 2. The variation of elongation at break of two screw speeds versus annealing time.

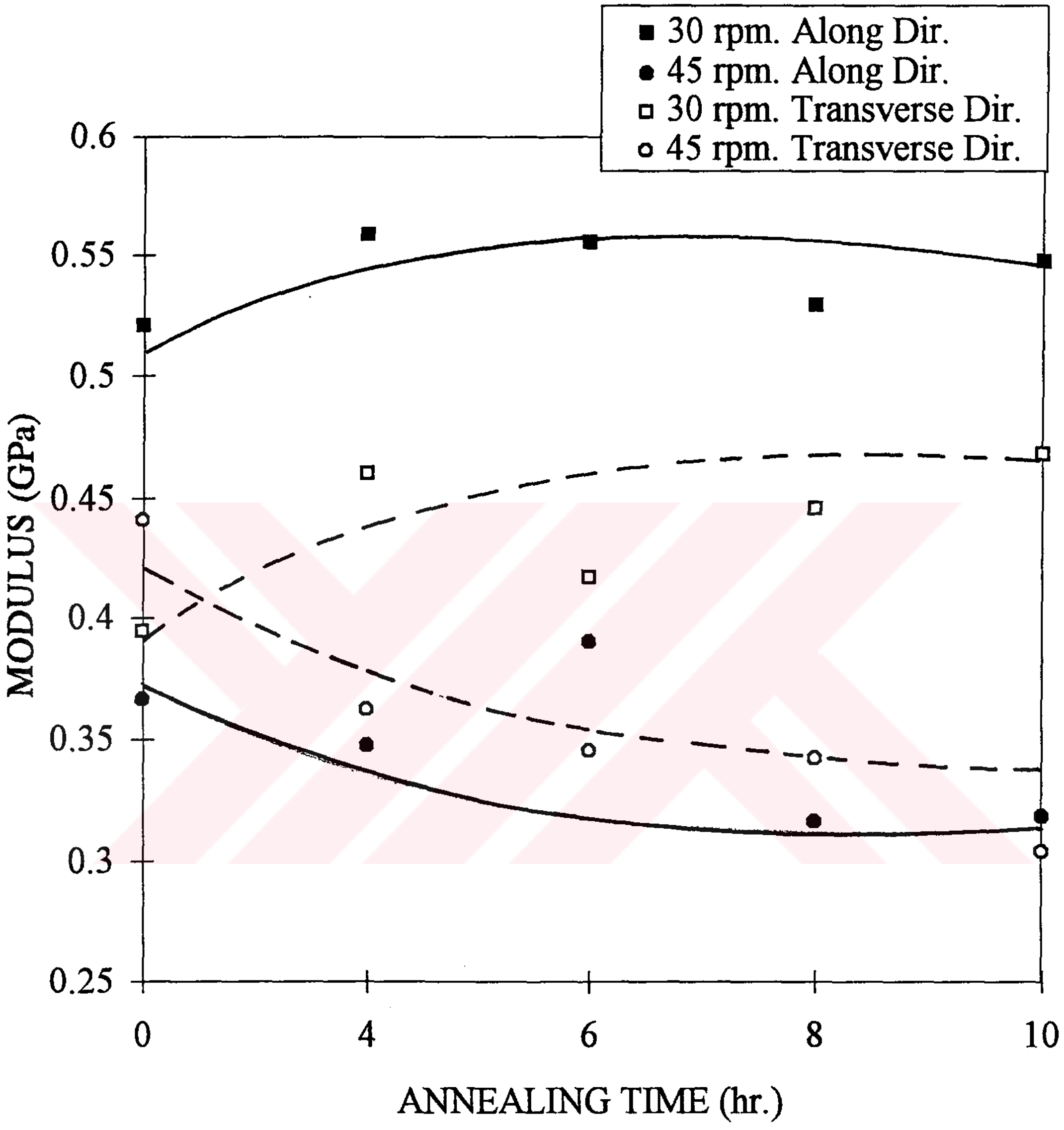


Figure 3. Modulus of two screw speeds versus annealing time at 90°C.

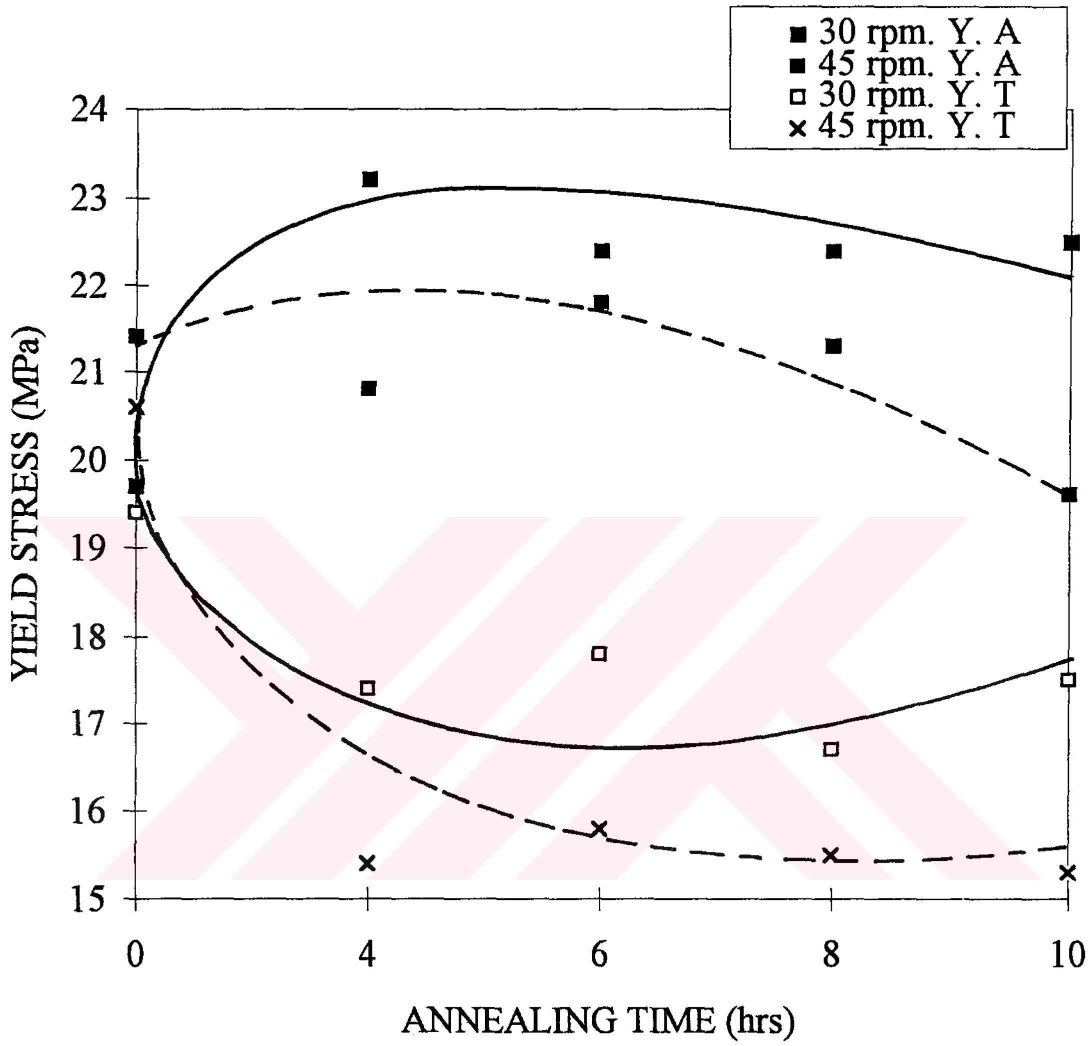


Figure 4. The variation of yield stress of two screw speeds versus annealing time. Y: Yield stress. A: Along travel direction. T: Transverse direction.

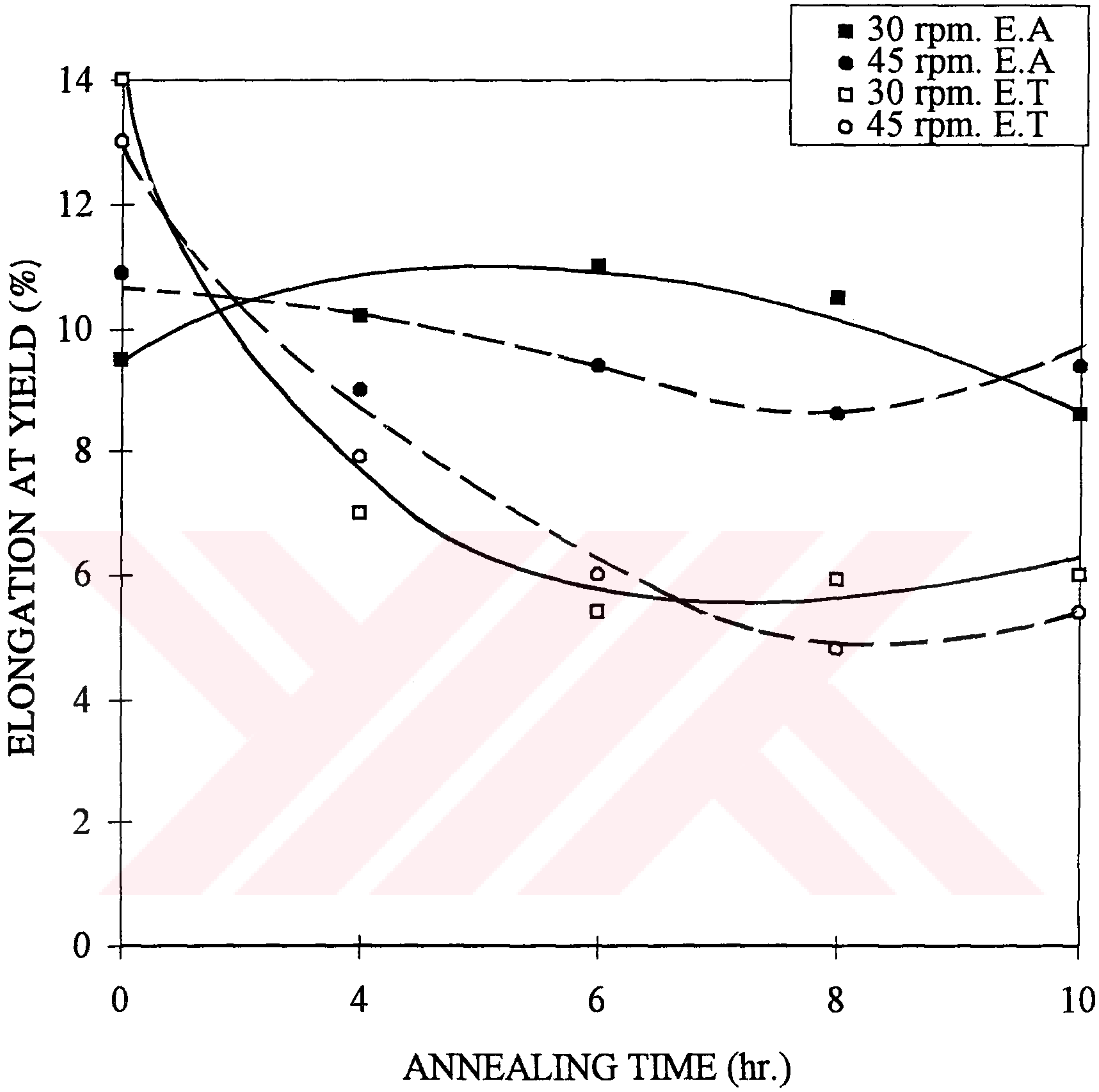


Figure 5. The variation of elongation at yield of two screw speeds versus annealing time. E: Elongation at yield. A: Along travel direction. T: Transverse direction.

The choice of processing temperature depends on whether the polymer is thermoplastic or crosslinkable. In crosslinked polymers a high temperature reduces the time needed to achieve a satisfactory crosslinked state, but there may be an increased risk of premature of crosslinking during movement, or shaping. The risk of degradation makes it undesirable for the polymer to spend long times at high temperature, to avoid this risk one should ensure that the polymer can flow smoothly through the extruder which makes the polymer more risk-tolerant.

An improvement in mechanical properties at 30 rpm, means that there is a smooth flow of the polymer melt and the polymer is more risk-tolerant compared to screw speed at 45 rpm, which have lower values of the mechanical properties. The above observations give a strong evidence on occurrence of melt deformation as a result of high friction forces which cause excessive temperature rise and supply further source of heat which enhance formation of dead spot in extruded polymer films at this screw speed (45 rpm). The shear rate at 30 rpm is lower than that of 45 rpm, the lower the shear rate the more opportunity for the molecules to arrange themselves in ordered manner. On the other hand the shear rate at 45 rpm is high enough to cause insufficient time for the polymer molecules to order themselves, which result in poor mechanical properties.

3.2.3 Mechanical properties along travel direction for 30 rpm. extrusion

Films extruded at 30 rpm, annealed at 70, 80 and 90°C, at several periods of annealing time.

Stress at break values of the polymer films were shown in Figure 6 and Table 3. 6. It is obvious that there is a considerable increase in tensile strength of the sample aged at 80°C especially at 8 hours of annealing.

Control of thermal and deformation history during processing allows microstructure of the polymer film to be changed to yield optimum performance. As the drawing proceeds some of the load is taken by the oriented material and some strain-hardening is observed. Failure occurs either because many molecules or part of them reach their breaking stress or because local defects start to grow in transverse direction. We observed a decrease in tensile strength values of samples annealed at 90°C at different time of annealing and slight decrease of tensile strength at 70°C when compared with annealing at 80°C. Although there was the expected increase in tensile strength with increasing degree of crosslinking, it was reported that the strength decreased again at very high degree of crosslinking [5, 6].

Since the effect of physical aging diminish after a critical time, which is a function of annealing temperature, and the critical aging time depends on how long it takes for non-equilibrium state to approach equilibrium [34]. Figure 7 and Table 3. 6. summarized strain at break variations of the polymer film with respect to annealing temperature and time of annealing. Sharp changes were observed in elongation at break for various annealing times in 90°C annealing temperature. In case of 80°C annealing, strain at break was increased with annealing time until 8 hours with almost no change up to 30 hours.

The decrease in strain at break may be due to increase in gel content at longer annealing time, in case of annealing at 80°C there was no change in elongation at break after 8 hours of aging may be due to the extent of crosslinking diminish after reaching the critical annealing temperature and the satisfactory time of annealing

Modulus of the polymer films were given in Figure 8 and Table 3. 6. It can be seen that the modulus increased with increasing annealing temperature, the highest modulus values can be observed at the longest annealing time 30 hours for all annealing temperatures.

Modulus increased with increasing annealing time due to the increase in extent of crosslinking in addition to a considerable increase of orientation along travel direction. The increase in modulus can be due to volume changes which depend on time scales of annealing, this behavior can be interpreted on the basis of changes in free volume, chemical crosslinking upon annealing, by bringing adjacent chain close together, reduce the free volume and hence raises modulus.It should be noted that modulus depends on test speed. A slow speed permits more disentanglement of molecular chains, and hence a lower modulus; a fast speed of test gives insufficient time for chains to uncoil and disentangle.

Table 3. 6. Mechanical properties of crosslinked polyethylene films extruded at 30 rpm, along travel direction of processing at 70, 80 and 90°C annealing temperatures.

Annealing temperature and time (hr.)	Tensile strength MPa	Elongation at break, %	Modulus GPa
70°C.			
0	37.5 ± 1.6	659 ± 26	0.521
4	36.3 ± 0.1	632 ± 8	0.376
6	38.5 ± 1.3	642 ± 22	0.304
8	35.3 ± 0.7	654 ± 12	0.290
10	38.4 ± 0.2	666 ± 6	0.322
12	36.9 ± 2.4	641 ± 31	0.329
30	36.5 ± 4.3	594 ± 67	0.577
80°C.			
4	31.0 ± 0.1	506 ± 15	0.503
6	38.9 ± 1.7	580 ± 78	0.507
8	37.4 ± 0.8	655 ± 6	0.527
10	38.3 ± 2.5	662 ± 22	0.474
12	37.6 ± 1.5	648 ± 33	0.516
30	38.4 ± 0.4	654 ± 23	0.580
90°C.			
4	33.2 ± 2.9	625 ± 71	0.558
6	32.0 ± 1.2	865 ± 10	0.555
8	29.8 ± 1.3	536 ± 18	0.529
10	31.6 ± 3.6	609 ± 54	0.547
12	34.0 ± 0.9	618 ± 29	0.501
30	30.9 ± 3.2	514 ± 103	0.588

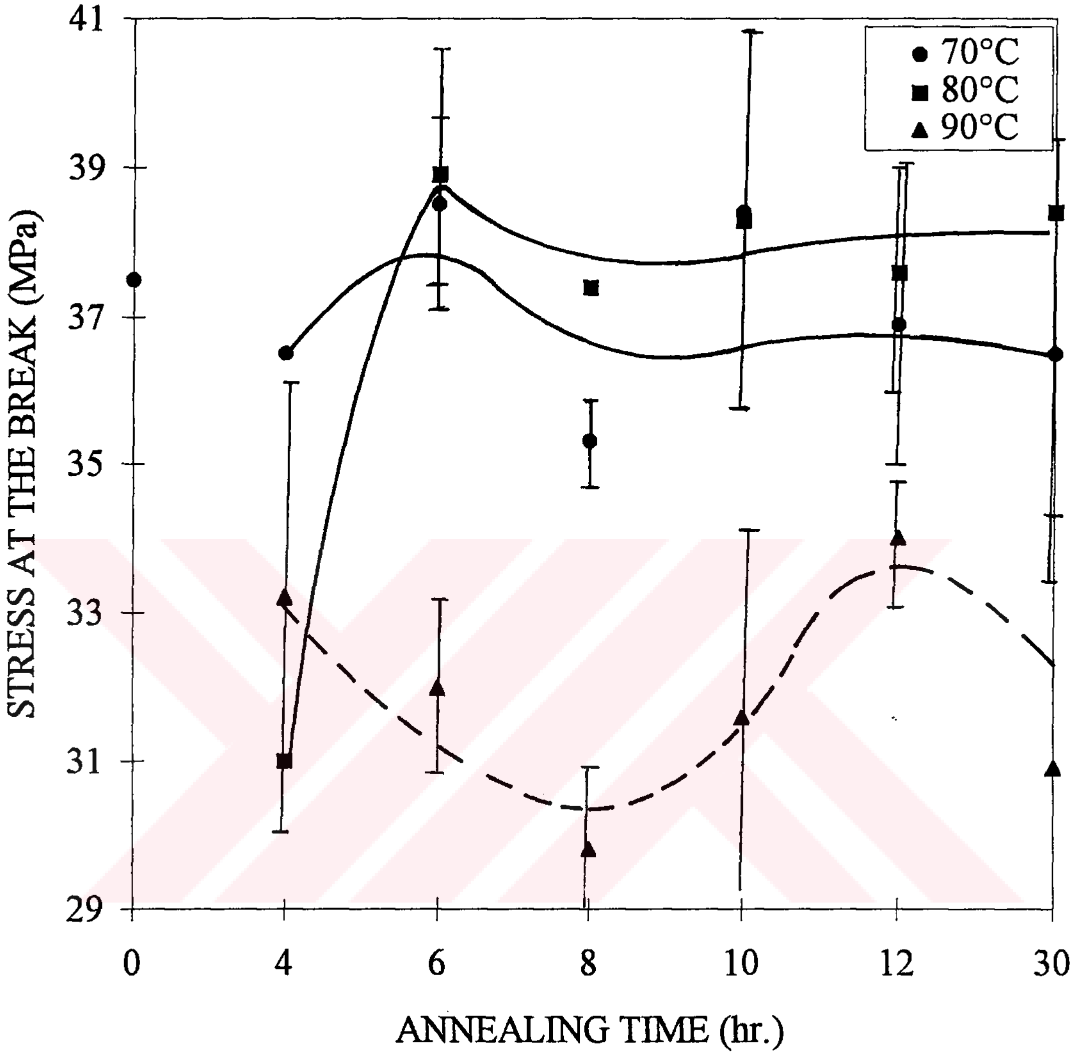


Figure 6. The variation of tensile strength versus annealing time along the travel direction.

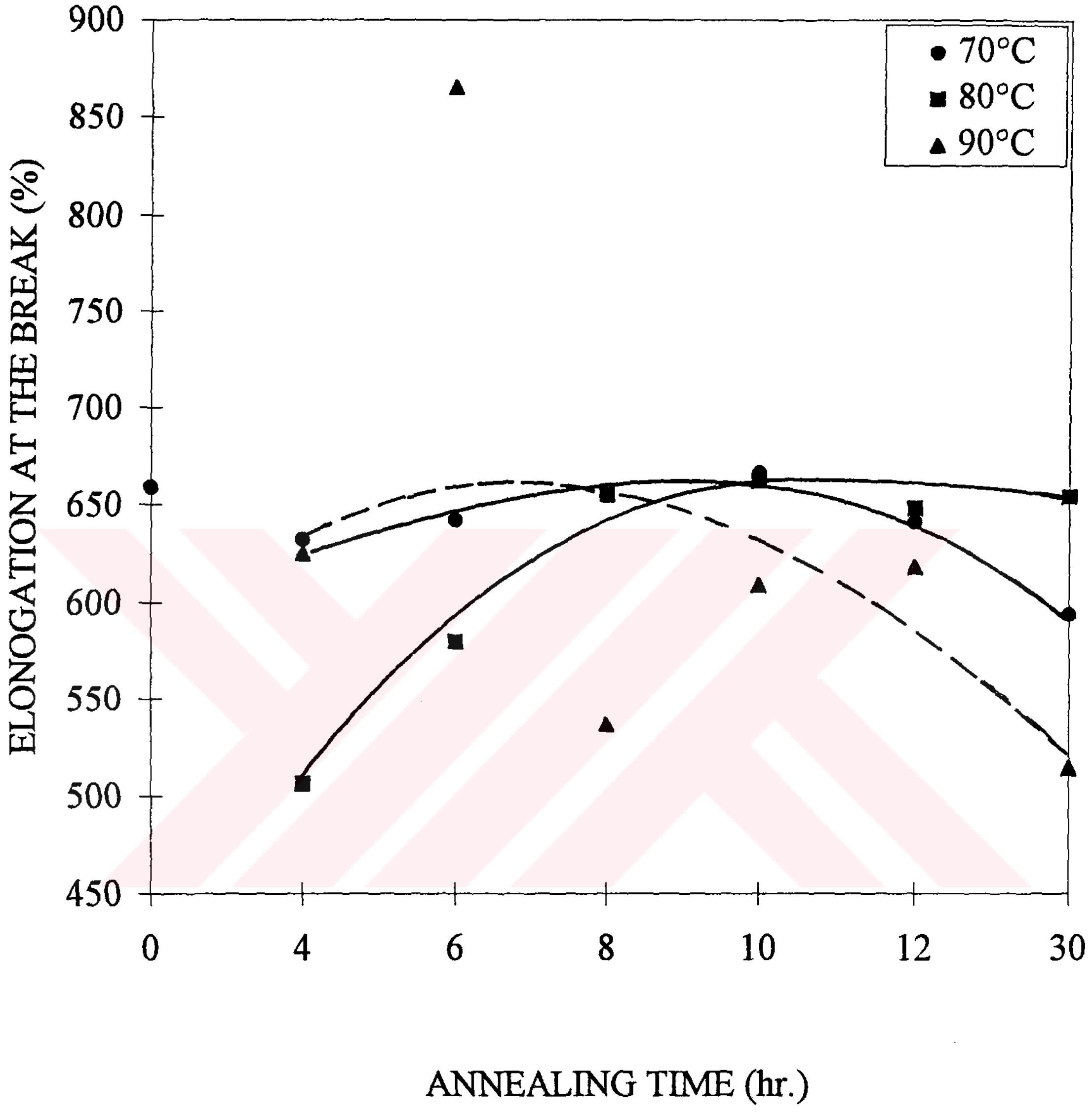
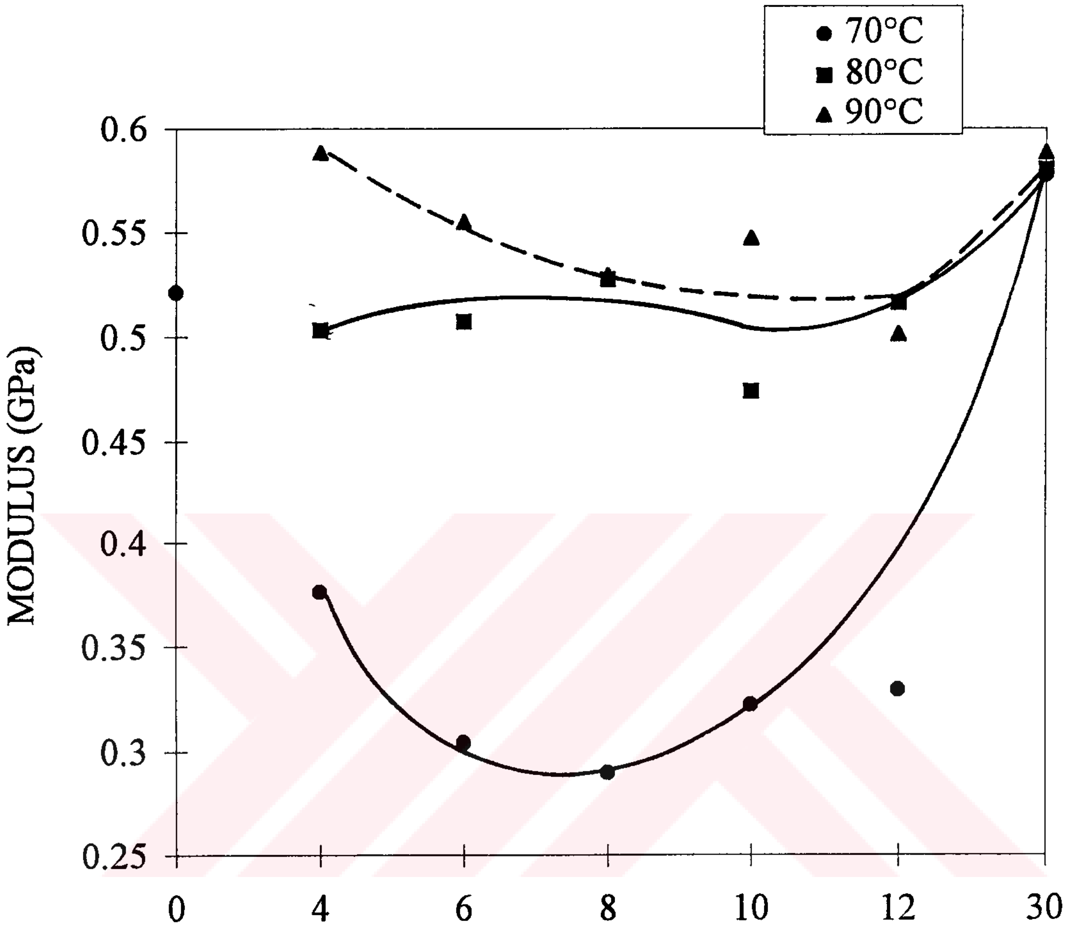


Figure 7. The variation of elongation at break versus annealing time and temperature along travel direction.



ANNEALING TIME (hr.)

Figure 8. The variation of tensile modulus versus annealing time and temperature along travel direction.

3.2.4 Mechanical properties of crosslinked polyethylene film in transverse direction, extruded at 30 rpm.

The mechanical properties (tensile strength, elongation at break and modulus) of the polymer film in transverse direction were shown in Figures 9, 10, 11, and Table 3. 7. We observed an increase in stress at break and modulus Figure 6, 8 along travel direction of processing when compared the same properties in transverse direction Figure 9, 11. An increase in elongation at break in transverse direction Figure 10 was observed when compared with elongation at break along travel direction Figure 7. In other words the resulting film is stiff and strong in the flow direction but flimsy in transverse direction.

These observations can be due to the forces between molecules in the polymer film are insufficient to hold the material together in the transverse direction, since the molecules become lined up during processing and are annealed in the lined-up configuration, which allowed for the molecules to relax in ordered way and enhanced the packing ability which resulted in easy bath for crosslinking, then the material become stiffer along the direction of alignment and more flexible in transverse direction.

Finally as annealing time increase, especially after 12 hours of annealing at all temperatures, an increase in modulus and tensile strength were observed but there was decrease in elongation at break in both directions due to increase in gel content.

Table 3. 7. Mechanical properties of crosslinked polyethylene films of transverse direction of processing, at 30 rpm, at 70°C, 80°C and 90°C annealing temperatures.

Annealing temperature and time (hr.)	Tensile strength MPa	Elongation at break %	Modulus GPa
70°C			
0	25.8 ± 4.6	857 ± 60	0.394
4	24.8 ± 8.5	791 ± 100	0.447
6	23.6 ± 2.0	794 ± 39	0.339
8	26.5 ± 1.8	915 ± 35	0.332
10	25.7 ± 2.0	897 ± 72	0.376
12	25.3 ± 3.0	725 ± 100	0.329
30	26.4 ± 0.4	806 ± 114	0.449
80°C			
4	27.3 ± 2.6	877 ± 78	0.34
6	27.8 ± 1.8	920 ± 78	0.351
8	25.7 ± 1.0	886 ± 67	0.38
10	24.5 ± 3.8	834 ± 100	0.331
12	28.6 ± 0.1	887 ± 53	0.354
30	25.8 ± 4.4	735 ± 100	0.438
90°C			
4	26.6 ± 2.2	863 ± 40	0.46
6	20.4 ± 3.0	683 ± 10	0.417
8	27.6 ± 1.0	925 ± 31	0.446
10	23.0 ± 2.0	785 ± 49	0.468
12	27.5 ± 1.3	938 ± 100	0.387
30	25.8 ± 2.0	750 ± 10	0.425

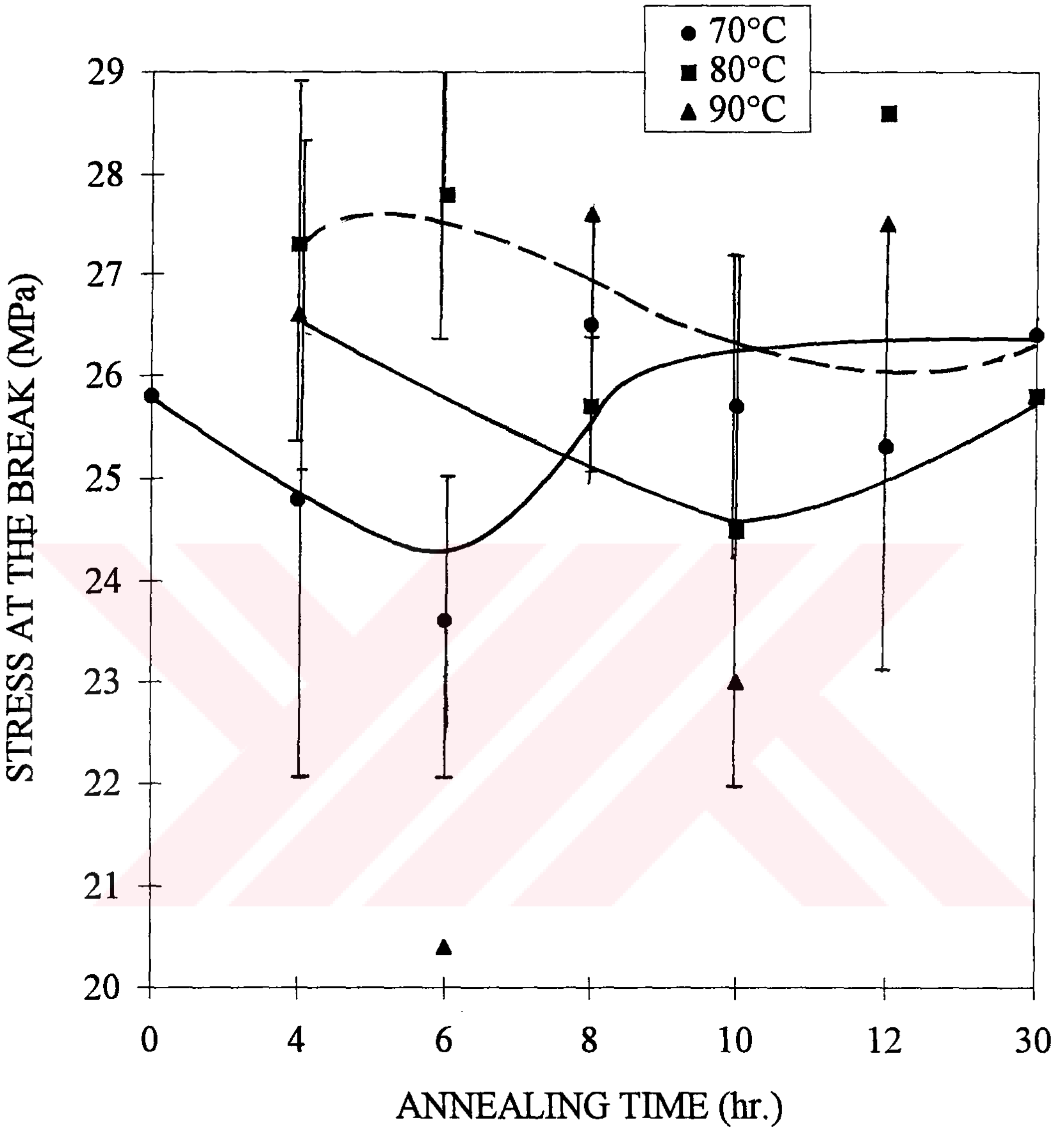


Figure 9. The variation tensile strength of transverse direction versus annealing time.

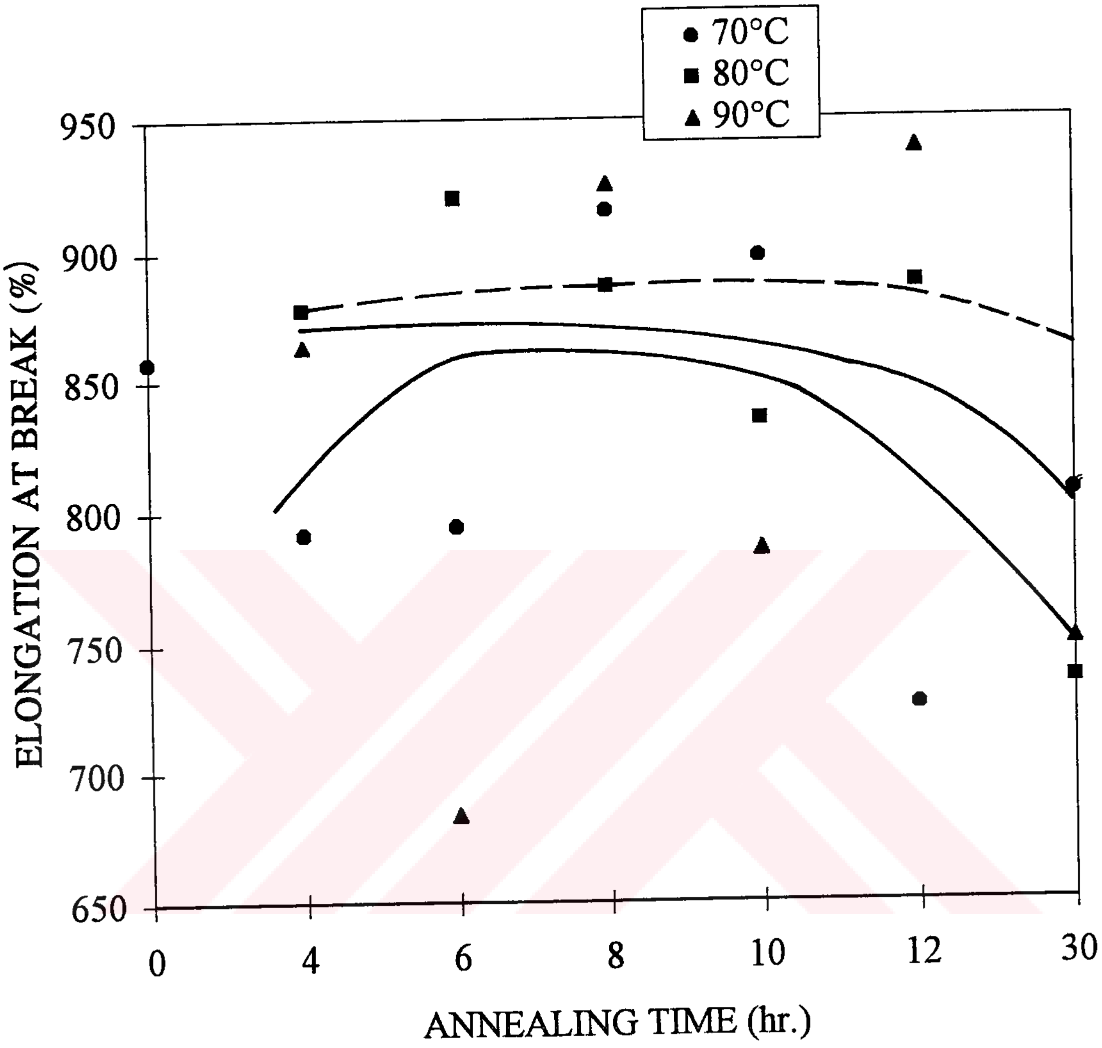


Figure 10. The variation of elongation at break of transverse direction versus annealing time and temperature.

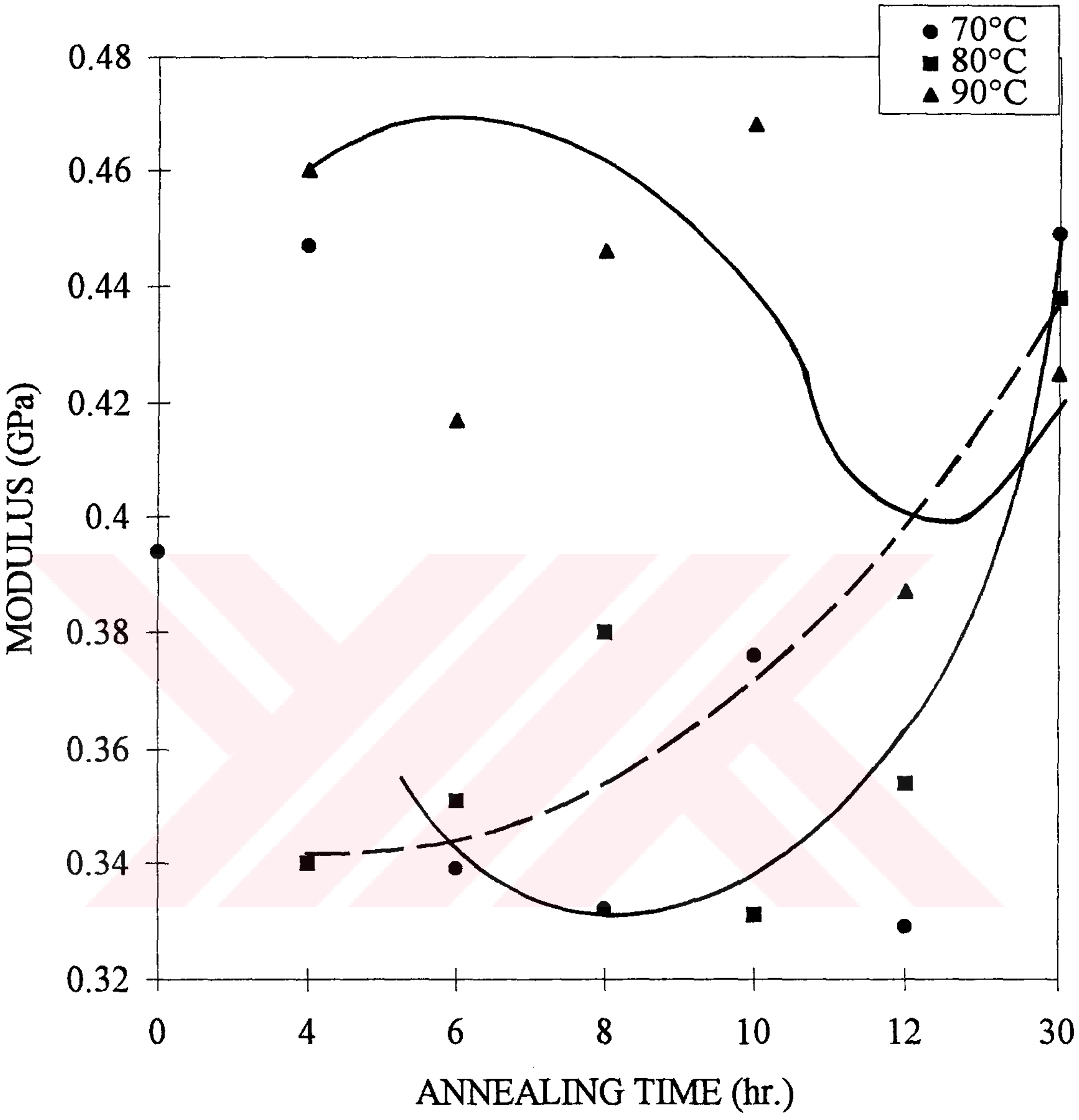


Figure 11. The variation of tensile modulus of transverse direction versus annealing time and temperature.

3.3 Yield Stress and Yield Strain

3.3.1 Deformation in the neck:

At yield point molecules start to slip past one another in a non-elastic manner and the microstructure change. However, below yield the molecular chains slip past each other, normally to a small extent which is largely, if not completely, recoverable, and there is kind of reordering of the microstructure. The polymer film deforms to develop a neck of voided whitened region, the molecules align themselves in the direction of the applied load: the alignment leads to strain-induced crystallization or even recrystallization and the material in the neck, therefore, becomes much stiffer in the direction of loading than the unnecked material. The neck is therefore stable and the shoulder of the neck travels along the specimen for as long as the load is applied, or until the neck reaches the wider ends of the spacemen where the cross-section is too large for yield to occur with out a dramatic increase in load [2].

3.3.2 Yield Stress:

The yield stress along travel direction of processing and yield stress in transverse direction with respect to annealing temperature and time of annealing were shown in Figure 12 and Table 3. 8. The variation of the yield stress in both directions with annealing time showed fluctuations, but on the average the yield stress was apparently increased to some extent. The above observations are due to relaxation process results in reorientation of macromolecule chains with the extent of crosslinking upon annealing.

3.3.3. Yield Strain:

Yield strain data with respect to test direction, annealing temperature and annealing time were summarized in Figure 13 and Table 3. 8. The elongation at yield along travel direction was bigger than that of transverse direction due to orientation. The yield elongation in transverse direction practically remained almost the same with annealing temperatures. However, the higher the annealing temperature (80 and 90°C) showed such a stability with annealing time in the yield elongation along travel direction.

Table 3. 8. Yield stress and elongation at yield of crosslinked polyethylene films, along and transverse direction of processing, at 30 rpm, at 70°C, 80°C and 90°C annealing temperatures, for several periods of annealing time in water bath.

Annealing Temp. and Time (hr.)	Yield stress[1] MPa	Elongation[1] at yield, %	Yield stress[2] MPa	Elongation[2] at yield, %
70°C				
0	19.3	10.6	17.1	8.3
4	19.7	11.4	17.7	8.3
6	19.7	11.4	16.6	9.2
8	18.4	11.4	17.0	10.0
10	19.7	11.4	17.5	10.0
12	19.5	11.4	17.3	10.0
30	20.3	12.0	18.0	10.0
80°C				
4	19.5	14.2	17.0	7.5
6	20.4	11.4	16.3	8.3
8	19.3	11.4	16.8	7.5
10	19.3	13.2	16.0	7.5
12	19.3	11.4	17.6	7.5
30	20.1	10.3	18.9	7.5
90°C				
4	18.4	11.4	16.2	9.5
6	18.6	12.3	16.9	10.0
8	18.7	14.2	16.4	9.1
10	19.5	14.2	17.0	9.1
12	19.0	14.2	17.2	9.1
30	20.6	11.0	17.5	10.0

[1] Along travel direction of processing.
[2] Transverse direction of processing.

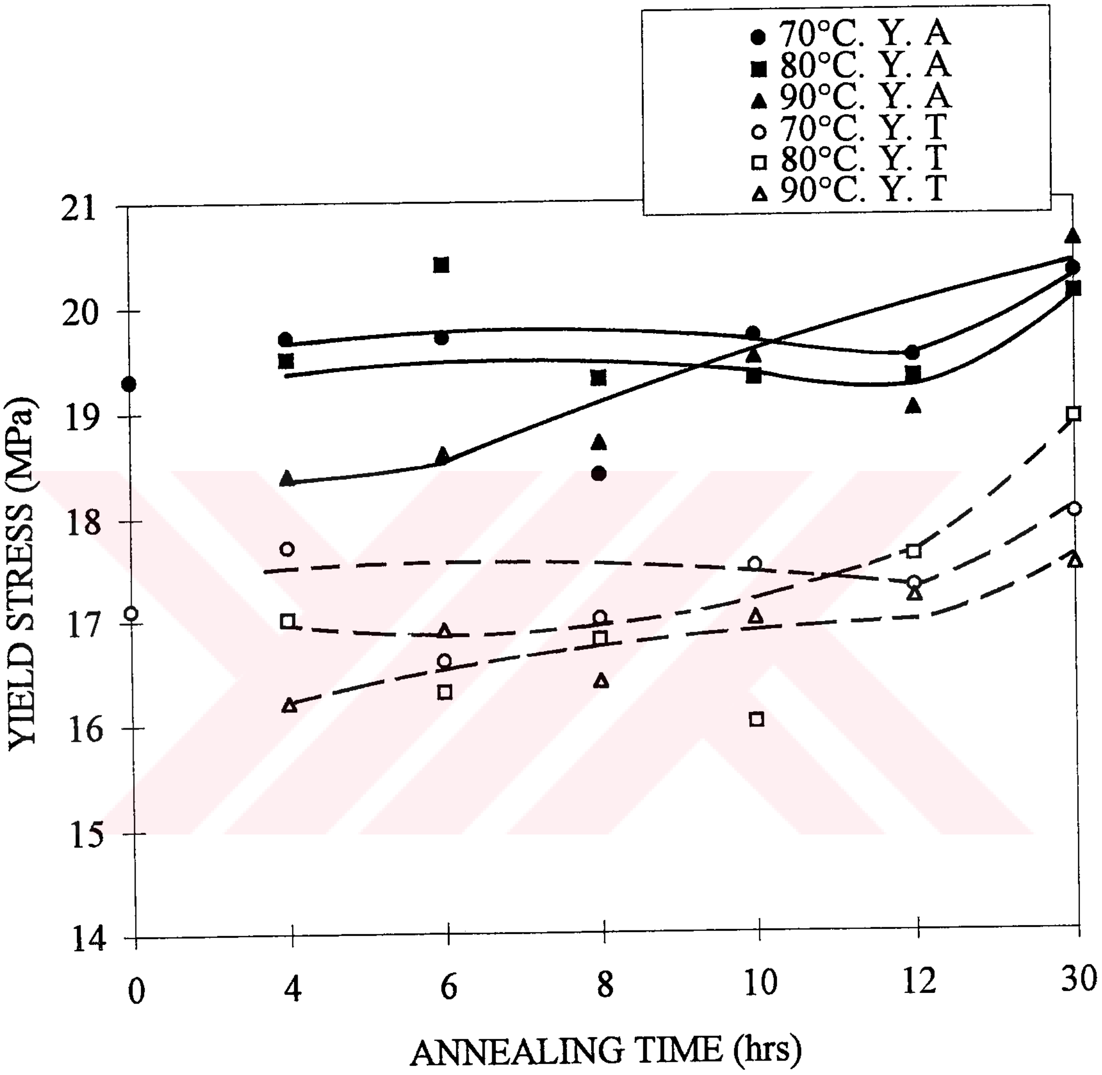


Figure 12. The variation of yield stress versus annealing time and temperature along travel and in transverse directions. Yield stress. A: Along travel direction. T:Transverse

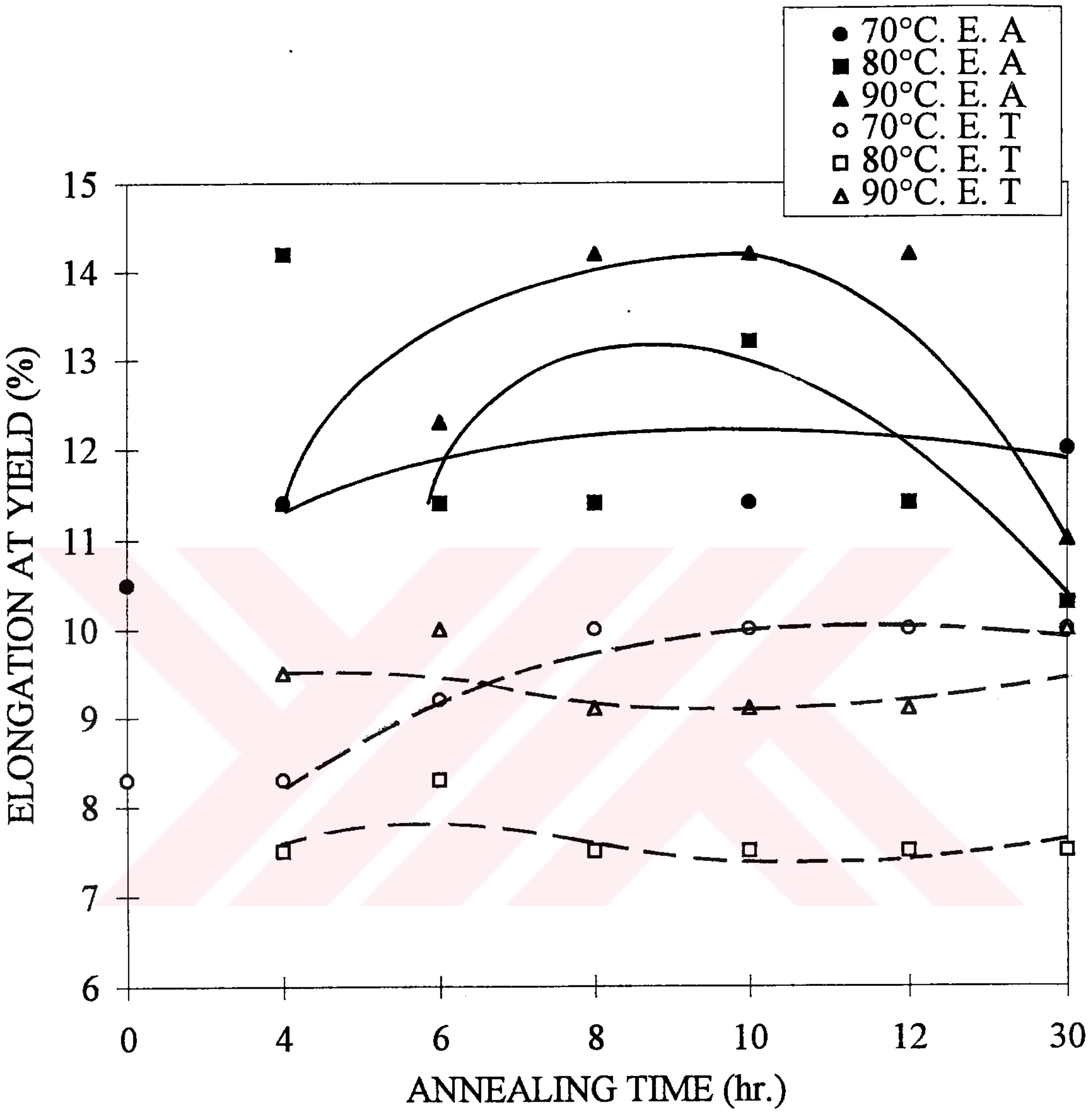


Figure 13. The variation of elongation at yield along travel direction and in transverse direction versus annealing time and temperature. E: Elongation at yield. A: Along travel direction. T: Transverse direction.

CHAPTER 4

CONCLUSIONS

1- Mechanical properties of two screw speeds: The mechanical properties were found to be better when extruded at screw speed 30 rpm compared with those extruded at 45 rpm. Because of the orientation, mechanical properties along travel direction of processing were larger than those of transverse direction. The optimal annealing time was 6 hours since all mechanical properties improved at this annealing time.

2- Mechanical properties as a function of annealing temperature and time of annealing: A relative considerable increase in tensile strength of the polymer film annealed at 80°C was obtained when compared with two other annealing temperatures. For all annealing temperatures an increase in elongation at break at short annealing time followed with a decrease at longer annealing time. However, almost no change in case of 80°C after 8 hours of annealing was observed.

Modulus increased as annealing time and annealing temperature increased and reached usually maximum at 30 hours of annealing.

3- Yield stress increased as annealing time increased with slight fluctuations in values at shorter annealing time but at longer annealing time there was a relatively considerable increase in yield stress with almost no change with respect to annealing temperatures. There was a marginal increase in yield strain as annealing temperature increased, yield strain decreased with increasing annealing time due to increase in gel content.

Quenching, annealing temperature and time of annealing of the polymer melt are important steps on production line, which play an important role in performing high product quality further more those steps will reduce the production cost. Finally the slow variation in structure as a function of annealing time depends on how long it takes for non-equilibrium state to approach equilibrium, thus the effect of physical aging diminish after a critical annealing time which is a function of annealing temperature.

The optimal annealing temperature was 80°C and that of annealing time was 8 hours. Since the obtained properties have the same if not better than those obtained at relatively high production cost of the pipe producing company. The previous annealing conditions are assumed to take role in reducing the pipe production cost

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