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Faculty of Textile Engineering

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Technical University of Liberec

Faculty of Textile Engineering

Department of Textile Technology

Polypropylene Multifilament Yarn For Technical Applications

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(PROJECT, ART WORK, ART PERFORMANCE)

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Rules for elaboration:

1. Compile a study on topic: The main geometrical parameters of the yarn (monofilament, multifilament). Yarn shrinkage. Mechanical parameters of fibers.
2. Measure selected parameters of polypropylene multifilament (fineness, twist, thermal shrinkage, strength).
3. Analyze results.

LIST OF NOTATION

Abbreviation

Ionex	Ion exchange
FCC	fluidized catalytic cracking
LPG	Light petroleum gases
PP or POP	Polypropylene
QC	computer software used to clean data (statistics)
Coeff.	Coefficient
LL	Low limit
HL	High limit
t/m	Turn/meter.
TUL	Technical University of Liberec
Mol	Molecular moles
C3	propane
CO_2	carbon dioxide
CO.	Carbon monoxide
DSC	Differential scanning calorimeter
Tm	Melting point
Tc	Crystallization point
ISO	International Standard organisation

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List of specialized literature:

[1] Militky, J.: Textile fibers, Faculty of Textile Engineering Technical University of Liberec. 2005

[2] Becker, 0., Chemiefasern, 30, p. 827 (1980)

[3] Militký J., Křemenáková, D., Košátková Hušková, M.: Thermal Sensitivity of Industrial Polyester Monofilaments Shrinkage Rate. 15th International Conf. STRUTEX, Structure and Structural Mechanics of Textiles, December 2008, Liberec.

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Mathematical Symbol

Symbol	Meaning
Rs	maximum shrinkage rate
A	Constant coefficient
B	Constant coefficient

Physical quantity

Quantity	Unity	Meaning
t	(tex)	fibre fineness filament fineness
m	(g)	fibre mass
l	(km)	fibre length
T	(tex)	bundle fineness
M	(g)	fibre bundle mass
ρ	(kg/m^3)	fiber density
V_f	(m^3)	fiber volume
A	(m^2)	equivalent cross-sectional area
s	(mm^2)	Cross-sectional area of the filament
d	(mm)	Diameter of the filament
n	(-)	Number of filament in parallel fiber bundle
μ	(-)	yarn packing density
V_y	(m^3)	total yarn volume
k	(-)	Twist intensity
β	(^{o})	An angle, slope of general twisted fibre (helix).
k	(-)	Twist intensity,
F	(N)	Force applied to a load

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Abstract

Monofilaments are used in the membrane Lamination process. Here in this report, 56 dtex of polypropylene multifilament yarn with 16 fibrous was evaluated for technical application (membrane lamination). Strength of fibers and fibrous bundles were very important parameters especially for industrial applications.

This project describes the bundle strength of POP multifilament's form statistical point of view. Bundles 1 to 10 filaments were tested. Yarns were twisted at 400t/m, 440t/m, 800z/m and 1200t/m count. Two type of twisting technologies were used, and those technologies were ply twister and ring spinning.

Based on the information provided by the Company initiated this project. And the results obtain during experiment. It were concluded that 1200t/m was the optimum yarn for a membrane lamination process. Ring spinning technology was recommended technology for twisting the yarn. The best operation condition for POP multifilament concluded was less the 120oC.

Keywords: POP multifilament, fiber, Lamination, Ply twister, ring spinning.

Table of Contents

1 INTRODUCTION

Here in this report the primary objective was to evaluate mechanical properties of Polypropylene multifilament used in technical application (laminated membrane application). The objective was driven by the cost and availability of POP multifilament yarns. And the project was initiated by one of the Czech membrane company.

5.6 tex with 16 fibrous POP multifilament untwisted yarns was provided as a raw material for project. TUL weaving technology laboratory was used to produce twisted yarns from raw material. Two types of technologies were used to produce four set of twisted yarns. Those technologies were ply twist and ring spinning without draft. Four sets were 400t/m 440t/m, 800t/m and 1200t/m. Only 400t/m was produced from ply twister technology and the rest were produced from a ring spinning technology.

TUL material testing laboratories were used to carry out the project objective. The membrane company was also used to investigate the membrane lamination effect at different twist factor using the raw material.

Theoretical, Polypropylene material is man-made, the fastest growing commodity polymer category globally, and is only surpassed by polyethylene in market size. Polypropylene has a very low density and good mechanical properties and is therefore very suitable for sectors where large volume, cost & weight are an issues. Polypropylene is the fibres material that is cheaper and produced by simple special technology. Polypropylene is a highly crystalline thermoplastic polymer produced by the chain growth polymerization of propylene, a gas obtained from petroleum cracking processes. [5]

2 LITERATURE REVIEW

2.1 Polypropylene production

2.1.1 Historical Discovery Polypropylene Production

Polypropylene has been produced for over 40 years and has a wide variety of applications including industrial uses, food packaging, membranes and many domestic uses.

In 1954 Giulio Natta and together with K. Ziegler discover a catalyst that can be used during the polymerization process to form polyolefin. The catalyst was called Ziegler type catalyst. The discovery in 1963 could bring about polymerization of propylene to linear polypropylene of high molecule weight. There research work, discovered an isotactic polypropylene. The term isotactic, which summarizes a concept of molecular structure, can be identified in three ways molecular structure. [5]

It was discovered that some polypropylene polymers have density of 0.91 and other have low density of 0.85. It was discovered that a polypropylene polymers melting point is not the same. Some polypropylene polymers have more crystallized than other polypropylene polymers. Most of these differences were obtained even the polypropylene polymers have the same molecular weight. [5]

2.1.2 Structure of polypropylene

Polypropylene interior structure consisted chemical molecules bonded together in a chains structures to produce a compound that has its own identification. The chains can be more or less, branched, or cleft structured group of polymers. That creates the similar compound with one molecular weight but with some similarity benefit and differences too. [5]

2.1.3 Chemical composition

Polypropylene fibers have following peculiar properties: low specific weight, high tenacity, high resistance to acids and caustic soda, high rubbing resistance, minimal thermal conductivity and low soiling thanks to low electrostatic charges and to water-repellence. Cause by the interior bonding of the compound. [5]

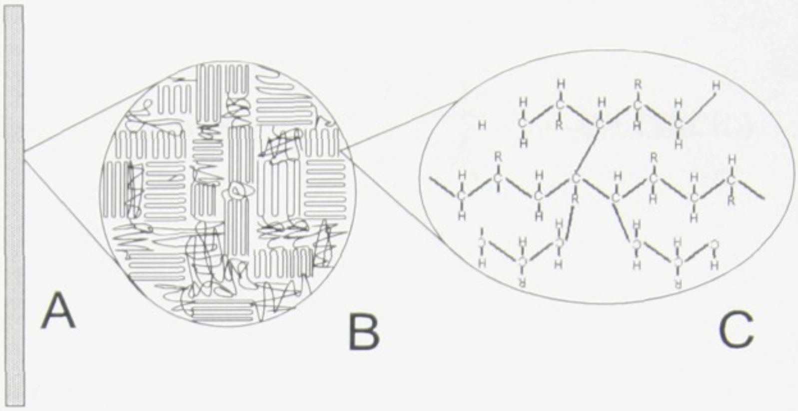


Fig. 2.1: The molecules structure of POP in the yarn filament.

A – POP Filament

B- This section shows that the polypropylene yarn, with crystallized and amorphous region.

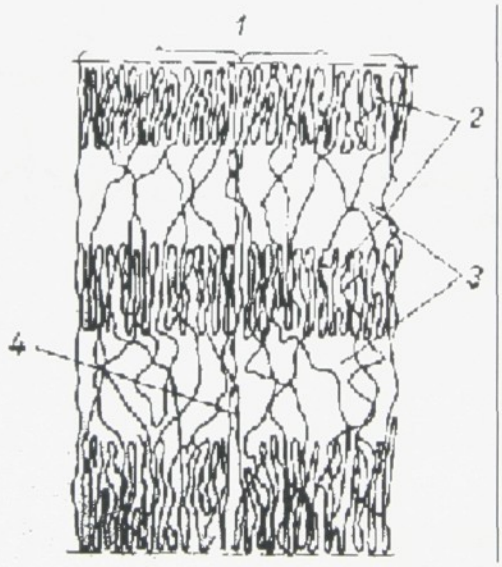
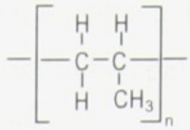


Fig. 2.2: *the POP* structure of model of semicrystallic fibers

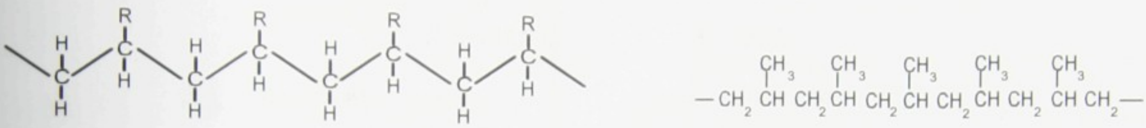
1 – micro fibrils, 2 – crystallites, 3 – amorphous intrafibrillic phase, 4 – amorphous interfibrillic phase [5].

2.1.3.1 Isotactic polypropylene

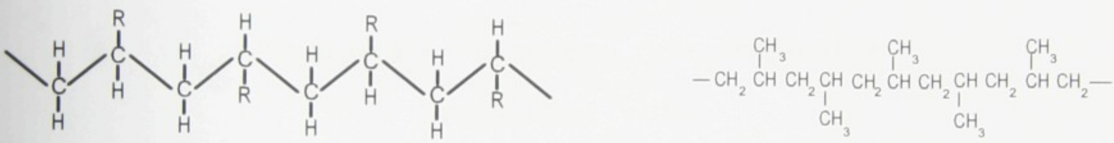
The term isotactic, which summarizes a concept of molecular structure, can be identified in three ways molecular structure and those structures are as follows.

Commonly used structure of POP  or $-CH_2CH(CH_3)-$

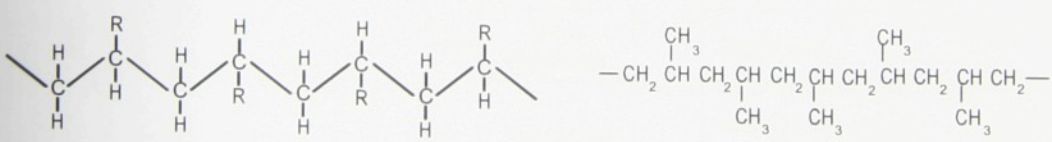
(1) Isotactic polypropylene



(2) Syndiotactic polypropylene



(3) Atactic polypropylene



[5, 18]

2.1.4 POLYPROPYLENE PRODUCTION

The initial processes for POP yarns are as follows; oil refinery, polymerization and extrusion process. All this processes are major processes to manufacture polypropylene yarns and do affect the polypropylene multifilament yarn quality and quantity.

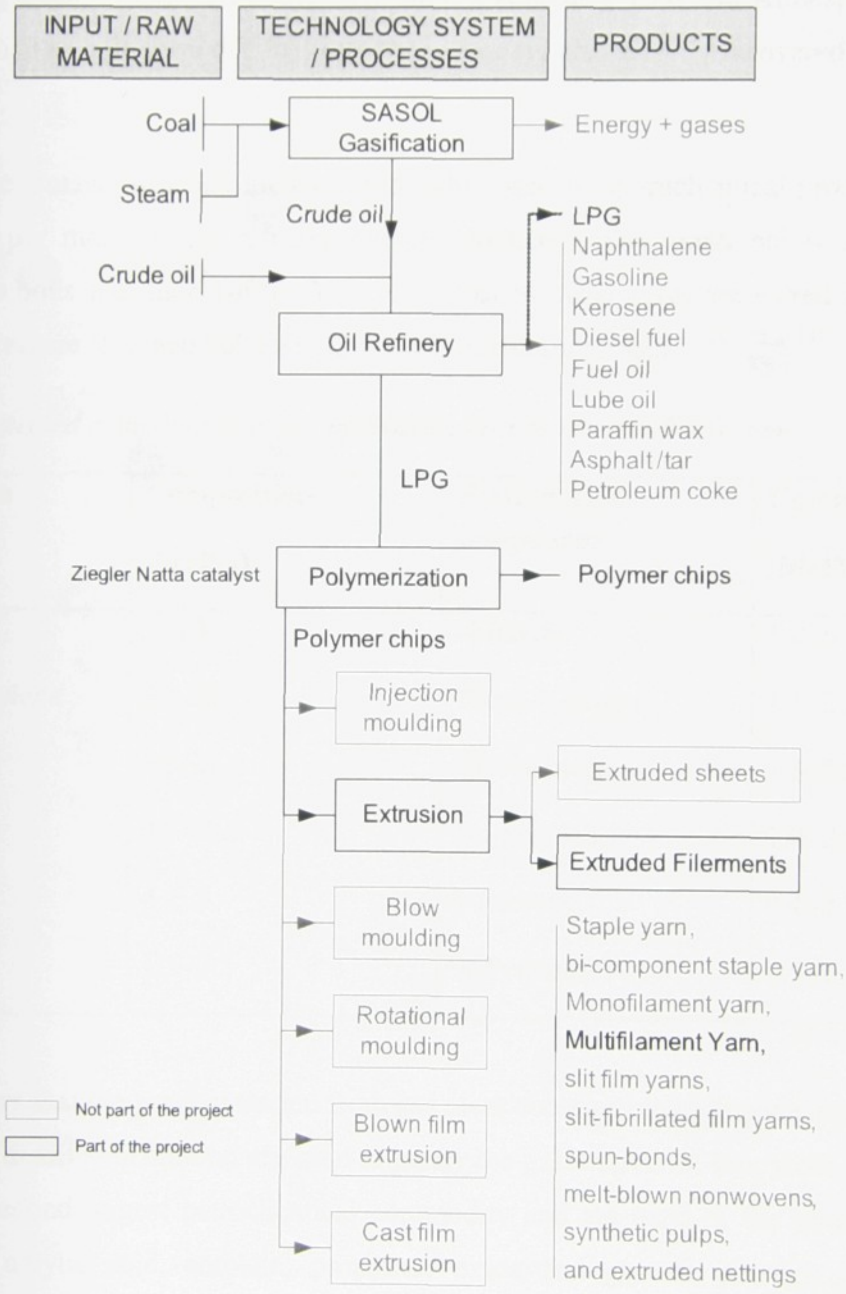


***Fig 2.3:** Simple process diagram for a POP multifilament yarn*

2.1.4.1 Oil Refinery process

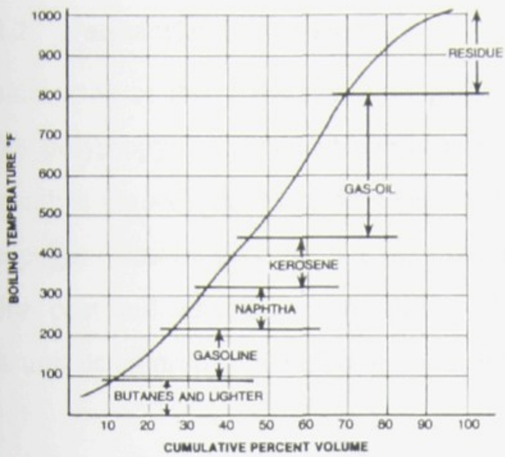
Liquefied Petroleum Gases (LPG) and light gases streams are actually a mixture of light gases produced in gas-oil refineries. And those gases are Methane, ethane, propane and butane, are separated accordingly for further products. The majority of LPG is produced at refineries from the following units; Fluidized Catalytically Unit, Vis-breaker Unit and Atmospheric distillation unit. Other smaller quantities of LPG and other gases are also directly recovered from all refinery process units.

In general the Butane, propane methane and light gases are petrochemical products range from 5% to 15% per mass of the refinery overall products. The graph below shows that light hydrocarbons boils less then 100°F (37.7 °C). Most of these gases are stored in a gases-liquid state at the pressure less than 200 PSI (13.6 atm) maximum pressure. [14, 15 & 18]

Table 2.1: Detected composition of the hydrocarbons present in LPG stream.

Hydrocarbon component	**Composition (Mol%)**	**Hydrocarbon component**	**Composition (Mol%)**
Methane	7–10	N-butane	5.0–6.5
Ethane, *c*-ethylene	20–22	*Trans*-2-butene	1.5–2.5
Propane	18–21	*Cis*-2-butene	1.5–2.5
Propylene	31–28.5	*Iso*-pentane	1.0–2.0
Iso-butane	4–5.5	1-Pentene	0.4–0.7
1-Butene	1.5–2.5	*n*-Pentane	0.5–1.5

Table2.1 shows that the product stream from gas plant contains more propane and Butane family. Strippers and distillation column are used to purify the gases streams. Propylene and propane are the world's second largest petrochemical commodity and are used in the production of POP, acrylonitrile, acrylic acid, acrolein, propylene oxide and glycols, plasticizer oxo alcohols, cumene, isopropyl alcohol, and acetone. Polymerization process is used to produces POP. [5 & 19]



Temperatures	Fraction
Less than 90°F	Butanes and lighter
90 - 220°F	Gasoline
220 - 315°F	Naphtha
315 - 450°F	Kerosene
450 - 800°F	Gas Oil
800°F and higher	Residue

Fig 2.4: *Crude Oil Distillation Curve and its Fractions*

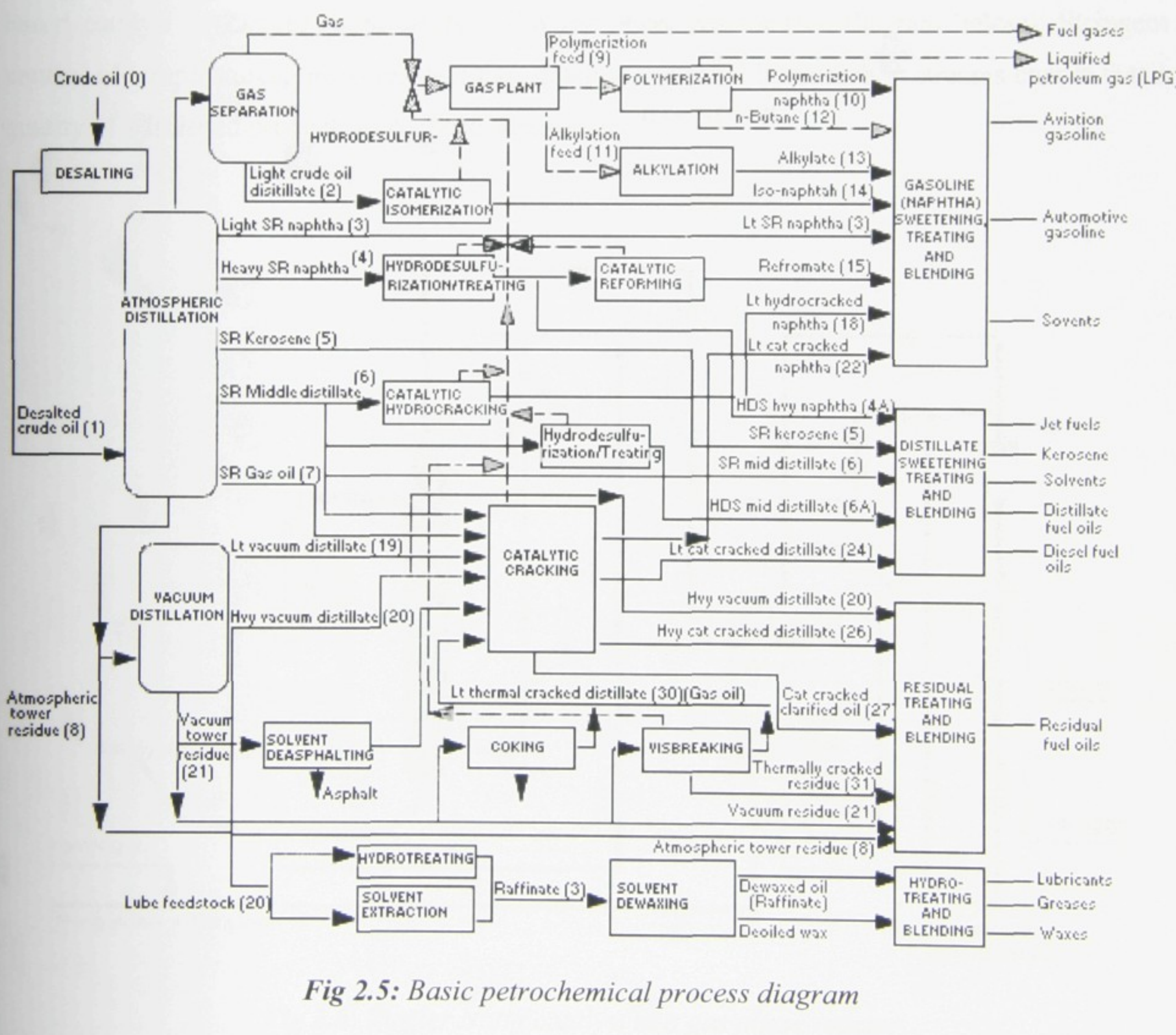


Fig 2.5: *Basic petrochemical process diagram*

2.1.4.2 Polymerization process

The main units in this polymerization process are reactors and strippers. The first process to produces polypropylene Ziegler Natta process, due to the fact that the catalyst used was Ziegler Natta catalyst named after German scientist. Nowadays there are lots of catalysts and processes for the polymerization process, but the principle is still the same only production rate, quality, operation cost and other factors do differ. The common process is C3 titanium based catalyst process unit using propylene and propane as a feedstock.

Polypropylene chips are produced by reacting propylene and propane gases over a titanium based catalyst or Ziegler Natta catalyst in a gas phase reactor (see diagram below). Stringent control of temperatures, pressures, additive, catalyst and other hydrocarbon streams ensure that a quality of a finished product is produced accordingly. [14,15, 18 & 17]

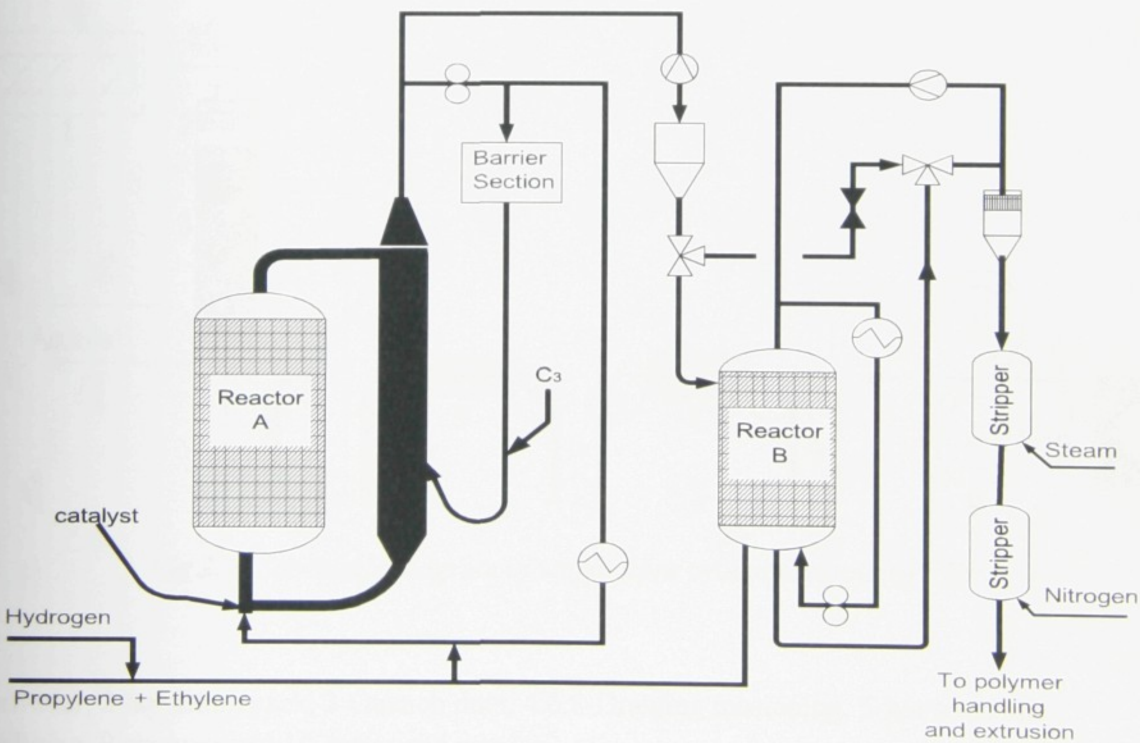


Fig 2.6: *Ziegler Natta catalyst in a gas phase reactor*

2.1.4.3 Extrusion Process

Polypropylene chips can be converted to fibre filament by traditional melt spinning process, though the operating parameters need to be adjusted depending on the final products. Spun-bonded and melt blown processes are also very important fibre producing techniques for nonwovens.

Polypropylene fibers are composed of crystalline and non-crystalline regions. The degree of crystallinity of POP fibre is generally between 50-65%, depending on processing conditions. Crystallization occurs between glass transition temperature (Tg) and the equilibrium melting point (Tm). The crystallization rate of POP is fast at low temperature. Heat setting removes the residual strains and produces a defect-free and stable crystalline structure to make fibre/fabrics dimensionally stable, during the process of heat setting at the temperature above 70°C. At 145°C the conversion is almost complete. High performance POP fibers have been made with high strength and high modulus. [14, 15, 16 & 18]

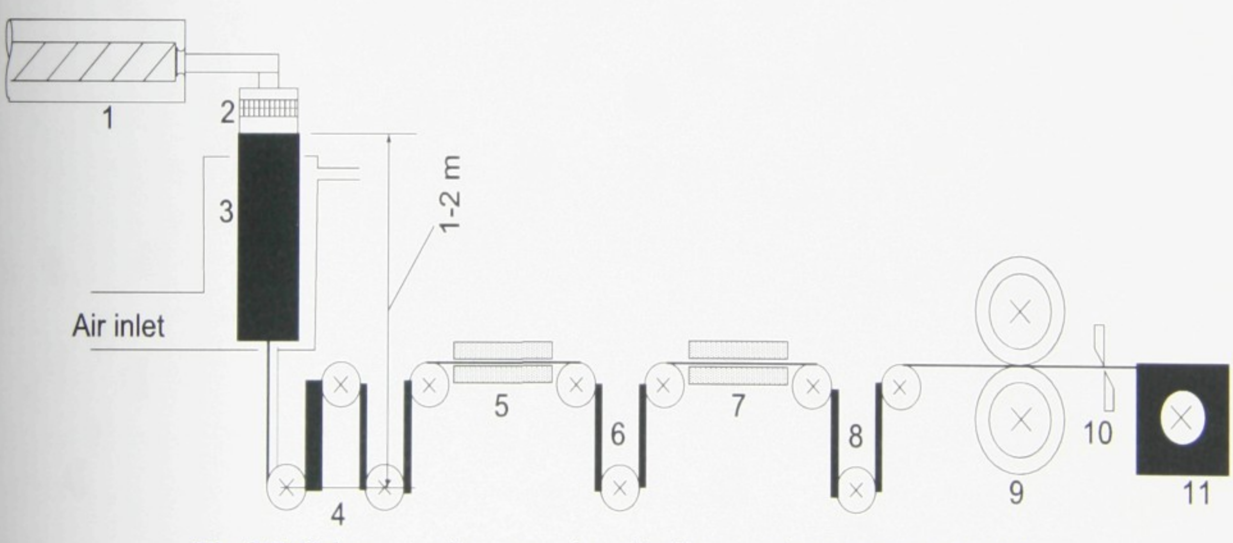


Fig 2.7: Schematic diagram of staple fibre production unit of POP

1-extruder, 2- spinning pack, 3-Ouench duct, 4.6.8-Drawing tensioning, 5-hot stretching, 7-stabilizing, 9-crimper and 10-cutter and winder.

2.1.5 Applications

Because of its superior performance characteristics and comparatively low-cost, POP fibre finds extensive use in the nonwovens industry. POP is a very important fibre in nonwoven processing and dominates in many nonwoven markets. The main application areas include: nonwoven fabrics, particularly absorbent product cover stock markets, home furnishings and automotive markets. It also used in industries under purification processes. It also used automotive industries and more. [5]

2.1.6 Other Properties of Polypropylene

In general, POP fibre has excellent chemical resistance to acids and alkalis, high abrasion resistance and resistance to insects and pests. POP fibre is also easy to process and inexpensive compared to other synthetic fibers. Its low moisture absorption helps aid the quick transport of moisture. [5]

2.1.7 TECHNICAL DATA OF POLYPROPYLENE FIBRES

2.1.7.1 *Mechanical and thermal properties*

Physical state: Solid, as fibers, crystal white in Colour

Fusion interval: 119ºC - 170ºC

Ignition temperature: >360ºC

Density: 0.85 - 0.93 g/cm3

PH: Not applicable.

Water solubility: Not soluble.

Solubility in other substances: Soluble in aromatic solvents at high temperatures.

Salt, acids and alkaline resistance: High.

2.1.7.2 *Stability and reactivity*:

Stability: Stable under normal circumstances.

Special conditions to avoid: Keep away from sources of heat. Avoid accumulation of little particles (scrap), especially in air-filled mechanisms.

2.1.7.3 *Ecological information:*

Environmental persistence/ degradation: The substance is not degradable. However it can be recycled.

Smooth

2.1.7.4 Handling information

POP is not a risky product, it suitable for domestic handling. No human health or ecology risk

Extinguishing methods for fire: Water, foam, CO^2, dry extinguishing methods. Dangerous products from thermal decomposition: It decomposes at temperatures higher than 320ºC, producing water, CO^2, and in case of incomplete combustion is formed CO. Its combustion produces irritating smokes.

2.1.7.4.1 Precautions of use and storage

Avoid accumulation of electrostatic charges and ignition sources. Use floor ground against static electricity. POP fibers should be stored in a dry place similar to cement conditions. Keep away from sun light.

2.1.8 Microscopically Images (non twisted)

- Images Of Polypropylene

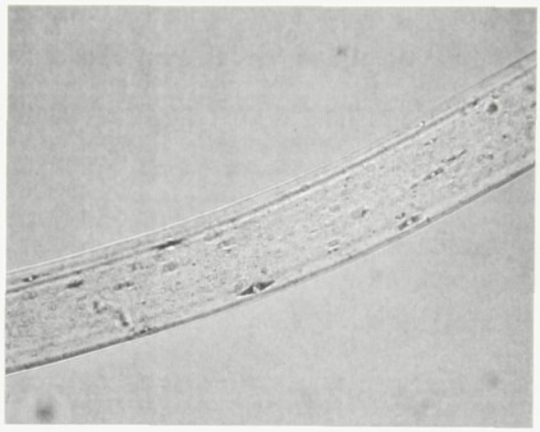


Image 1 : 20X0.6 light microscope

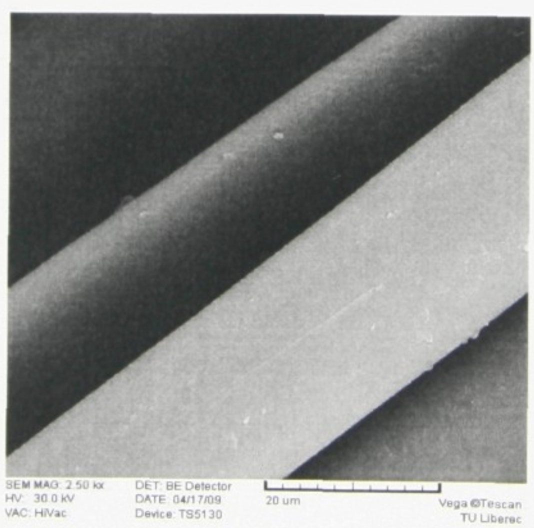


Image 2: 30kv electrical microscope

2.1.9 DSC Value Measurement

DSC is an abbreviation of Differential scanning calorimeter. It is an instrument use to determine the temperature changes and the impact of thermal conditions.

There are compounds that give heat and those compounds are called exothermic compound. And others are absorbing heat energy and are called endothermic compound. Heat flux and temperature gradient are used to evaluate thermal effect of the compound.

Graphical recorded relationships of a specific compound dependence on temperature gradient are observed as the heat flux changes. The temperature increases as the heat flux increases until the compound reaches the liquid state, then cooled down as heat flux decreases until the compound reaches the crystallization or solidification state. [6]

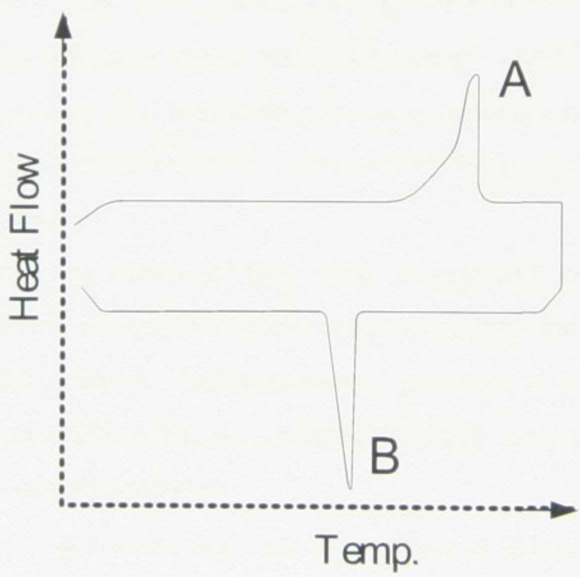


Fig. 2.8: Typical DSC curve

A – Melting point (Tm)

B – Crystallization point (Tc)

2.1.10 Modified Polypropylene Multifilament fibers

Polypropylene is the second world polymer product that is used globally. It is also a cheapest compound or polymer. POP fibre cost is 50% less polyester fibers and nylon fibers cost per kilogram. Latest technological are employed daily to modify POP yarns for different end use produced.

2.1.10.1 <u>The main methods of modification to optimise POP multifilament</u>

- chemical modification,
- Physical modification.

The most common chemical modifications are

- isotactic polypropylene discovered structures and take place in this units
  - **Refinery**
    - Crude oil refineries use range of crude oil grade. Some of this crude oil have high gas yield. Most refineries in South Africa were design to process 50% Iranian Light and 50% Iranian heavy crude oil to produce a range of 5 to 15 % mass product of a total refinery. When a refineries runs a blended crude oil with high solids like Venezuela crude oil, gas yield do drop to minimum point depending on a bland ration. Blending with bonny light (Nigerian crude oil) light crude oil the gas yield increases up to 25%.
  - **Gasification Refinery**
    - A gasification refinery uses Coal (any range of graphite coal), steam and addictive. SASOL plants were design to process coal to produce more than 40 % Gas mass product of a total refinery. Refinery normal produces a constant range of gases at normal operation condition. But the quality changes as operational conditions changes.
  - **Polymerization of polypropylene**
    - Polymerization process takes place on the surface of the catalyst inside the reactor. The system is capable to recycle gases that did not polymerized. But the change in operation condition, quality feed gases from refinery and quality of the catalyst does affect the polypropylene product quality.

The most common Physical modifications take place in these units

- ***Filament production***
  - **Extrusion**
    - At extruder uses polypropylene polymer chips, heat them to an extrusion operation condition. Pressure or force is used to push melted polymers to a spinning pack. The filament are cooled down and drawn. The nozzle size of spinning pack, cooling ratio, drawing speed and heat energy use are responsible on the mechanical properties of the filament.
    - Drawing tensioning, hot stretching, stabilizing, crimper and winder do have also the major role play. The operation condition can change also the quality of the polypropylene filaments. [15]

Benefits of chemical and physical modification are;

- changes in a relative molecular mass and structure,
- change of cross-section,
- change drawing and fixation conditions,
- arrange crystallization,
- reduction of oxidation,
- Controlled surface heat and light sensitivity.
- lower tendency to pilling,
- shrinkage of fibers for a preparation of bulky structures,
- improved orientation of a filament

2.1.11 Separation and simple basic Reaction

- Crude oil refinery
  - Crude oil is a mixture of hydrocarbon. Consist of short chain, meddle chain, long chain and complex chain of hydrocarbon. Distillation and strippers units are used to separate according to molecular weight and boiling temperature. Reactors (e.g. vis. breakers, fluidized catalytically cracking (FCC) and other) are use to break long and complex chain of hydrocarbons to a required specification. Also Reactors (e.g. reformation unit, polymerization unit, isomerisation and other) are used to rearrange and build up hydrocarbon from light molecule hydrocarbon to form a required specification.

1. **Separation**

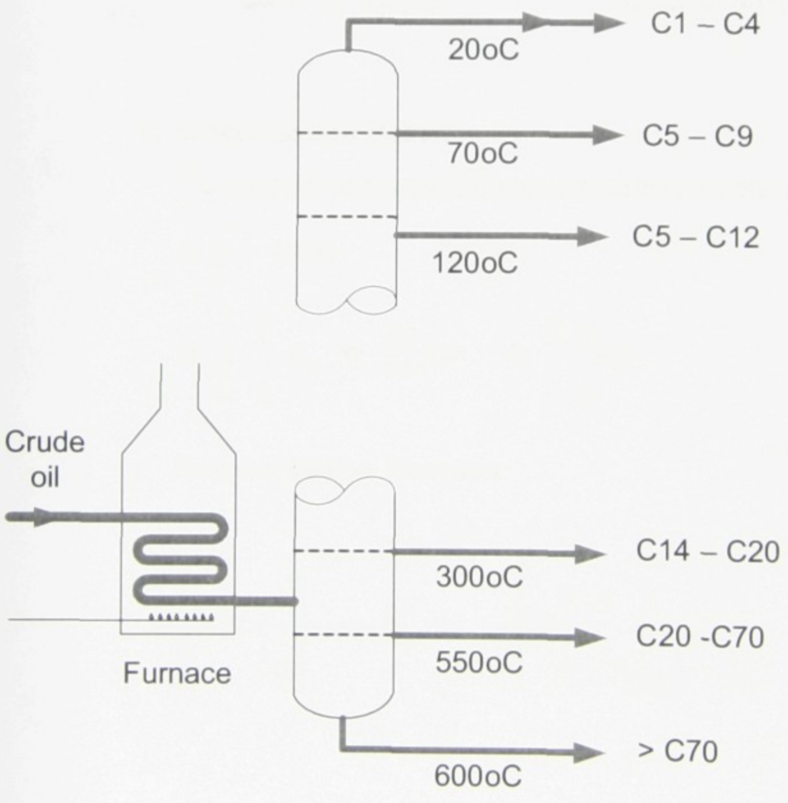
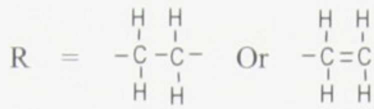


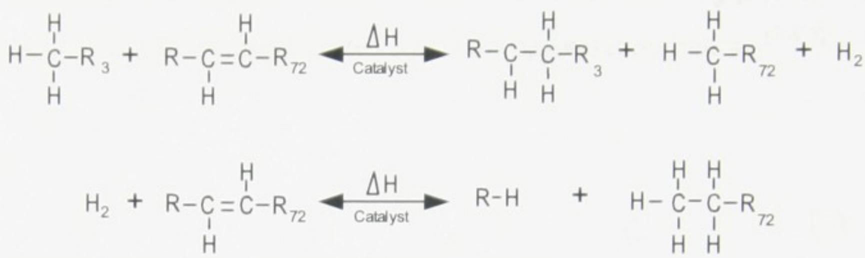
Fig. 2.9: Typical Distillation column

2. Basic Reactions

Let Assuming that R is representing ethane or ethylene group as shown below.



a. Hydrocracker and refinery polymerization Reaction



Build up process Break up process

b. Isomerisation Reaction

To simplify isomerisation is molecule restructuring

E.g. (ABC - BCA)

c. Polymerization Reaction

2.2 *GEOMETRICAL PARAMETERS OF FIBRES*

2.2.1 **Yarn fineness and diameter** *(monofilament or multifilament)*

The fibre or filament fineness (t) is expressed in tex or dtex. Tex is actually a fibre mass (m) in grams per length (l) in kilometre. There are a number of systems and units that expressing yarn fineness. The common units for ISO standard are fibre fineness (t), bundle fineness (T) fibre mass (m), fibre bundle mass(M), fibre length(l) bundle length (L), fiber density (ρ), fiber volume (V) and equivalent cross-sectional area (A) represented by (s) on the equation below. [2 & 5]

$$t = \frac{m}{l} = s\rho = \frac{\pi \rho d^2}{4} \quad (1)$$

Assuming that the fiber equivalent cross sectional diameter is circular

t – Fineness of the filament [tex],

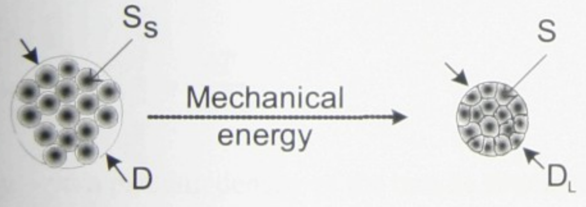
m – Mass of the filament [g],

l – Length of the filament [km],

ρ - Density of the filament [g/m^3], and

s - Cross-sectional area of the filament [mm^2].

d – Diameter of the filament [mm].



Assume that mechanical energy or equipment is used to close the air space between filaments. For multifilament yarn fineness bundle (T) the following mathematical expression or equation is used to determine the equivalent fibre diameter (D) from determine cross sectional area (S)[2].

$$T = \frac{M}{L} = S\rho = \frac{\pi \rho D_L^2 L}{4} \quad (2)$$

$$D_L = \sqrt{\frac{4T}{\pi\rho}} \quad (3)$$

D_L = this is the slowest yarn diameter without air gaps in between fibers.

$$n = \frac{T}{t} \quad (4)$$

T – Fineness of the bundle filament [tex],

t – Fineness of the single filament [tex],

n – Number of filament in parallel fiber bundle [-],

M – Mass of the bundle filament [g],

L – Length of the filament [km],

ρ - Density of the filament [g/m^3], and

S – Sum of cross-sectional areas of the filament [mm^2].

D – Diameter of the bundle [mm].

When twisting yarn, the fibrous are compressed to form what is called a substance diameter (d_s) from real yarn diameter (D) that assumption. From real yarn diameter and substance diameter it's possible to define yarn packing density (μ) as a ratio between filament volume (V_f) and the total yarn volume (V_y).

$$\mu = \frac{S}{S_s} = \frac{D_L^2}{D^2} = \frac{4T}{\pi D^2 \rho} \quad (5)$$

μ – yarn packing density of the bundle filament [-],

V_f – Ratio between filament volumes of the bundle filament [mm^3],

V_y – total yarn volume of the bundle filament [mm^3],

ρ - Density of the filament [g/m^3],

d – Diameter of the filament [mm].

D – Diameter of the filament [mm].

The yarn diameter can be derived at the following equation,

$$D = \sqrt{4T/\mu\pi\rho} \qquad (6)$$

2.2.1.1 Yarn twist

Bundle is more than one fibre or filament. Twist process is a process used to bind filaments or yarn together in a continues strand, accomplished in spinning or plying operation. The direction of a twist may be right, described as Z or left described as S twist.

Theoretical a Packing density of a yarn increases with the increasing of a yarn twist. In a multifilament yarn consist of fibrous with a constant tex, assume that substance diameter increases as tex of a yarn increases.

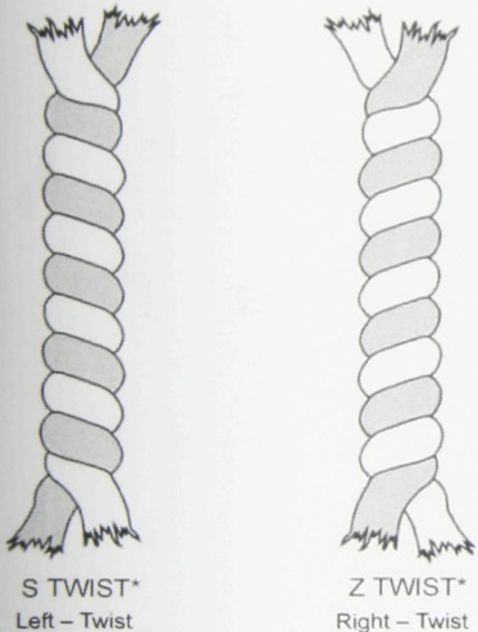


Fig. 2.10: Typical Distillation column

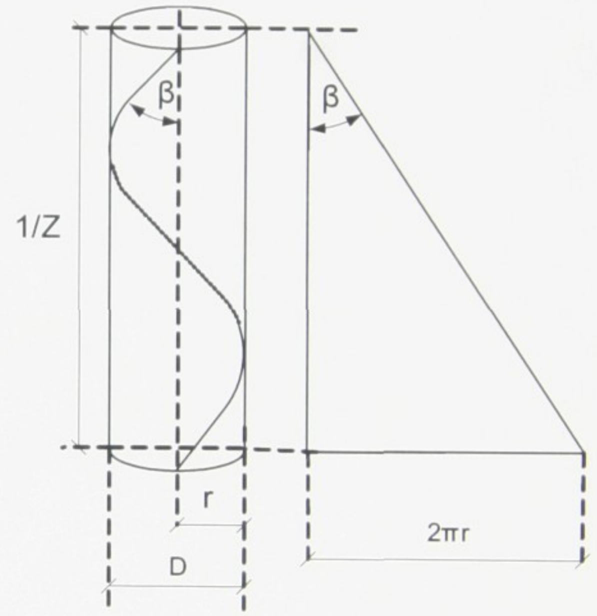


Fig. 11: ***Yarn helical model***

- **Simple Helical Model**

The manners in which the fibers are packed in the yarn cross sectional area are very important to effect of frictional contract of fiber on yarn properties. If the fibers are not closely packed the fibers moves independent and the yarn look bulky and the yarn diameter is larger due to air gaps between fibers.

Twist intensity (k) is dimensionless due to the fact that it is a product of a twist [m^{-1}] and yarn diameter [m]. In most cases it is multiply with the pi (π) In this case, the twist intensity is also the tangent of angle β ($Tg\,\beta$) of this fibre. See fig 11.

$$Tg\,\beta = 2\pi r Z = DZ\pi = k \quad (7)$$

β - An angle, slope of general twisted fibre (helix).

r– Radius of a general twisted fibre

k - Twist intensity, Diameter (D), Twist coefficient (a), Packing density (μ)

When Length of the twisted yarn is described as 1/Z

2.3 TENSILE STRESS STRAIN

2.3.1 Stress-Strain

If a fiber is subjected to tensile loading, then demands are made on both its strength and elongation. Strength and elongation are therefore inseparably connected. This relationship is expressed in the so-called stress/strain diagram (force/length change diagram). For polypropylene stress stain curve differ into three types due to the fact that this polymer has three different steric structures and during spinning process. During spinning process, filaments or yarns are oriented different. The degree of orientation achieved by drawing the filaments during spinning and extrusion process influences the mechanical properties. During production process the greater the degree, the higher the tensile strength and the lower the elongation. There are number of factors that affect strength of the yarn or filament like part geometry, loading, constraint conditions and more.[7]

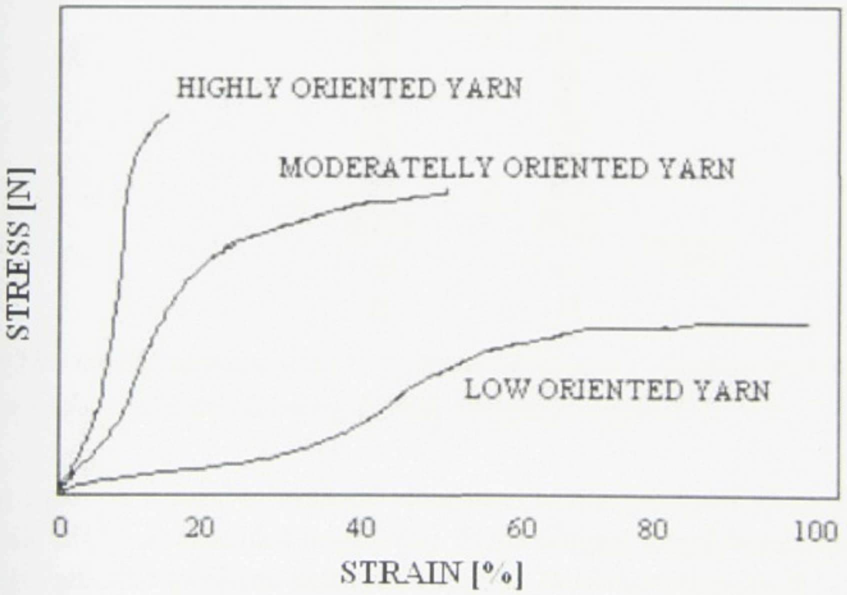


Fig 2.12*. (a) Stress stain curve for POP filament or yarn at different oriented*

It is important to consider the relevant stress-strain behaviour that corresponds to the primary (and, commonly, the multiple) load state(s) at the operation temperature and strain rate. [7]
The figure below depicts the tensile bar test sample and the deformation under a pre-set, constant load. The stress (σ) and deformation at break (ε) are defined as:

$$\delta = \frac{F}{t} = \frac{F}{A\rho} \tag{12}$$

(F)– Force applied to a load, while *(A)* is a cross sectional area of the specimen.

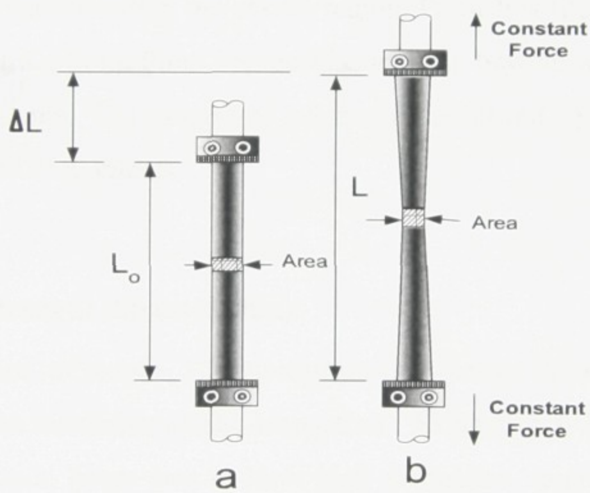


Fig 2.13. *(a) The tensile test bar with a cross-sectional area, A, and original length L_0. (b) Tensile test bar under a constant loading, F, with elongated length, L.*

The following equation is used to evaluate elongation of the specimen. ($E_{\%}$) is a elongation in percentage while *(Δl)* is an extended length. *(lo)* is the original length before testing process, (l) is the total length after the specimen extended it length. *Deformation at break*

$$\varepsilon_n = \frac{\Delta l}{l_0} \tag{13}$$

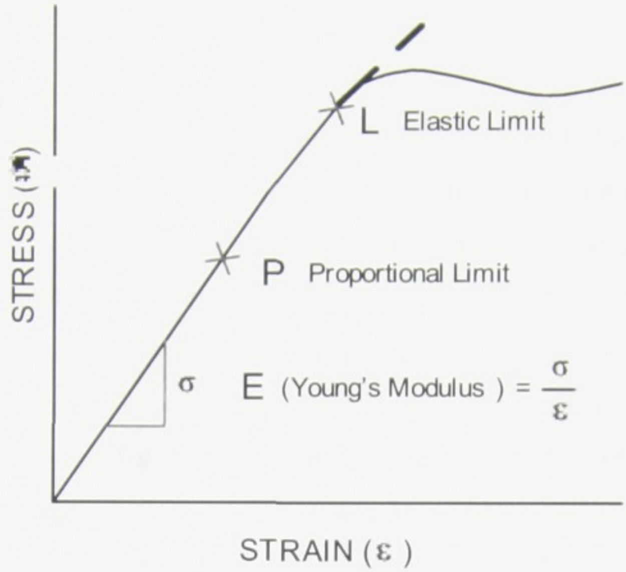


Fig 2.14. Stress-strain curve for a typical thermoplastic polymers.

Horizontally to show the details within the elastic region. Point P is the proportional limit, most often used as the design strain limit. Point I is the Elastic limit, beyond which the plastic part will not recover its original shape. The degree of orientation achieved by drawing influences the mechanical properties of POP filaments.

2.3.2 Elongation and strength (Stress-Strain)

Elongation is a deformation of length. The elongation is a part of the extension through which the fiber does not return on relaxation elastic elongation. Elongation is specified as a percentage ratio. Polymers or manmade fibers tern to have high elongation compare to natural fibers for example, polypropylene (polymer) = 65 - 100% depending on production orientation; cotton = 6 -10%; wool = 25 -45%. [1]

2.4 THERMAL ENERGY & SHRINKAGE

The fiber, yarn or filament shrinkage is generally considered as a huge factor in the textile products. Also the structure of the fabrics, yarns or filament that resulting into dimensional changes becomes a waste if shrinkage was not taken into consideration. There are many mechanisms that cause textile structures to shrinkage. Naming the fewer, thermal shrinkage (dimension of a textile specimen changes when heat radiation or conventional energy is applied), relaxation shrinkage (dimension of a textile specimen changes when recovery from deformed), swelling shrinkage (dimension of a textile specimen changes when swelling) and more. All the mechanical changes of the specimen do take place at a certain thermal relationship called thermal kinetic curve, where a degree of change take place a certain temperature. [1, 15 & 16]

2.4.1 Thermal Properties

Polypropylene fibers have a softening point in the region between range of 115 °C and 150°C and a melting point at 160-170°C. At temperatures of 70°C or lower, POP fibers retain their excellent flexibility. At higher temperature (but below 120°C) POP fibers nearly remain their normal mechanical properties. POP fibers have the lowest thermal conductivity of all commercial fibers. In this respect, it is the warmest fibre of all. The thermal conductivity of common textile fibers is shown in table below. [2, 3, 4]

Table 2.4.1.2: *Thermal Conductivity of textile fibers*

Material	Thermal Conductivity
Air	1.0
POP	6.0
Wool	6.4
Acetate	8.6
Viscose	11
Cotton	17.0

2.4.2 Thermal Shrinkage of Polymers

Polyolefin are inherently prone to degradation by oxidation and heat radiation, which become more serious as the temperature increases. This phenomenon does affect the production of polymers during the extrusion and the strength. The oxidation breakdown of POP does get accelerated by light, and the unprotected filaments are sensitive to heat and ultra-violet radiation.

During the production of yarn, the filaments used are drawn at high temperatures in order to orientate the molecules in the length direction of material. Afterward, heat cause a certain molecular disorientation coupled with shrinkage in the length direction that phenomena called heat shrinkage.

2.4.3 Thermal Shrinkage

Thermal Shrinkage is generally defined as an irreversible shortening of fibre length when exposed to a heat radiation. The energy needed to cause shrinking is called the shrinkage work and the stress developed during the shrinking is called the shrinkage stress (mechanically). Under thermal conditions is called thermal shrinkage stress.

In general, solids expand on heating and contract on cooling space, but plastics mainly polymers does expand on heat and get deformed, when cooling does not return to its original shape.

The strain associated with change in temperature will depend on the coefficient of thermal expansion of the material and the magnitude of temperature drop or rise, special on the crystallized region. Under extreme high temperature conditions, ordinary crystallized region, structures do suffer more and little or no distress from changes in ambient temperature. [1, 5 & 15]

2.4.3.1 Effective Thermal Shrinkage

When analyzing shrinkage there are aspects that are taken into consideration like shrinkage effective. This means shrinkage (length change) of a specific material take place at a given particular energy (temperature change), with respect to a time-period at a constant tension.

Mathematical expression; shrinkage is amount of shortening of a rod or material after exposed to a particular environment at a particular time.

$$S[\%] = \frac{(L_o - L_s) \times 100}{L_o} \tag{14}$$

Where L_o is an initial length and L_s is shrink length.

2.4.3.2 Effective Thermal Shrinkage force

When analyzing shrinkage force of a yarn or specimen, there are aspects that are taken into consideration like shrinkage effective and force applied. This means shrinkage (length change) of a specific material take place at a given particular energy (temperature change), with respect to time-period at a constant yarn or specimen tension force.

In polymers fibers have two basic contraction mechanisms leading to macroscopic shrinkage that can be distinguished. These are amorphous and crystalline contractions or regions. The other shrinkage mechanism is the crystalline contraction. Is occurs especially in differential shrinkable fibers. This type of contraction is provoked by rearrangement of the crystalline phase, connected with the formation of "perfect" crystallites with folded chains. [1, 5 & 15]

2.4.3.3 Maximum Thermal Shrinkage

The maximum thermal shrinkange is maximum shrinkage of a specimen. At higher temperatures, most specimen provide maximum shrinkage. Amorphous region or part has most effect then crystallised part or region during shrinking and drawing.

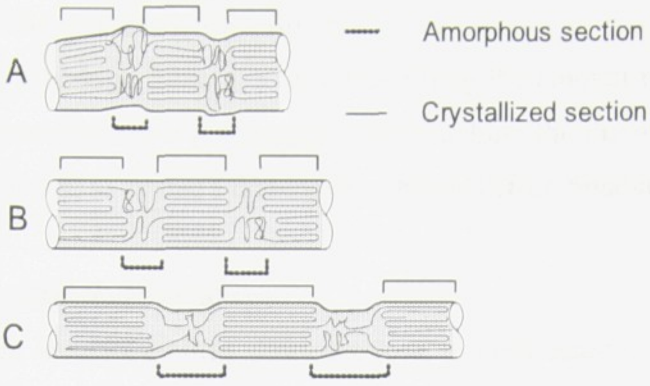


Fig. 2.15: ***shrinking and drawn filament***

A - Shrinked fillerment, B- normal fillerment, C-Over drawn fillerment or yarn (all have amorphous an crystallized region.

2.4.3.4 Maximum Thermal Shrinkage Force

Crystallized regions have less effect during shrinkage and drawing. Thermal shrinkage maximum force is a maximum potential shrinkage point of the yarn or fillerment force at a particular environment. A maximum drawing force is a point at which the fillerment or yarn snap off when it further drawn at maximum force of yarn or filament.

When the fibre is allowed to shrink during heat-setting, there are no external constraints to structural re-organization and a significant part of the residual stresses present in the non heated drawn yarns relaxes. [1, 2, 4, 5 & 15]

2.4.3.5 Residual Thermal Shrinkage

The residual thermal shrinkage is a term describing the amount of shrinkage remaining in a fabric, yarn, or filament after finishing the thermal process, expressed as in percentage of the dimensions change before finishing the thermal process. The potential shrinkage that remains in a fibre, yarn or fabric after treatment designed to reduce or eliminate shrinkage. During measuring of effective shrinkage, residual is also measured after.

2.4.3.6 Residual Thermal Shrinkage force

The residual thermal shrinkage force is a term describing the amount of a force remaining in a fabric, yarn, or filament that cause a shrinkage after finishing the thermal process, expressed as in force applied or required to course a dimensions change before finishing the thermal process.

2.4.3.7 Minimum Thermal Shrinkage

A shrinkage minimum is different than shrinkage loss, in most cases is being used as similar. A shrinkage minimum means a specific material is shrinking at minimum rate as compare to it potential shrinkage at a given point. A shrinkage loss is a shrinkage energy that is gives out at specific period, special take place unexpectedly.

2.4.3.8 Thermal Sensitivity

Sensitivity is the ability to respond to affective changes in a particular environment. Polymers are too sensitive at high temperature above the glass transition temperature to melting temperature. Sensitivity shrinkage has linear relationship below the glass transition, mostly polymers. Sensitivity Maximum shrinkage rate is defined as a tangent of the straight line from least regression (A). For the wide temperature intervals the behaviour of fibre shrinkage R_s with respect to temperature T can be expressed approximately by the formula below. [1, 5 & 15]

$$R_s = AT + B \qquad (15)$$

Where A and B are constants

A is a slope of a straight line

B is a Maximal shrinkage rate intercept of a straight line

3 EXPERIMENTAL PART

3.1 Experimental background

Since the main objective was to evaluate POP multifilament yarn for technical application. In order to determining the yarn characteristics for technical application, one should evaluate the mechanical properties.

The second objective is to evaluate the compatible yarn for a development of ion exchange membrane using a polypropylene multifilament yarn. Currently an existing ion exchange membrane is made of Polyester monofilament yarn. Due to durability of polyester, polypropylene monofilament is the substitute material to develop the ion exchange material, but POP multifilament is cheaper and available.

3.2 Characteristic of used material

Sampling was conducted on 100% polypropylene multifilament yarn. A Material specification from the supplier was provided. A data sheet clearly state that a yarn is 100% polypropylene Multifilament yarn, Tex 56/16 fibrous not twisted, and its Cristal white in colour.

Based on the main objective, yarns were twisted as follows 400turns/meter, 440turns/meter 800turns/meter, and 1200turns/meter from supplied untwisted yarn. Two type of twisting were used and those technologies were ply twister and ring spinning without draft. The twisting of yarns ware done at the TUL weaving laboratory and the twister tester was used to confirm the twist count. (CSN 80 0701)

3.3 Instrument and equipments used during experiment

- Scissor
- Warp reel machine
- Mass balance
- Material Testing Machine
- Thermal Shrinkage rate Tester
- And more

3.4 Used fineness testing equipments

A fineness for all provided twisted and untwisted multifilament Polypropylene yarns were carried out in the textile material testing laboratory at room condition, (23°C temperature and 1ATM). A hank machine (warp reel machine) was used to measure the length of POP yarns.

Hank Machines is an electrical machine operates at automatically bases. Press and hold for 5 second a tart button, then the machine will collect an accurate one meter length yarn. Mass balance was used to measure a mass or weight of 100m POP yarns.

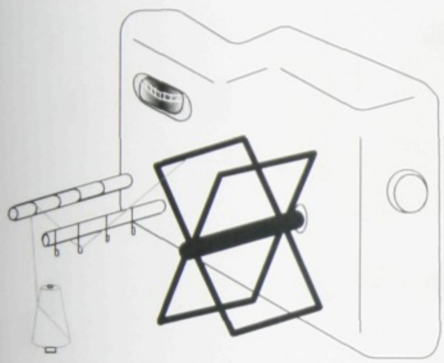


***Fig 3.1**: wrap reed and yarn from bobbin*

***Picture 3.1**: electrical mass balance*

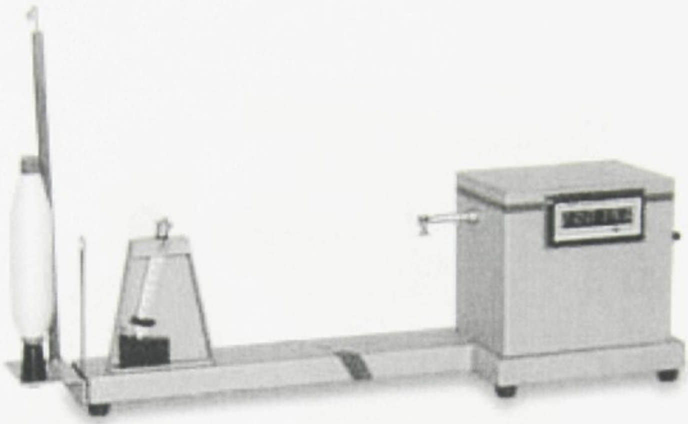
Procedure for operating a wrap reed and mass balance CSN80 0071

- A bobbin yarn was place on a rail bobbin bar.
- Yarn from bobbin was attached to a warp reed roller that it's responsible to collect a 1m yarn.
- Five runs per yarn type. (zero twist, 400t/m, 440t/m, 800t/m, 1200t/m)
- Yarns ware place on a mass balance scalar area separately (individually) before tare.

All mass results were noted and recoded for all POP multifilament yarns, fineness were calculated accordingly.

3.5 Used of Twist tester

Twist tester was used to evaluate counts for all twisted polypropylene multifilament yarns. This equipment is capable to determine counts of S twist and Z twist. It only takes measurement of half a meter yarn and provide values of twist count per meter.



Picture 3.2: *Material Testing Machine*

During practical experiment, 30 runs were adequate to provide precise result. All twisted polypropylene yarns have consisting of the same number of fibrous (16) since they were all from untwisted polypropylene multifilament yarn. CSN 800701

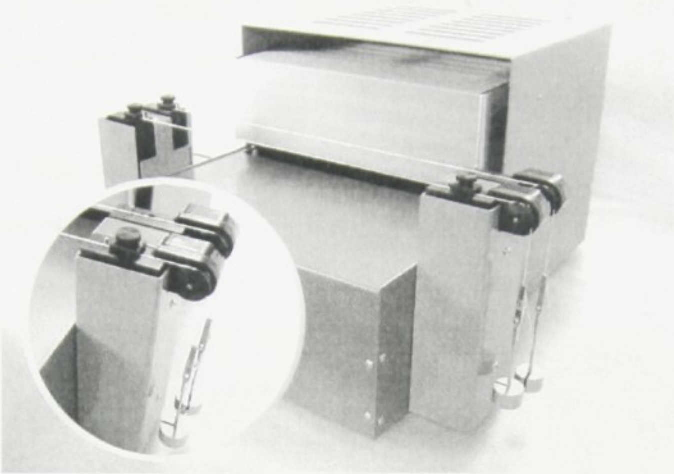
Machine Setting used for twist count tester for POP twisted yarn

- Since all yarns were less then 9.1tex the pretention weight used was 3grams.
- All twisted yarns were Z twist, the instrument speed was set at maximum for all yarns.

3.6 Use of Thermal shrinkage tester

The Thermal Shrinkage rate Tester (TST 2) was used determine the thermal shrinkage; shrinkage force of yarns (twisted and not twisted) while being heated at a preset defined temperature for a specified period. TST 2 is an automatic apparatus, that is too sensitive to surrounding due to it design and perfection operation performance. The precise temperature control of the heater, guarantee stable testing conditions and very accurate and reproducible results.

The system is automated determination of thermal shrinkage and shrinkage force according to ASTM D4974. The system is modernized to produce thermal shrinkage effective, residual and maximum. The instrument is computerized, most results were analyzed accordingly



Picture 3.3: TST 2 Tester

During practical experiment, one minute was an adequate time. From a POP multifilament Polypropylene yarns, plus 0.5 minute time for residual. 20 series of runs were done at different temperature 50, 70, 90, 100, 110,120, and 140°C for each set of twisted and untwisted yarns. Due to the shortage of other set of yarns 20 series of runs were recommended. Two parameters that were taken in to consideration and those parameters were thermal shrinkage and thermal shrinkage force. The maximum shrinkage rates were calculated from those calculated thermal parameters. The pre-stress of 0.2 g was selected based on the POP testing standard.

Hand pedals were used to operate clampers that hold the yarns ends.

Procedure for operating a TST2 for thermal shrinkage rate and thermal force

- *Thermal shrinkage rate:* POP yarn fix clamped on one end and the pretension weight of 200g was free hanging on other side.
- *Thermal shrinkage force rate:* POP yarn fix clamped on both end after pretension weight of 200g was free hanging on one side.
- When pressing the start testing button on the PC screen. The heater automatically moves to a measuring position and cover the overall measuring length of the sample.

3.7 Electrical microscope and NIS Element microscope

The electrical microscopes ware used to view the microscopically effect after spinning of yarns.

Picture 3.4: Microscope, processer and personal computer.

During practical experiment, POP multifilament Polypropylene yarns, samples were taken from all twisted and untwisted yarns. Five samples from each yarn type were adequate.

Procedure for operating a microscope

- POP yarn fix clamped on both ends
- The microscope set on the scale of 4 X 0.6 at 3.67um/Pixel
- Images were viewed and analysed using the NIS element Software
- Note: only the qualified laboratory technician was allowed to operate the electrical microscope.

4 RESULTS & DISCUSSION

The objective was to evaluate mechanical properties of Polypropylene multifilament used in technical application (laminated membrane application). And the project was initiated by one of the Czech membrane company.

4.1 FINENESS

Czech Standard CSN EN 12751 (800070) and CSN EN ISO 2060 (80 0702) ware used to sample and measure the yarn fineness for non twisted and twisted multi filament polypropylene yarns.

Four different types of twisted yarns (400t/m, 440t/m, 800t/m and 1200t/m) were produced from a supplied non twisted yarn of 56 dtex with 16 fibrous.

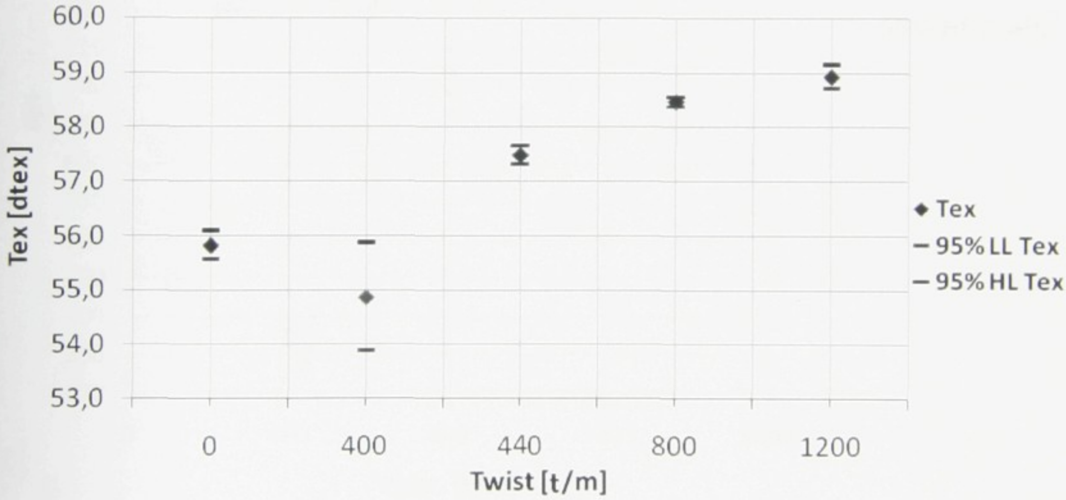


***Fig 4.1.1:** fineness for all POP yarns (non twisted and twisted yarn)*

From a figure above, result shows that a measured fineness value and provided information value from a POP suppler were identical (untwisted yarn). Fineness of 400t/m yarn was statistical dependent to a fineness of 0t/m (untwisted yarn) and the value was 55 dtex which was a lowest fineness value. Yet the fineness of 440t/m, 800t/m and 1200t/m yarns were statistical independent, and values were57.5 dtex , 58.5dtex and 59dtex consecutive.

Fineness for twisted yarns from ring spinning technology was increasing as the twist count increases. From the figure above, it was clear that ply twister technology does stretch or draw up the filaments. The ring spinning technology does not stretch or draw up the filaments.

4.2 YARN TWIST

Yarn twist sampling was done using CSN 800701, standard and recommended procedure. 30 samples per yarn were tested.

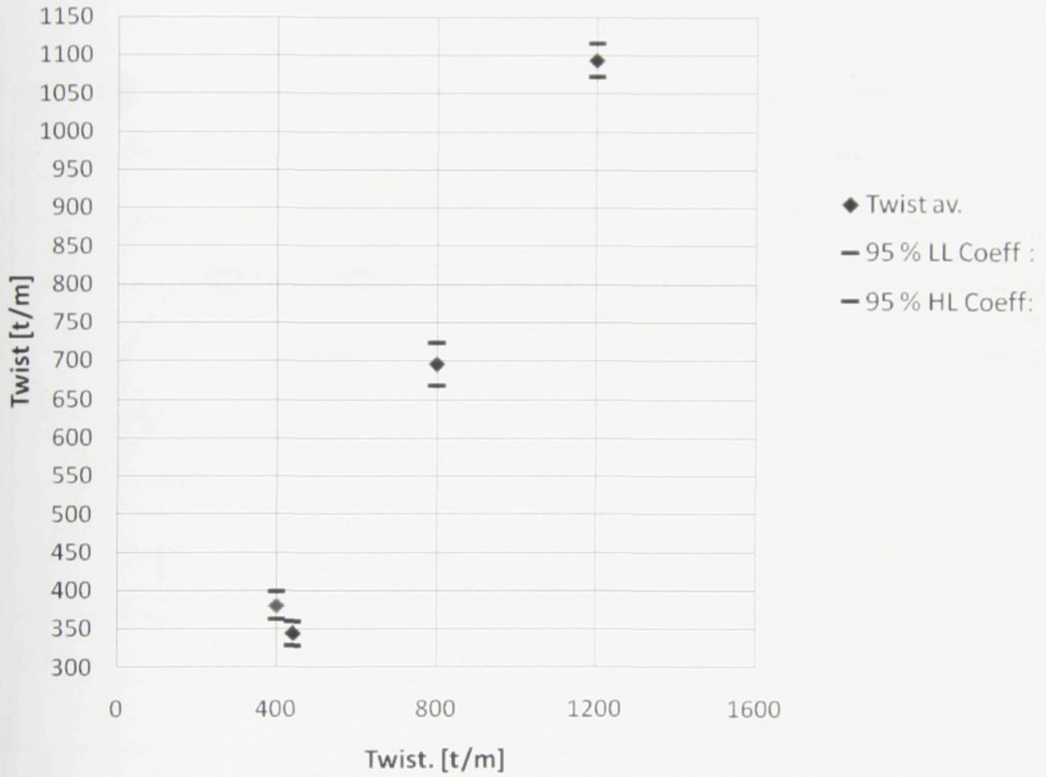


Fig4.2.1: *POP multifilament yarns at different twist (400t/m,440t/m, 800t/m, and 1200t/m)*

Figure shows that all twisted set were below the required amount of twist count .The values measured per average were 380 t/m for 400t/m required, 344 t/m for 440t/m requried,696 t/m for 800t/m required, 1094t/m for 1200t/m required. 400t/m twisted yarn sets was 5% less accurate and deviate below a targeted twist count. 440t/m, 800t/m and 1200t/m were 14%, 14% and 9% consecutive. In this cases technology was a factor, ply twisted was more accurate the ring spinning.

4.3 STRESS STRAIN

This section is divided into two parts, the first part based on the twist effect on the POP strength force and the second part based on the bundle effect on the POP strength (force).

EN ISO 2062 was the standard procedure used to evaluate and operate the instrument used to measure stress train and other mechanical properties that are associated with stress stain.

4.3.1 *Part 1*

Evaluating POP Stress strain at different twist (0t/m, 400t/m, 440t/m, 800t/m, 1200t/m)

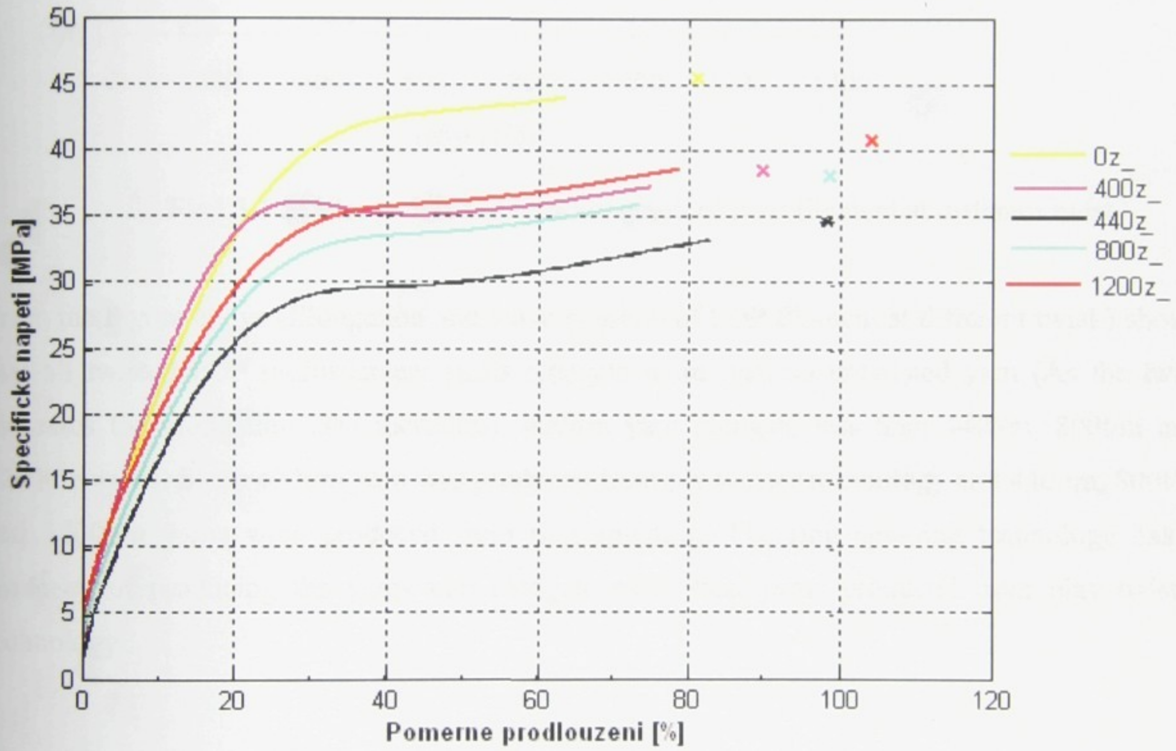


Fig4.3.1.1 *stress stain Curves for 0t/m, 400t/m,440t/m, 800t/m, 1200t/m*

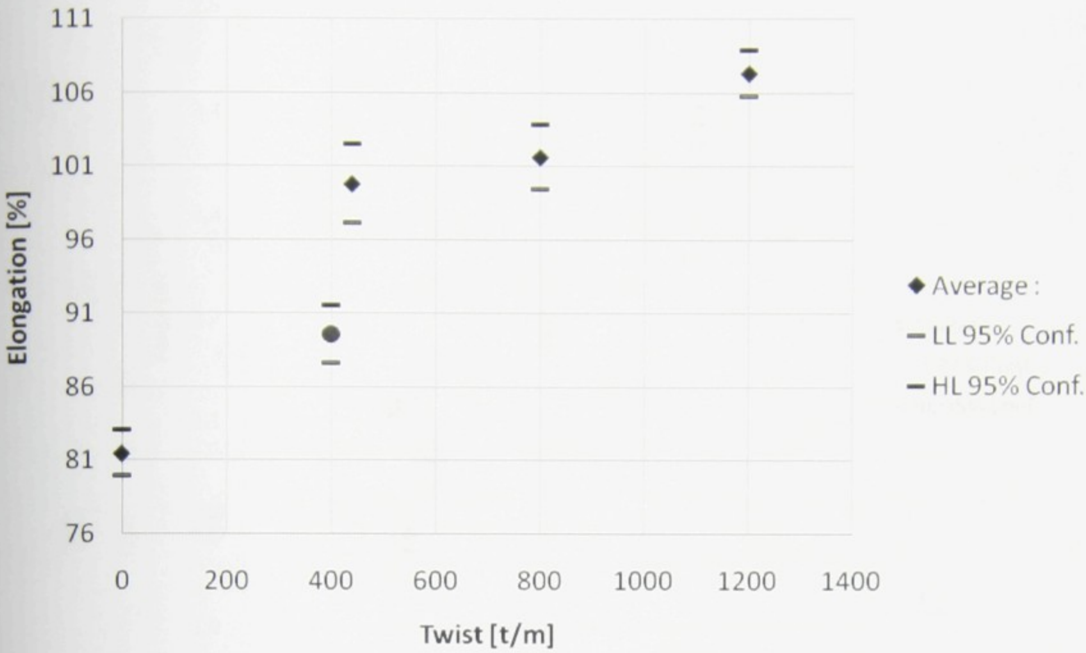


Fig4.3.1.2: Elongation and tenacity graph of POP filament at different twist

From the Figure above (Elongation and tenacity graph of POP filament at different twist) shows that all twisted POP multifilament yarns elongate more than an untwisted yarn (As the twist increases the elongation also increases). 400t/m yarn elongate less than 440t/m, 800t/m and 1200t/m yarns. Since 400t/m yarn was produced from ply twister technology and 440t/m, 800t/m and 1200t/m yarns were produced from ring spinning. The ring spinning technology has a tendency of producing the yarns that elongate more than yarns produced from play twister technology.

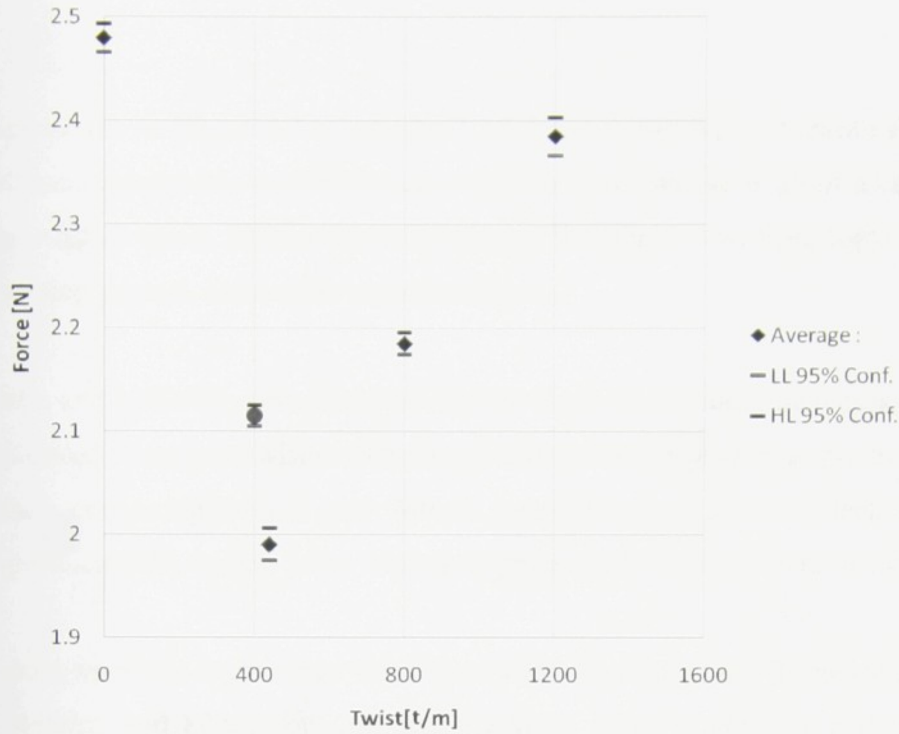


Fig4.3.1.3 *Stress strain force at different twist (0t/m, 400t/m, 440t/m, 800t/m, 1200t/m)*

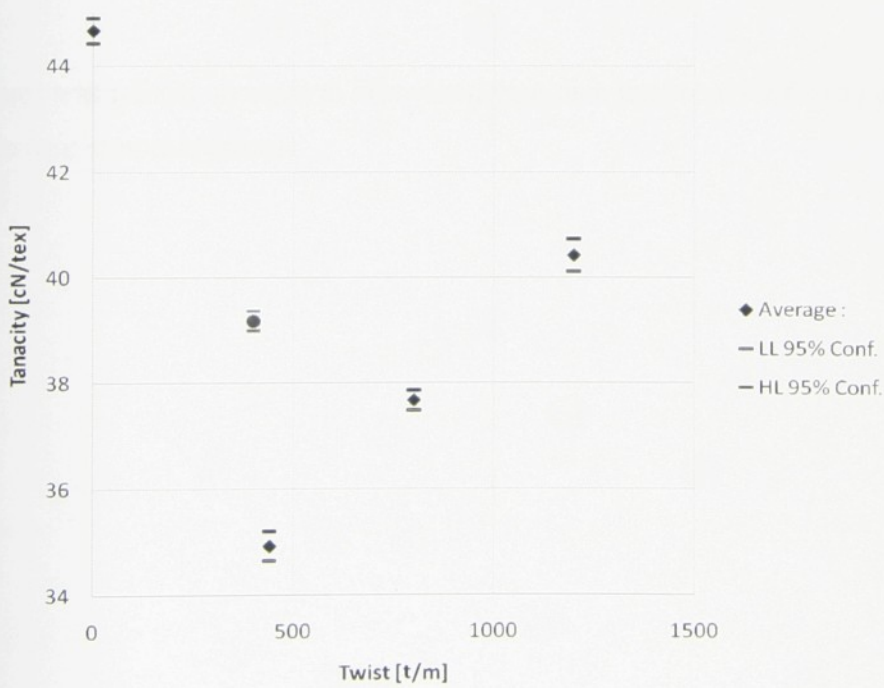


Fig4.3.1.4 *tenacity at different twist (0t/m, 400t/m,440t/m, 800t/m, 1200t/m)*

From the Figures above (figure 4.3.1.1, figure 4.3.1.3 and figure 4.3.1.4) shows that all twisted POP multifilament yarns were weaker than an untwisted yarn (the strength of an untwisted yarn was more the twisted yarns). The strength of polymer filaments are weaken, rupture, fragmented during the twisting process when cohesion and adhesion.

440t/m, 800t/m and 1200t/m yarns strengths increase as the twist count increases. Since 400t/m yarn was produced from ply twister technology and a 440t/m yarn was produced from ring spinning, when comparing 400t/m and 440t/m yarns, the ring spinning technology have a tendency of producing the weaker yarns than yarns produced from play twister technology.

Tenacity of 0t/m yarn was higher than tenacity of all twisted yarns and Tenacity of 400t/m was higher than 440t/m, and 800t/m but less tenacity value when compure it with 1200t/m yarn. Tenacity increases as twist increases from 440t/m to 1200t/m (ring spinning technology only). During the twisting process, filaments are rupture when cohesion and adhesion, that rearrange the structure of the POP multifilament.

If the tex values was remain constant to all twisted yarn then the behavior of Tanacity and stress stain would remain almost identical.

4.3.2 *Part 2*

Evaluating POP Stress strain at different bundles (bundle 1 -10)

During an experiment there were lot of human errors due to the fact that is it easy to operate and monitor one bundle of yarn then many bundle. Those errors were visible during experiment and during evaluating and analysing the results.

Basic noticeable Human errors were;

- to put all yarns at the same tension during testing,
- yarn crossing causing yarn to be pulled at an angle, not parallel
- some yarns were not fully clamped during testing,

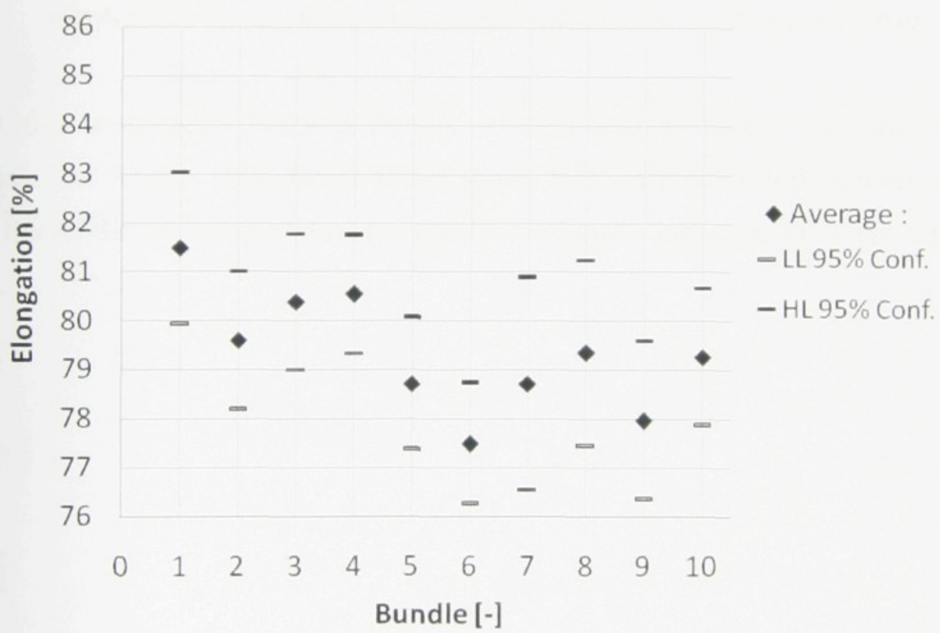


Fig 4.3.2.4: *Elongation for different bundle. (non twisted yarn)*

There were 60 samples per bundle; sampling was done per set of bundles. bundle one (one yarn) to bundle 10 (10 yarns) of untwisted yarns. Result shows that as the bundle increases the elongation decreases.

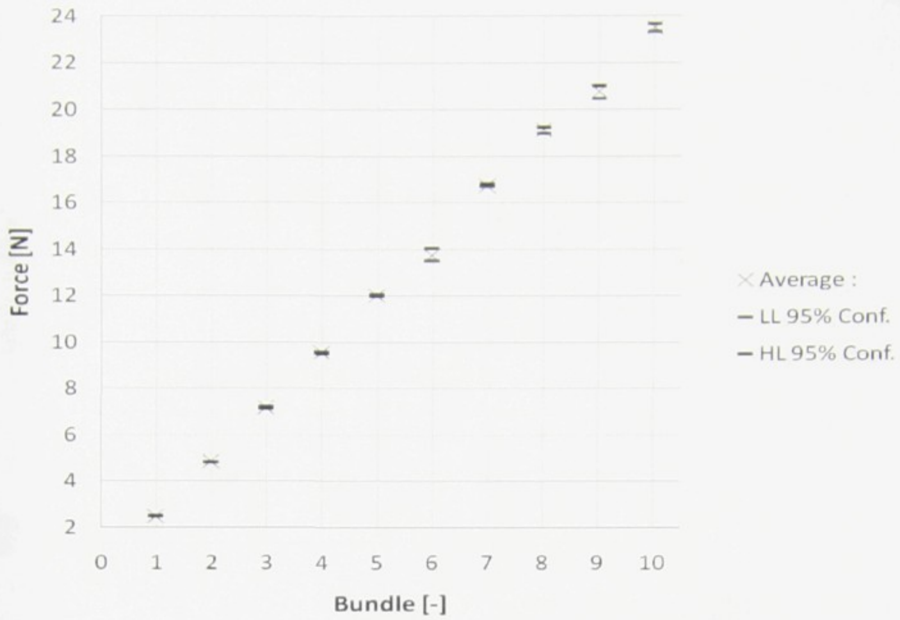


Fig 4.3.2.5: *Stress strain force at different bundle. (non twisted yarn)*

Obviously the relationship between bundle strength and number of bundle was directly proportional. The Results from figure above shows that the relationship between strength and bundle is linear, directly proportional (as number of bundle increases the bundle strength also increases).

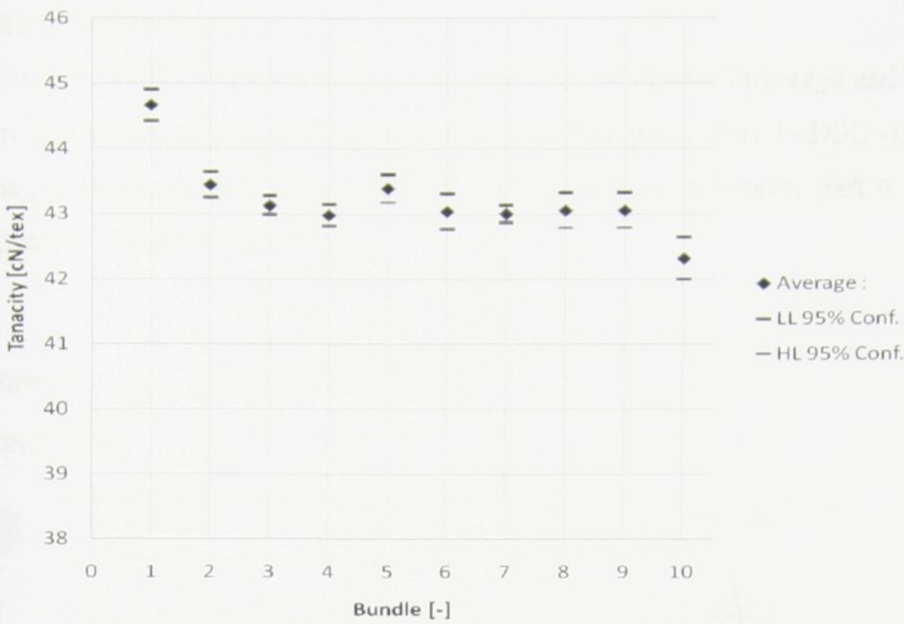


Fig 4.3.2.6: *Stress strain force at different bundle. (non twisted yarn)*

Results show that the relationship between tenacity and number of bundle was inversely proportional (as number of bundle increases the bundle tenacity decreases).

4.3.3 THERMAL SHRINKAGE

There are different procedures that are used to measure and evaluate the Shrinkage and shrinkage effect and different instrument, this section is divided into five parts. Part 1- DSC (Differential scanning calorimetric) curve, part 2- Kinetic curves, part 3 thermal shrinkage, part 4 - thermal shrinkage force, part 5 – thermal sensitivity.

4.3.3.1 Part 1

- DSC curve.

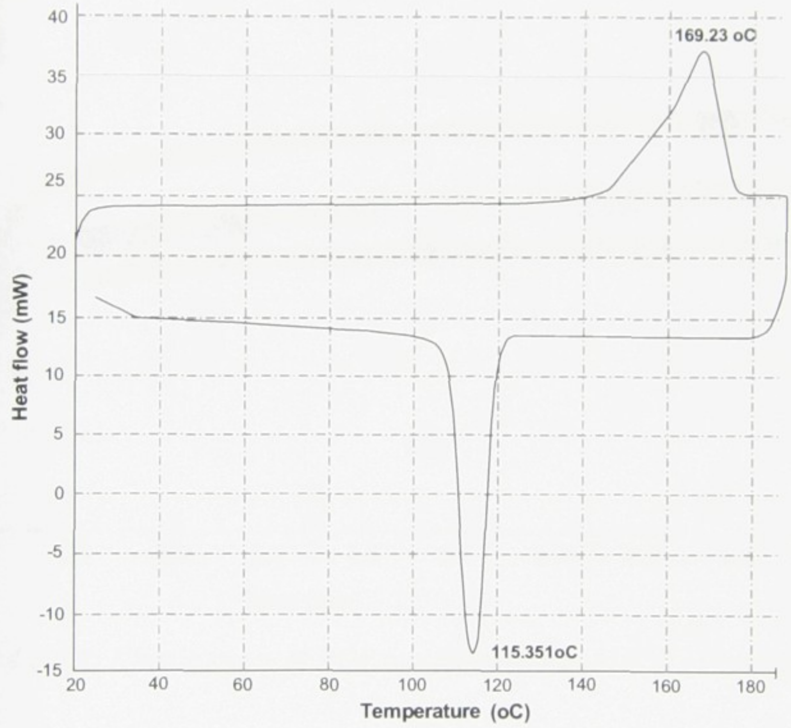


Fig 4.3.3.1: *DSC curve for multifilament POP Yarn. Temperature [°C] vs. heat flow [mW].*

Fig 4.3.3.1 show an endothermic and exothermic heat and temperature intervals. DSC curve for raw material used in this thesis. Melting temperature ranges in the interval 160. – 180°C, value of the "peak" is approx. 169°C. The heat received by the sample is 108,473 Jg^{-1}. The temperature of re-crystallization is in the interval of 99.9 – 125°C, the "peak" is approx. 115°C. The heat released by the sample is -114,480 Jg^{-1}.

4.3.3.2 Part 2

- Kinetic curves. (Twist effect)

Since Shrinkage testing procedure does not regulated by a certain International standard. Testing Manual was used to evaluate the shrinkage, and shrinkage force for all POP multifilament yarns (twisted and not twisted).

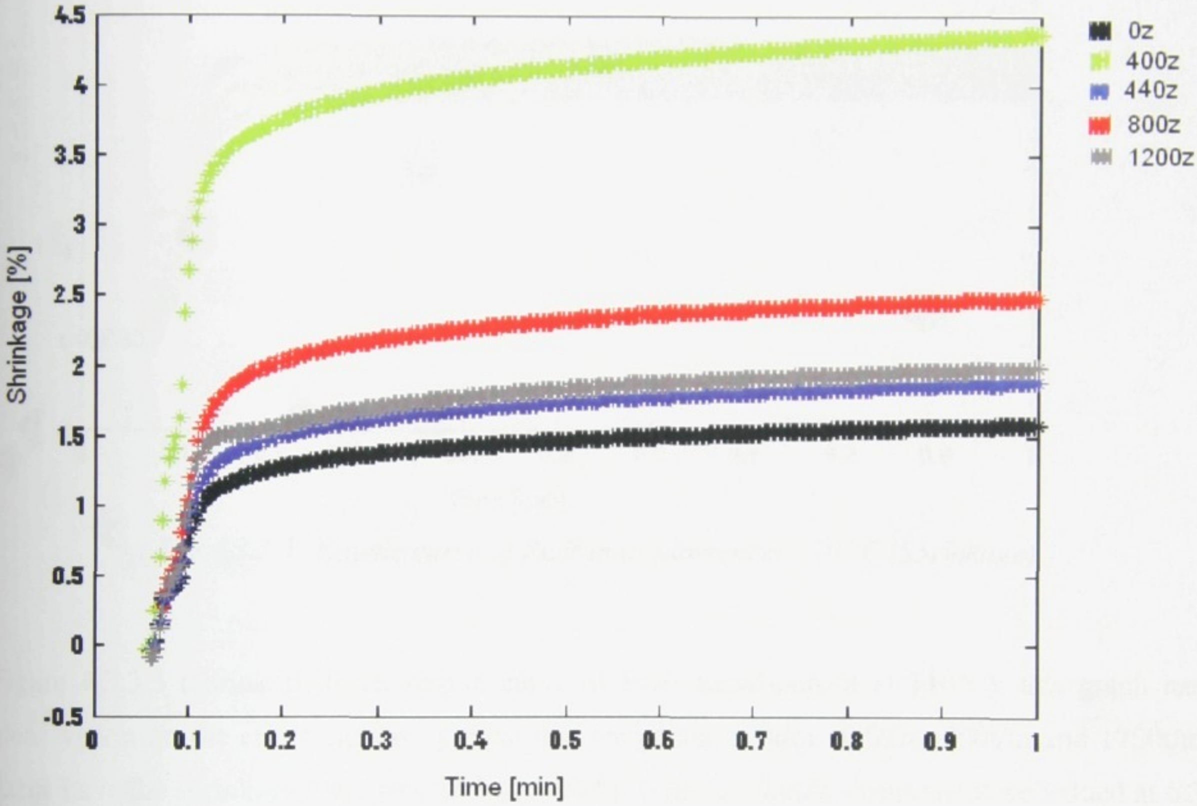


Fig 4.3.3.2: *Kinetic curve of POP multifilament at 110 °C (Shrinkage)*

Figure 4.3.3.2 (kinetic curve of POP multifilament at 110°C); this graph has clear vision on the effect caused by twist and temperature. 0t/m, 440t/m 800t/m and 1200t/m yarns have the shrinkage less than 2 %. 400t/m (green line) yarn has more than 2 % shrinkage, infect is double when compare it with 0t/m, 440t/m 800t/m and 1200t/m yarns. The cause is that, during the twisting process filaments are rupture when cohesion and adhesion, that rearrange the structure of the POP multifilament.

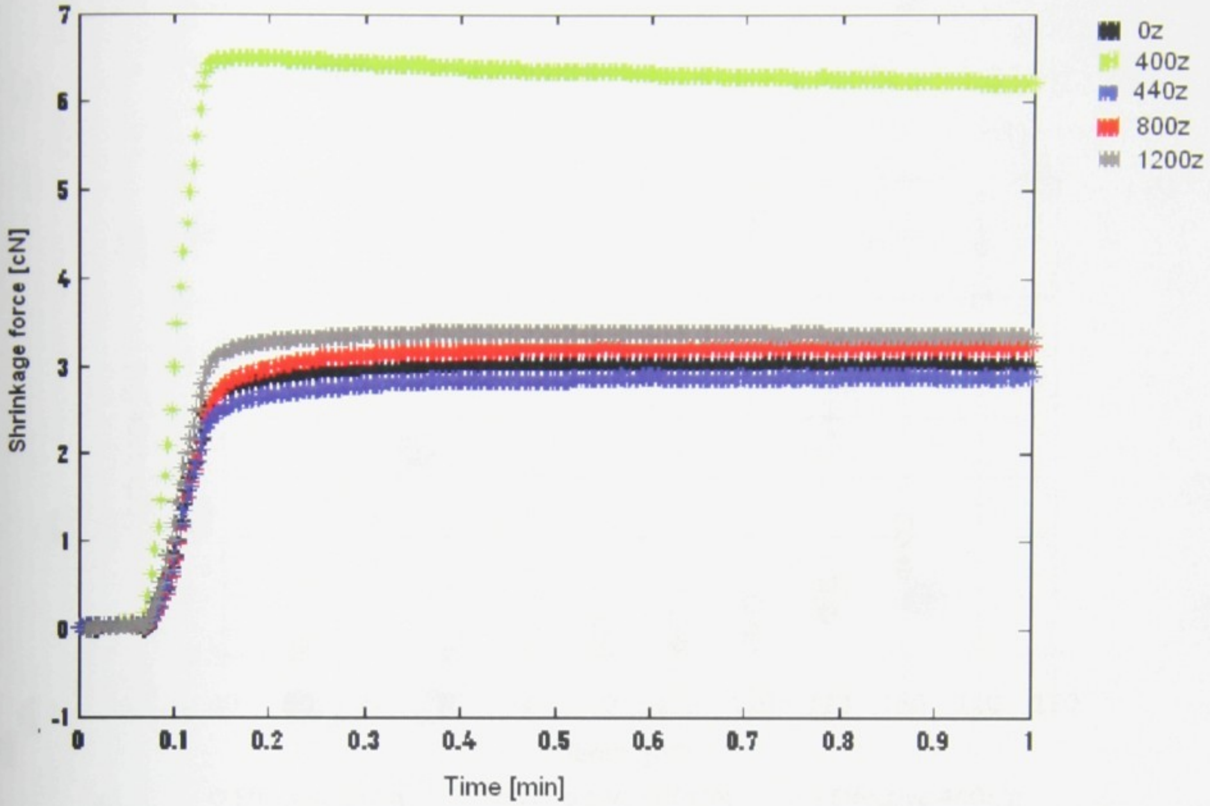


Fig 4.3.3.3: Kinetic curve of POP multifilament at 110 °C (Shrinkage)

Figure 4.3.3.3 (shrinkage force kinetic curve of POP multifilament at 110°C); this graph has clear vision on the effect caused by twist and temperature. 0t/m, 440t/m, 800t/m and 1200t/m yarns have the shrinkage force around 3cN. 400t/m yarn has double shrinkage force valued at 6.3 cN when compare it with 0t/m, 440t/m, 800t/m and 1200t/m yarns. The cause was that, during the twisting process filaments are rupture when cohesion and adhesion, that rearrange the structure of the POP multifilament. At a small twist a certain part in the twisted fillerment has a shrinkage force, but when further twist the fillerment at no stress (pulling force) that shrinkage force get shortened and be equivalent to than an untwisted filaments.

4.3.3.3 Part 3

- Thermal shrinkage. (Twist effect)

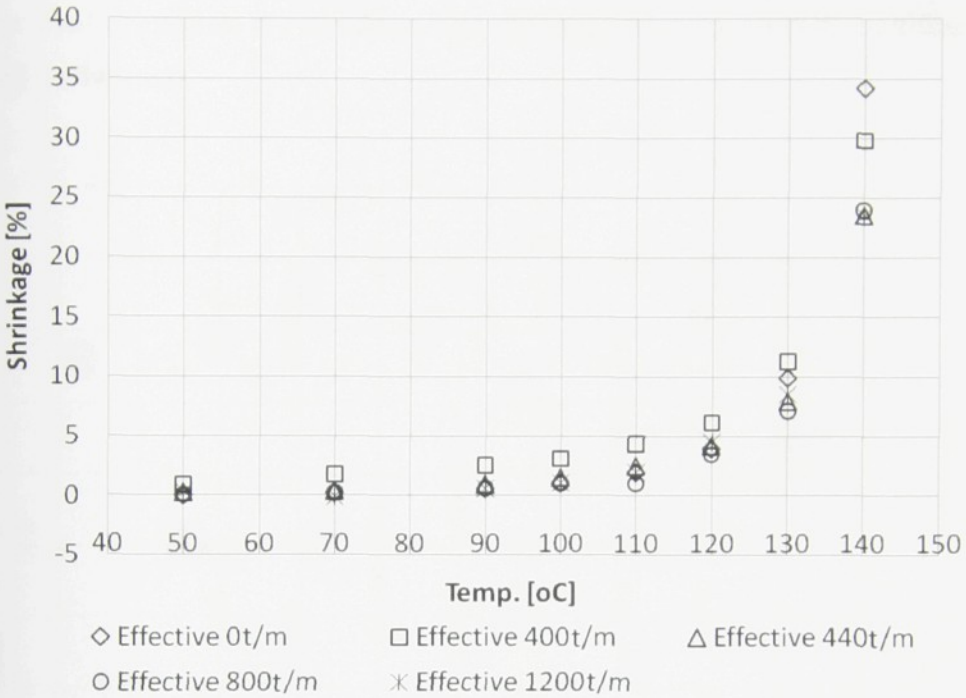


Fig.4.3.3.3.1: *Effective Shrinkage for all POP yarns (non twisted and twisted yarn)*

The shrinkage values of 400t/m twisted yarn were high values at all temperature interval. The shrinkage values of 440t/m, 800t/m and 1200t/m twisted yarns were almost identical at all temperature interval.

If shrinkage of 400 t/m twisted yarn produced by ply twister was high than the shrinkage of yarns produced by ring spinning that means that ply twister technology is producing thermal sensitive twisted yarns.

If shrinkage of 400 t/m twisted yarn produced by ply twister was high than the raw material (untwisted POP multifilament) shrinkage that means that ply twister technology is producing thermal sensitive twisted yarns.

4.3.3.4 Part 4

- *Thermal shrinkage force*

Since Shrinkage testing procedure does not regulated by a certain International standard. Testing Manual was used to evaluate the shrinkage, and shrinkage force for all POP multifilament yarns (twisted and not twisted).

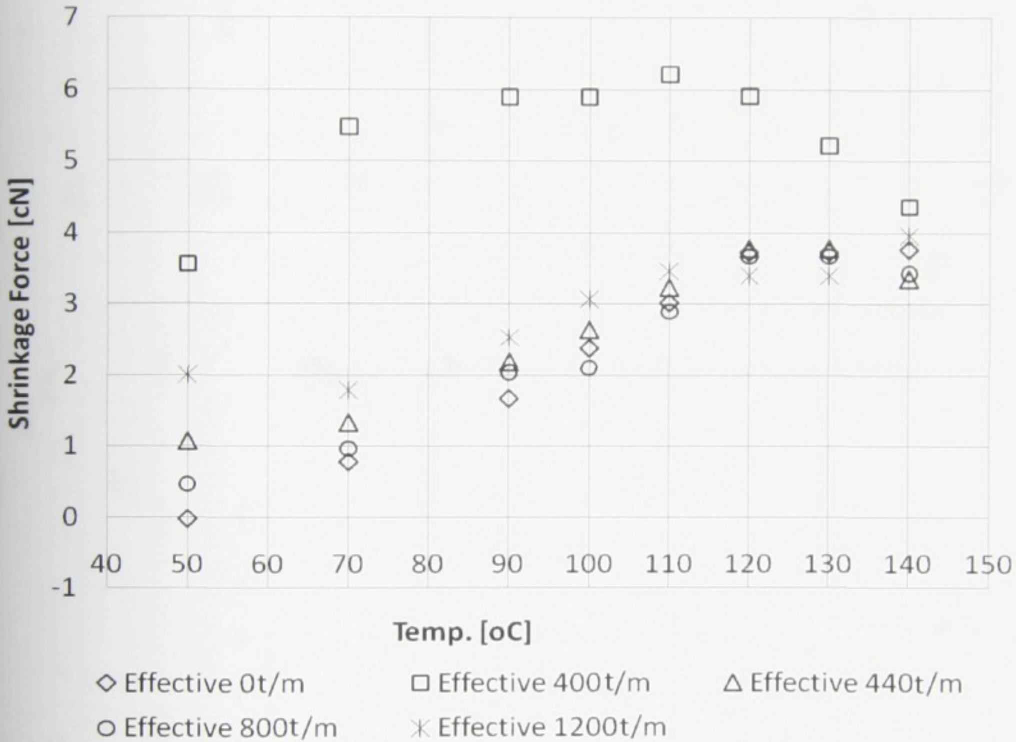


Fig.4.3.3.4.1: *Effective Shrinkage force for all POP yarns (non twisted and twisted yarn)*

The shrinkage force values of 400t/m twisted yarn were high values at all temperature interval. The shrinkage values of 440t/m, 800t/m and 1200t/m twisted yarns were almost identical at all temperature interval. Per average shrinkage force values of 1200t/m yarn were high at temperatures below 110°C.

If shrinkage force of 400 t/m twisted yarn produced by ply twister was high than the shrinkage force of yarns produced by ring spinning that means that ply twister technology is producing thermal sensitive twisted yarns.

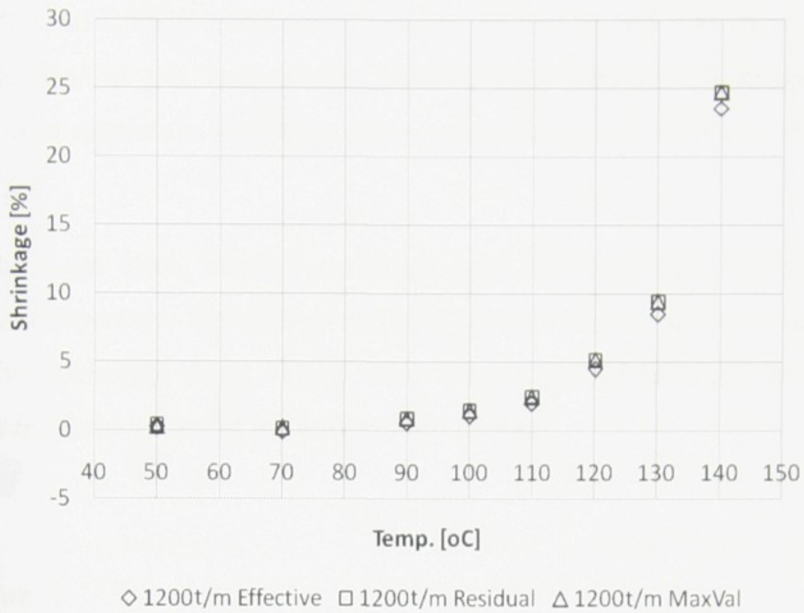


Fig.4.3.3.4.2: Shrinkage for POP yarns at 1200t/m

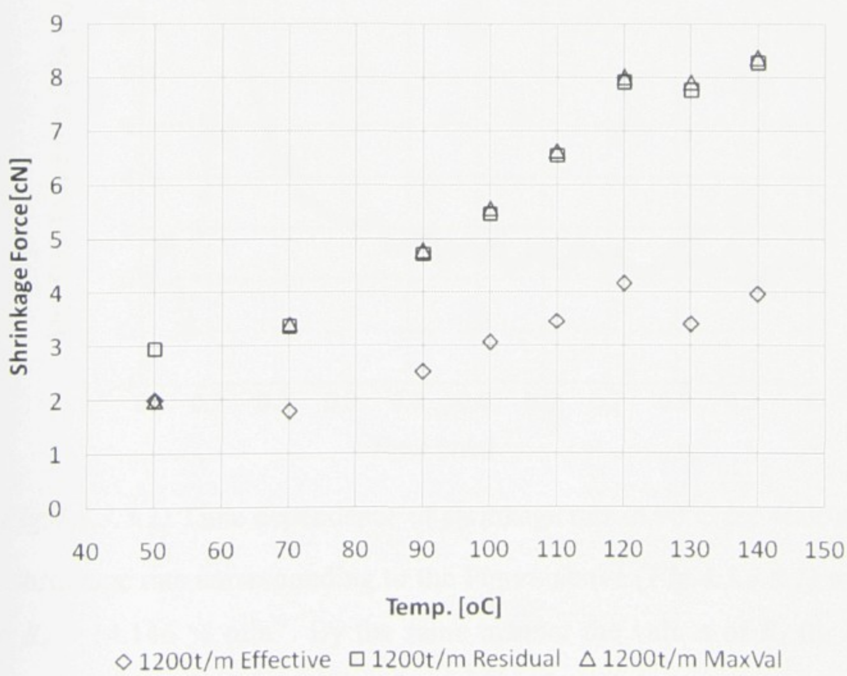


Fig.4.3.3.4.3: Shrinkage force for POP yarns at 1200t/m

From figures above (*Fig.4.3.3.4.2& Fig.4.3.3.4.3)* shows that for 0 t/m or 400t/m, 440 t/m, 800t/m, or 1200t/m an Effective shrinkage, residual shrinkage and maximum shrinkage values were almost identical at per temperature interval. But Effective shrinkage force, residual shrinkage force and maximum shrinkage force values were not identical at per temperature interval.

The effective shrinkage force, residual shrinkage force and maximum shrinkage force values were increases as temperature increase up to 120°C, remain almost constant from 120 °C to 140 °C. The Effective shrinkage force values were almost half of residual shrinkage force and maximum shrinkage force values at per temperature interval.

*4.3.3.5 **Part 5***

- Thermal sensitivity

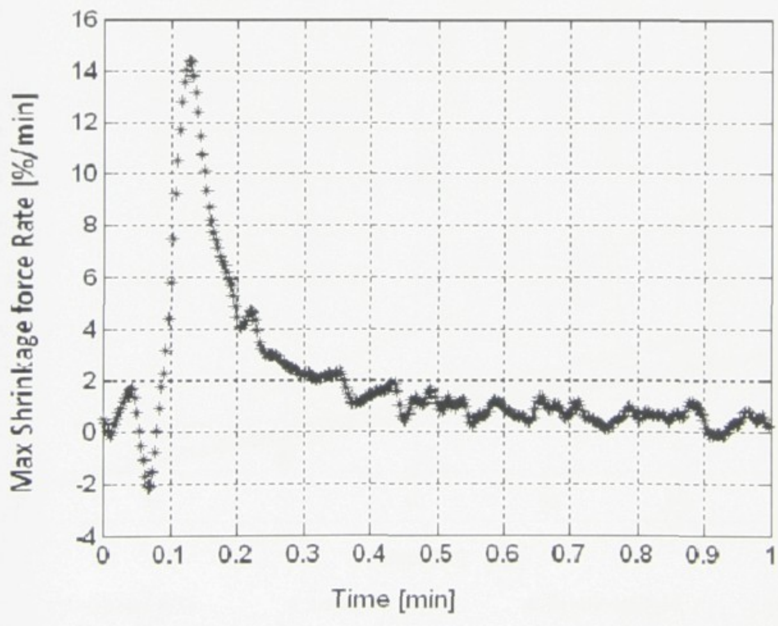


Fig.4.3.3.5.1: Time dependence of shrinkage rate at 90°C for 400t/m

The maximum shrinkage rate corresponding to the Figure above (***Fig.4.3.3.5.1)*** was evaluated to be equal to the R_s = 14.146 % min^{-1}. By the same manner the values of R_s for all investigated yarns were evaluated at deferent temperatures interval.

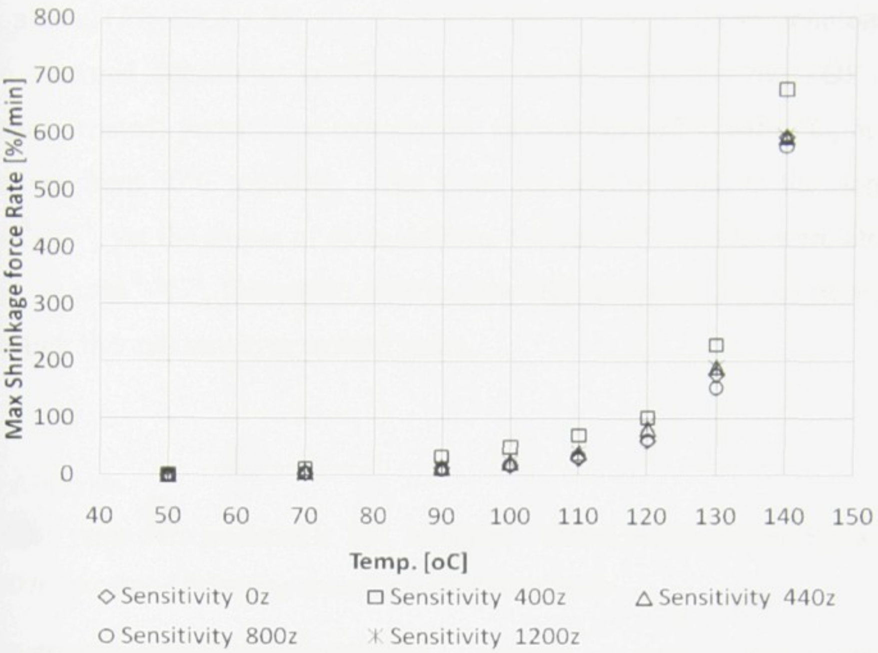


Fig.4.3.3.5.2: *Max. Shrinkage force rate for POP yarns at dif twist (0z, 400z, 800z and 1200z)*

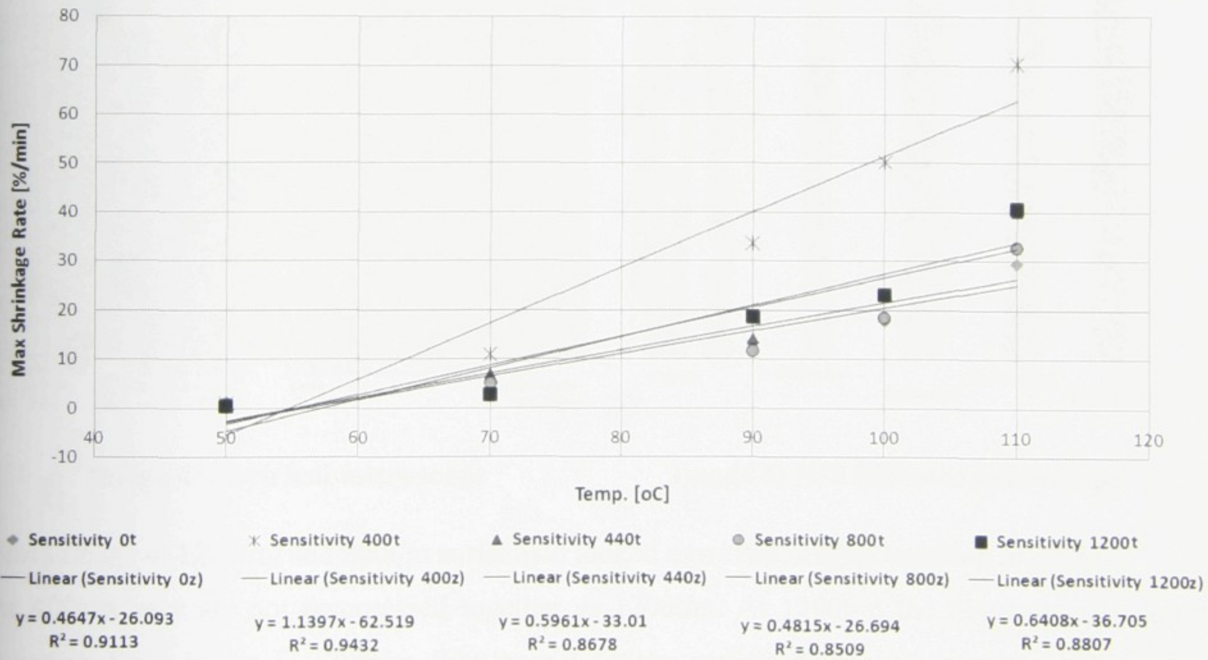
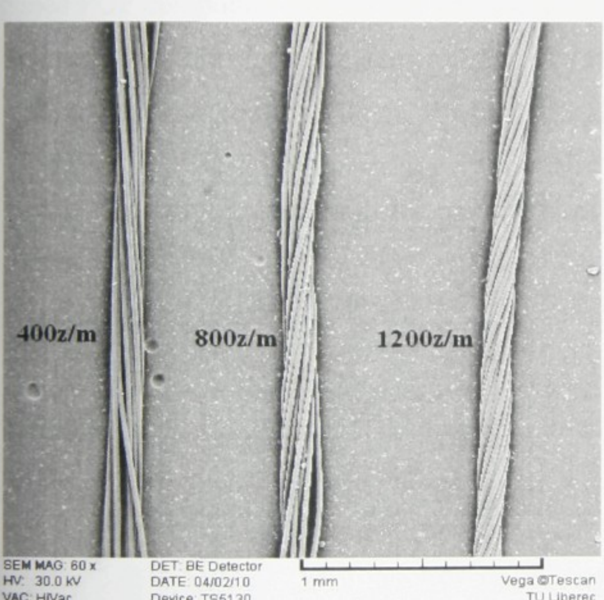


Fig.4.3.3.5.3: *Temperature dependence of maximum shrinkage rate (temp. less than 120°C)*

From figures above (*Fig.4.3.3.5.2& Fig.4.3.3.5.3)* shows a non linear relationship between shrinkage rate (thermal sensitivity coefficient) and temperature for the POP multifilament (twisted and none twisted) yarns when temperature ranges from 50°C to140°C, but linear when temperature ranges from 50°C to120°C. The slope for 400t/m equal to the slope i.e. **SRT = 1.1397 % min^{-1} °C^{-1}**, yet the slopes of 0t/m, 440t/m, 800t/m and 1200t/m were almost the same i.e. **SRT = 0.51 % min^{-1} °C^{-1}**. Generally, 400t/m yarn SRT indicates that ply twisted technology produces the higher thermal sensitive twisted yarns.

4.3.4 Image Analysis

Note: all the twisted yarns were produced at TUL laboratory. 400t/m produced from ply twist and 440t/m, 800t/m and 1200t/m produced from ring spinning without any draft.



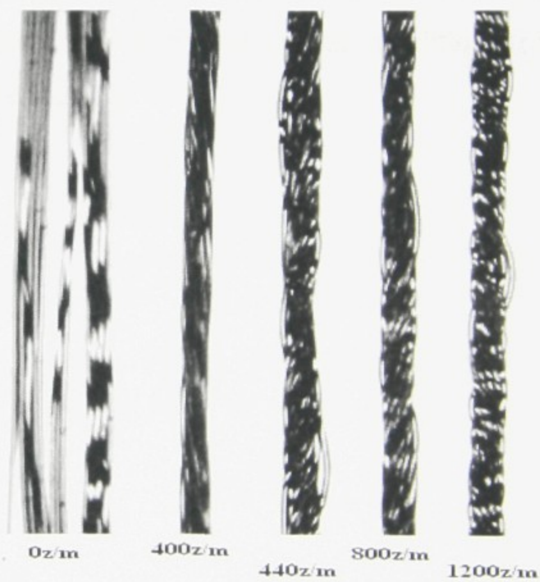


Image 4: electrical microscope **Image 5: NIS Element microscope**

From image 4: 1200t/m and 800t/m surface do looked more ruptured as compare to 400t/m.

At 400t/m yarn are not compressed together as 1200t/m. At 1200t/m the filaments are closed together. From image 5: 1200t/m, 800t/m and 440t/m surface do looked more twisted. 400t/m yarn does look twisted and it seems as if the pulling force was used during the twisting. 0t/m the filaments looked loss and separated not much cohesion force to bold all the filaments together.

5 RECOMMENDATION

The mechanical properties evaluation of POP multifilament was successful and it was a good tool to investigate the strength of the POP filament at certain twist and observing the mechanical effect caused by a two type of twisting technologies.

The untwisted POP multifilament was not suitable for membrane lamination. 1200t/m yarn was the optimum yarn for membrane lamination process that was information provided by the membrane company. If so it is recommended to twist the filament at maximum and prevent a pulling force to be used during the twisting. The high the twist, more compact (high parking density) yarn is produced.

Since POP compound melt at 169 and the glass transition is at 115°C. It is recommended to used this material (POP multifilament) at any environment below 115°C, at ambient conditions (room temperature and pressure) the material operate at it optimum.

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7 APPENDIX A – (Tables)

7.1 *Fineness*

Table 7.1.1: Fineness for all POP yarns (non twisted and twisted yarn)

	0t/m	400t/m	440t/m	800t/m	1200t/m
Fineness [tex]:	55.817	54.867	57.483	58.467	58.917
95 % LL Coeff :	55.556	53.870	57.303	58.381	58.692
95 % HL Coeff:	56.077	55.864	57.664	58.552	59.141

7.2 *Yarn twist*

Table 7.2.1: POP yarns Twist statistics for twisted yarn (400t/m, 440t/m, 800t/m, 1200t/m)

	400t/m	440t/m	800t/m	1200t/m
Average :	380.7333	344.2333	696.1667	1094.133
95 % LL Coeff :	362.63	327.9125	668.1144	1072.498
95 % HL Coeff:	398.8367	360.5542	724.2189	1115.768
Differences [%]:	**5%**	**13%**	**13%**	**9%**
No.	30	30	30	30

7.3 *Stress strain*

7.3.1 *Stress strain for different yarn twist (0t, 400t, 440t, 800t and 1200t)*

Table 7.3.1.1: Mechanical properties of POP twisted yarns

Twist [t/m]	Fineness [tex]	Elongation [%]	Tenacity [N]	Strength at break [cN/tex]
0	5.581667	81.48	2.48	44.67
400	5.3911	89.58	2.12	39.18
440	5.748333	99.82	1.99	34.92
800	5.846667	101.65	2.19	37.67
1200	5.891667	107.36	2.39	40.42

Table 7.3.1.2: Elongation (%) for POP yarns bundles (none twisted)

Yarn twist [t/m]	0	400	440	800	1200
Average :	81.48	89.58	99.82	101.65	107.36
LL 95% Conf.	79.93	87.61	97.15	99.45	105.83
HL 95% Conf.	83.04	91.56	102.49	103.85	108.89

Table 7.3.1.3: strength at break (cN/tex) for POP yarns bundles (none twisted)

Yarn twist [t/m]	0	400	440	800	1200
Average :	2.480	2.115	1.990	2.185	2.385
LL 95% Conf.	2.466	2.105	1.975	2.175	2.367
HL 95% Conf.	2.493	2.125	2.006	2.196	2.404

Table 7.3.2.4: Tenacity (N) for POP yarns bundles (non twisted)

Yarn twist [t/m]	0	400	440	800	1200
Average :	44.67	39.18	34.92	37.67	40.42
LL 95% Conf.	44.42	38.99	34.64	37.49	40.11
HL 95% Conf.	44.91	39.36	35.19	37.85	40.73

7.3.2 Stress strain for different bundles (bundle 1 -10)

Table 7.3.2.1: Mechanical properties for POP yarns bundles (none twisted)

Bundle	Fineness	Elongation	Tenacity	Strength at
[-]	[tex]	[%]	[N]	break [cN/tex]
1	5.55	81.48	2.48	44.67
2	11.1	79.60	4.83	43.45
3	16.65	80.39	7.18	43.13
4	22.2	80.54	9.54	42.99
5	27.75	78.71	12.04	43.40
6	33.3	77.49	13.77	41.36
7	38.85	78.72	16.73	43.01
8	44.4	79.35	19.12	43.06
9	49.95	77.97	20.75	43.06
10	55.5	79.27	23.49	42.32

Table 7.3.2.2: Tenacity (N) for POP yarns bundles (non twisted)

Unit (N)	Bundle 1	Bundle 2	Bundle 3	bundle 4	bundle 5	bundle 6	bundle 7	bundle 8	bundle 9	bundle 10
Average :	2.5	4.8	7.2	9.5	12.0	13.8	16.7	19.1	20.7	23.5
LL 95%	2.5	4.8	7.2	9.5	12.0	13.5	16.7	19.0	20.5	23.3
HL 95%	2.5	4.8	7.2	9.6	12.1	14.0	16.8	19.2	21.0	23.7

Table 7.3.2.3: strength at break (cN/tex) for POP yarns bundles (none twisted)

	bundle 1	bundle 2	bundle 3	bundle 4	bundle 5	bundle 6	bundle 7	Bundle 8	Bundle 9	bundle 10
Average :	44.67	43.45	43.13	42.99	43.40	41.36	43.01	43.06	43.06	42.32
LL 95%	44.42	43.26	42.99	42.83	43.18	40.56	42.87	42.79	42.79	42.00
HL 95%	44.91	43.64	43.27	43.15	43.61	42.17	43.15	43.33	43.33	42.65

Table 7.3.2.4: Mechanical properties for POP yarns bundles (none twisted)

	bundle 1	bundle 2	bundle 3	Bundle 4	bundle 5	bundle 6	bundle 7	bundle 8	bundle 9	bundle 10
Average :	81.48	79.60	80.39	80.54	78.71	77.49	78.72	79.35	77.97	79.27
LL 95%	79.93	78.19	79.01	79.34	77.36	76.25	76.55	77.45	76.34	77.87
HL 95%	83.04	81.01	81.78	81.74	80.06	78.73	80.89	81.25	79.60	80.67

7.4 Shrinkages

Table 7.4.1: Effective Shrinkage for all POP yarns (non twisted and twisted yarn)

Temp.	Effective				
(°C)	0t/m	400t/m	440t/m	800t/m	1200t/m
50	-0.014	0.887	0.247	0.101	0.298
70	0.2125	1.782	0.377	0.272	-0.066
90	0.549	2.536	0.921	0.625	0.59
100	1.0345	3.107	1.493	1.037	1.075
110	1.9445	4.361	2.485	1.037	1.985
120	3.946	6.161	4.192	3.46	4.515
130	9.9015	11.296	7.926	7.142	8.533
140	34.213	29.81	23.54	23.966	23.53

Table 7.4.2: Residual Shrinkage for all POP yarns (non twisted and twisted yarn)

Temp.	Residual				
(°C)	0t/m	400t/m	440t/m	800t/m	1200t/m
50	0.094	0.992	0.386	0.172	0.411
70	0.399	1.963	0.613	0.466	0.164
90	0.8145	2.808	1.268	0.899	0.913
100	0.8145	2.536	5.591	1.349	0.59
110	2.305	4.798	3.05	2.404	2.495
120	4.446	6.74	4.955	4.147	5.2
130	10.6605	12.084	8.94	8.07	9.444
140	35.2635	30.898	25.112	25.194	24.715

Table 7.4.3: MaxVal Shrinkage for all POP yarns (non twisted and twisted yarn)

Temp.	MaxVal				
(°C)	0t/m	400t/m	440t/m	800t/m	1200t/m
50	0.094	0.992	0.386	0.21	0.418027
70	0.094	1.963	0.386	0.466	0.418027
90	0.8145	2.808	1.269	0.899	1.342453
100	1.3205	3.449	1.911	1.349	2.05241
110	2.305	4.798	3.05	2.404	3.167883
120	4.446	6.74	4.955	4.147	5.067667
130	10.671	12.084	8.94	8.07	9.093353
140	35.895	30.901	25.115	25.21	25.797

Table 7.4.4: Effective Shrinkage force for all POP yarns (non twisted and twisted yarn)

Temp.	Effective				
(°C)	0t/m	400t/m	440t/m	800t/m	1200t/m
50	-0.0275	3.558	1.078	0.46	2
70	0.7755	5.479	1.34	0.967	1.788
90	1.6705	5.895	2.194	2.04	2.525
100	2.381	5.895	2.643	2.105	3.064
110	3.0205	6.212	3.239	2.894	3.461
120	3.733	5.906	3.787	3.669	3.402
130	3.733	5.22	3.787	3.669	3.402
140	3.7735	4.361	3.361	3.433	3.963

Table 7.4.5: Residual Shrinkage force for all POP yarns (non twisted and twisted yarn)

Temp.	Residual				
(°C)	0t/m	400t/m	440t/m	800t/m	1200t/m
50	0.7495	4.462	2.164	1.415	2.955
70	2.284	6.985	3.115	2.465	3.372
90	3.6	7.95	4.731	4.175	4.72
100	4.575	8.277	5.591	4.23	5.466
110	5.5155	9.201	6.91	6.245	6.551
120	6.469	9.328	8.267	7.243	7.915
130	6.9775	9.057	8.848	8.451	7.76
140	6.771	8.142	8.463	8.206	8.273

Table 7.4.6: Maximum Shrinkage force for all POP yarns (non twisted and twisted yarn)

Temp.	MaxVal				
(°C)	0t/m	400t/m	440t/m	800t/m	1200t/m
50	0.8095	4.535	2.226	1.461	1.461
70	2.3695	7.069	2.226	2.516	2.516
90	3.6895	8.066	4.798	4.221	4.221
100	4.6805	8.365	5.684	4.318	4.318
110	5.583	9.301	7.011	6.36	6.36
120	6.573	9.441	8.387	7.567	7.567
130	7.098	9.191	8.998	8.451	8.451
140	6.955	8.338	8.687	8.357	8.357

Table 7.4.7: Shrinkage for POP yarns at no twist

Temp.	0t/m		
(°C)	Effective	Residual	MaxVal
50	-0.014	0.094	0.094
70	0.2125	0.399	0.094
90	0.549	0.8145	0.8145
100	1.0345	0.8145	1.3205
110	1.9445	2.305	2.305
120	3.946	4.446	4.446
130	9.9015	10.6605	10.671
140	34.213	35.2635	35.895

Table 7.4.8: Shrinkage for POP yarns at 400t/m

Temp.	400t/m		
(°C)	Effective	Residual	MaxVal
50	0.887	0.992	0.992
70	1.782	1.963	1.963
90	2.536	2.808	2.808
100	3.107	2.536	3.449
110	4.361	4.798	4.798
120	6.161	6.74	6.74
130	11.296	12.084	12.084
140	29.81	30.898	30.901

Table 7.4.9: Shrinkage for POP yarns at 440t/m

Temp.	440t/m		
(°C)	Effective	Residual	MaxVal
0.247	0.247	0.386	0.386
0.377	0.377	0.613	0.386
0.921	0.921	1.268	1.269
1.493	1.493	2.643	1.911
2.485	2.485	3.239	3.05
4.192	4.192	4.955	4.955
7.926	7.926	8.94	8.94
23.54	23.54	25.112	25.115

Table 7.4.10 Shrinkage for POP yarns at 800t/m

Temp.	800t/m		
(°C)	Effective	Residual	MaxVal
0.247	0.101	0.172	0.21
0.377	0.272	0.466	0.466
0.921	0.625	0.899	0.899
1.493	1.037	1.349	1.349
2.485	1.037	2.404	2.404
4.192	3.46	4.147	4.147
7.926	7.142	8.07	8.07
23.54	23.966	25.194	25.21

Table 7.4.11: Shrinkage for POP yarns at 1200t/m

Temp.	1200t/m		
(°C)	Effective	Residual	MaxVal
50	0.298	0.411	0.992
70	-0.066	0.164	1.963
90	0.59	0.913	2.808
100	1.075	0.59	3.449
110	1.985	2.495	4.798
120	4.515	5.2	6.74
130	8.533	9.444	12.084
140	23.53	24.715	30.901

Table 7.4.12: Shrinkage force for POP yarns at 0t/m

Temp.	0t/m		
(°C)	Effective	Residual	MaxVal
50	-0.0275	0.7495	0.8095
70	0.7755	2.284	2.3695
90	1.6705	3.6	3.6895
100	2.381	4.575	4.6805
110	3.0205	5.5155	5.583
120	3.733	6.469	6.573
130	3.733	6.9775	7.098
140	3.7735	6.771	6.955

Table 7.4.13: Shrinkage force for POP yarns at 400t/m

Temp.	400t/m		
(°C)	Effective	Residual	MaxVal
50	3.558	4.462	4.535
70	5.479	6.985	7.069
90	5.895	7.95	8.066
100	5.895	8.277	8.365
110	6.212	9.201	9.301
120	5.906	9.328	9.441
130	5.22	9.057	9.191
140	4.361	8.142	8.338

Table 7.4.14: Shrinkage force for POP yarns at 440t/m

Temp.	440t/m		
(°C)	Effective	Residual	MaxVal
1.078	1.078	2.164	2.226
1.34	1.34	3.115	2.226
2.194	2.194	4.731	4.798
2.643	2.643	5.591	5.684
3.239	3.239	6.91	7.011
3.787	3.787	8.267	8.387
3.787	3.787	8.848	8.998
3.361	3.361	8.463	8.687

Table 7.4.15: Shrinkage force for POP yarns at 800t/m

Temp.	800t/m		
(°C)	Effective	Residual	MaxVal
1.078	0.46	1.415	1.461
1.34	0.967	2.465	2.516
2.194	2.04	4.175	4.221
2.643	2.105	4.23	4.318
3.239	2.894	6.245	6.36
3.787	3.669	7.243	7.567
3.787	3.669	8.451	8.451
3.361	3.433	8.206	8.357

Table 7.4.16: Shrinkage force for POP yarns at 1200t/m

Temp.	1200t/m		
(°C)	Effective	Residual	MaxVal
50	2	2.955	4.535
70	1.788	3.372	7.069
90	2.525	4.72	8.066
100	3.064	5.466	8.365
110	3.461	6.551	9.301
120	3.402	7.915	9.441
130	3.402	7.76	9.191
140	3.963	8.273	8.338

Table 7.4.17: Max. Shrinkage force rate for POP yarns at dif twist (0z, 400z, 800z and 1200z)

Temp.	Sensitivity				
(°C)	0z	400z	440z	800z	1200z
50	0.1676	1.0211	0.6514	0.9108	0.4758
70	3.6693	10.9643	6.9434	4.9952	2.6894
90	13.4116	33.6097	14.1507	11.6088	18.6402
100	17.904	50.1556	23.5158	18.4076	23.0533
110	29.5449	70.3108	40.0423	32.8385	40.764
120	61.1721	101.7667	82.7985	62.703	90.3977
130	176.92	229.1576	191.0949	154.1928	191.1593
140	591.348	675.0279	592.5188	575.4247	593.7654

Table 7.4.18: Max. Shrinkage force rate for POP yarns at dif. twist (temp. less than 120°C)

Temp.	Sensitivity				
(°C)	0z	400z	440z	800z	1200z
50	0.1676	1.0211	0.6514	0.9108	0.4758
70	3.6693	10.9643	6.9434	4.9952	2.6894
90	13.4116	33.6097	14.1507	11.6088	18.6402
100	17.904	50.1556	23.5158	18.4076	23.0533
110	29.5449	70.3108	40.0423	32.8385	40.764

8 APPENDIX B – (Graphs)

8.1 Fineness

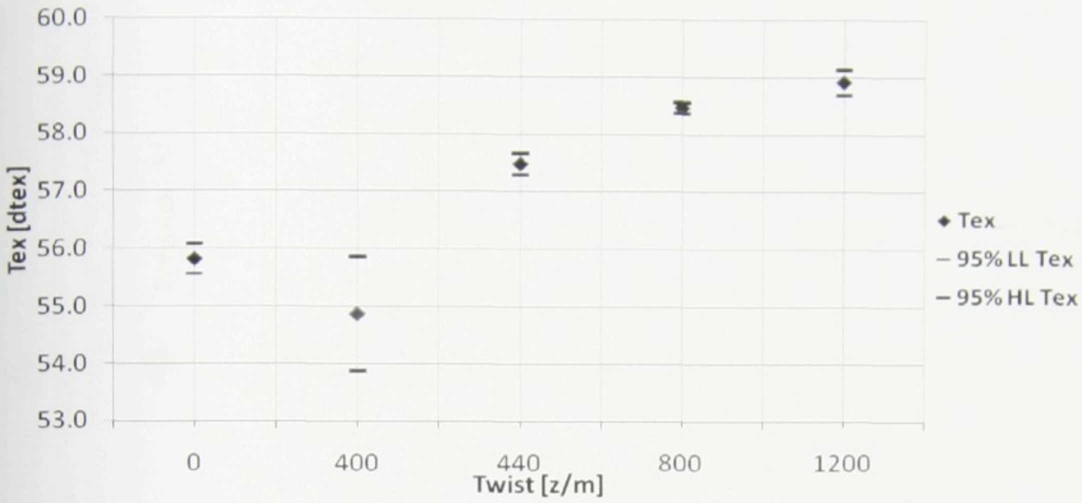

Fig 8.1.1: fineness for all POP yarns (non twisted and twisted yarn)

8.2 Yarn twist

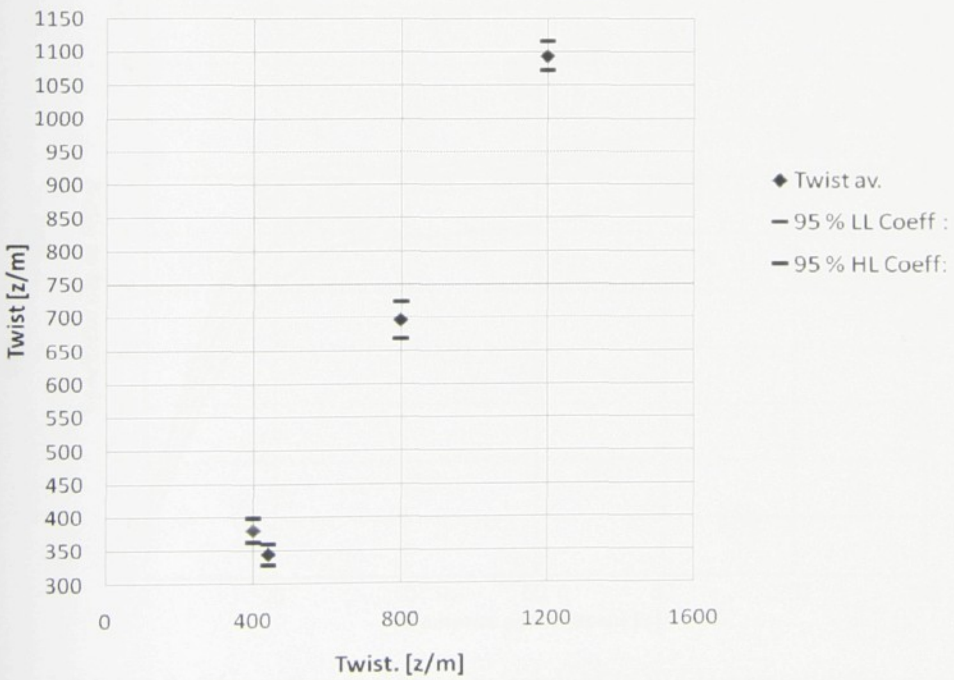

Fig8.2.1: POP yarns Twist statistics for twisted yarn (400t/m, 800t/m, 1200t/m)

8.3 Stress strain

8.3.1 Stress strain for different twist (400t/m, 800t/m, 1200t/m)

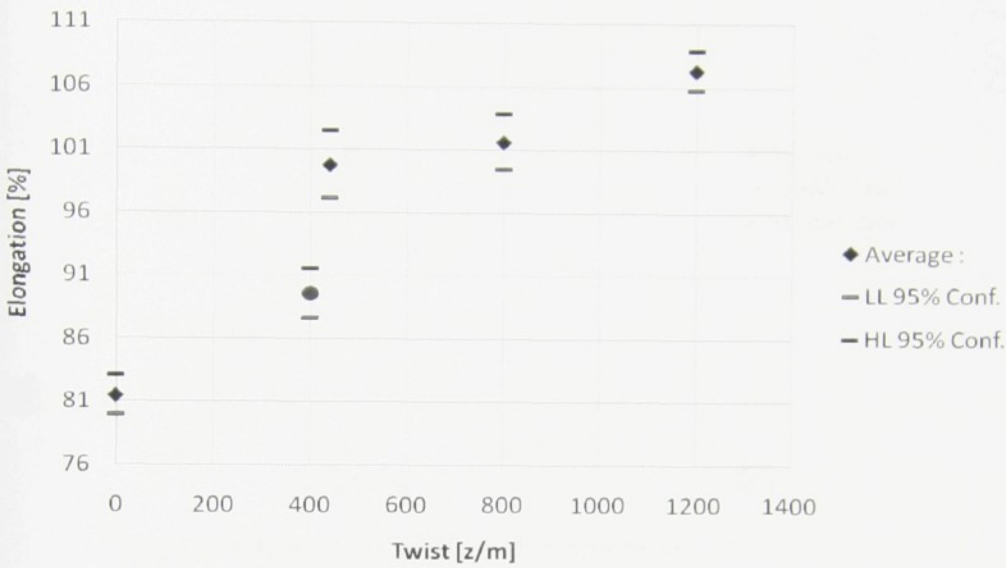

Fig 8.3.1.1: Elongation of POP multi-filament yarn at different twist

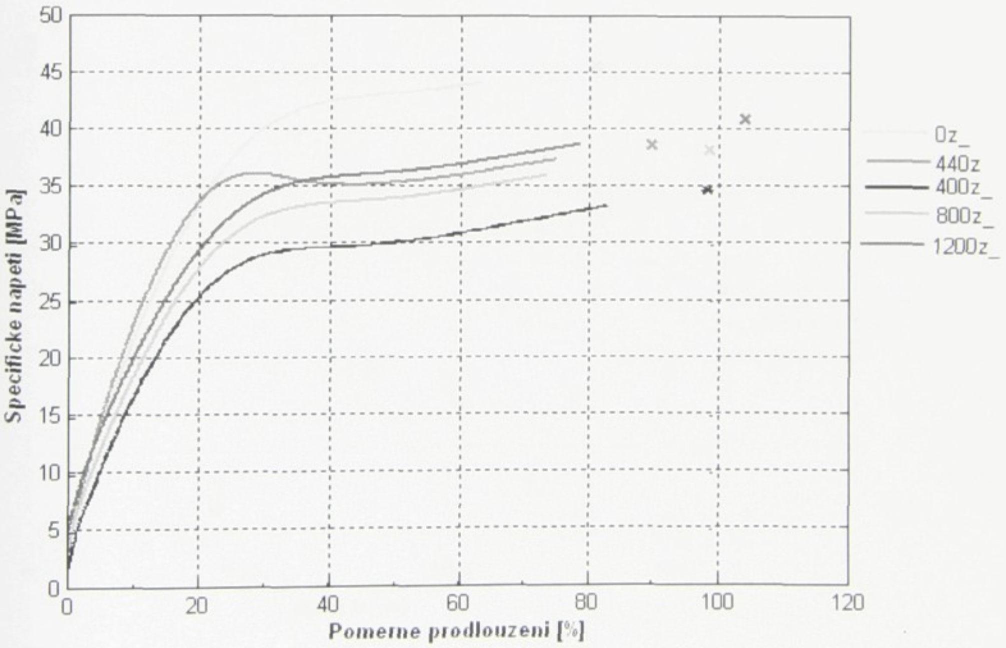

Fig8.3.1.2: Elongation and tenacity graph of POP filament at different twist

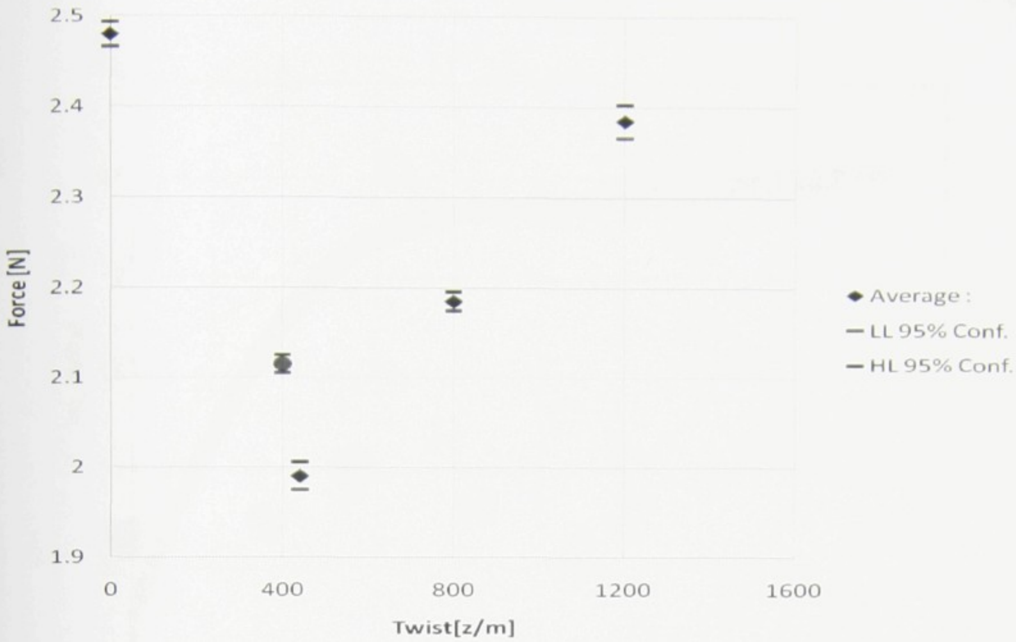

Fig 8.3.1.3: strength graph at different twist

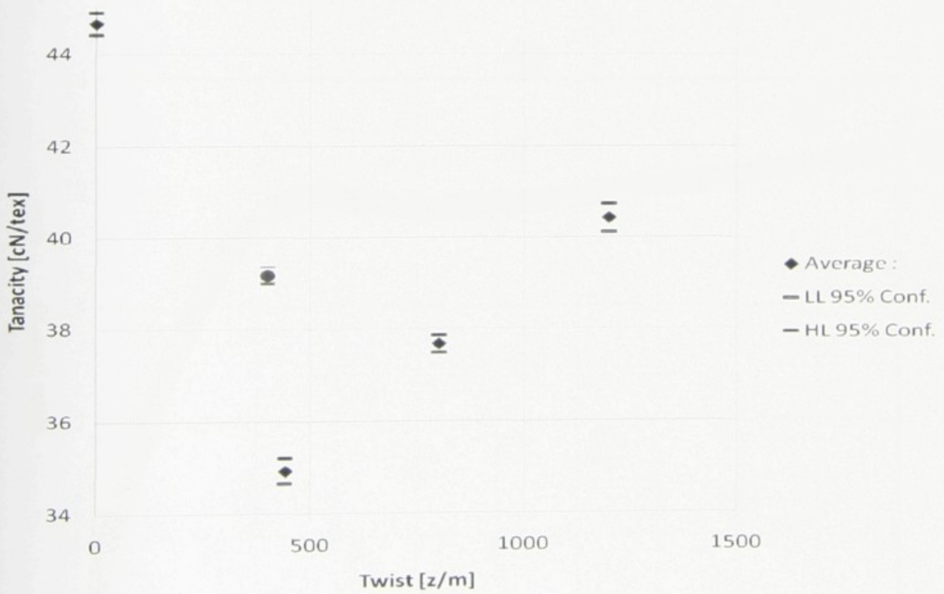

Fig 8.3.1.4: Tenacity graph at different twist

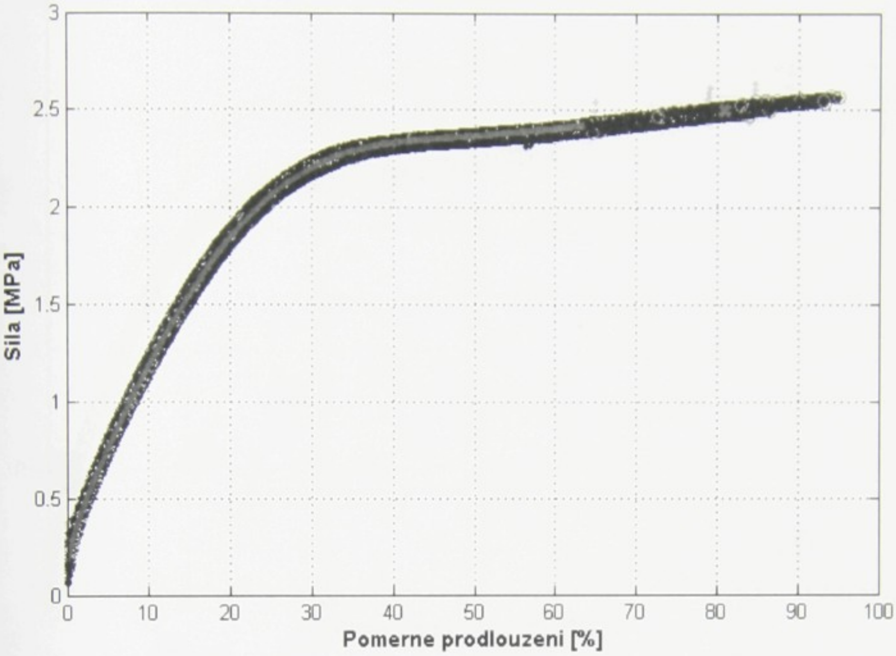

Fig 8.3.1.4: Strength at break for POP filament at 0 twist (0t/m)

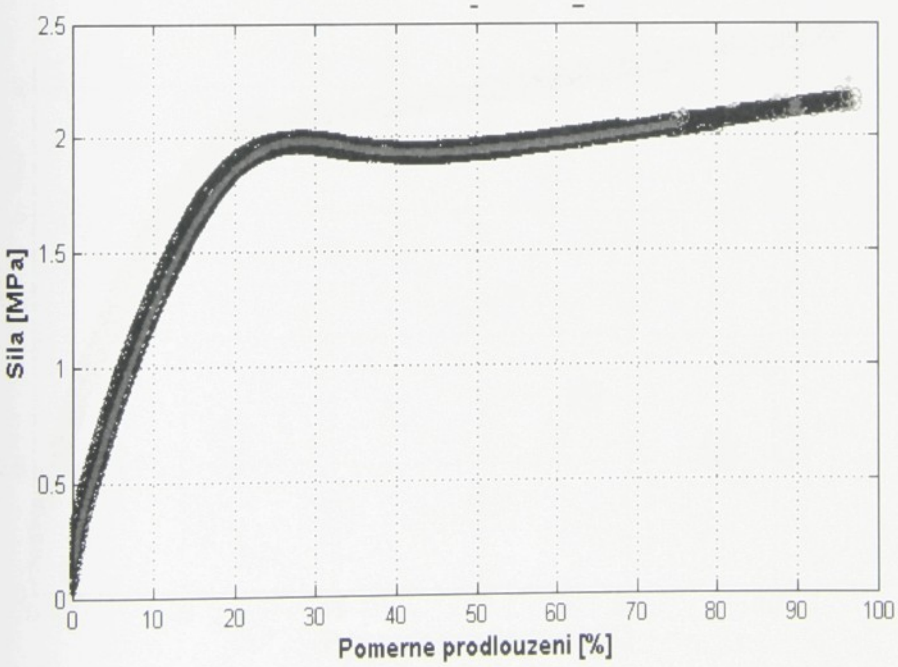

Fig 8.3.1.5: Strength at break for POP filament at 400 twist (400t/m)

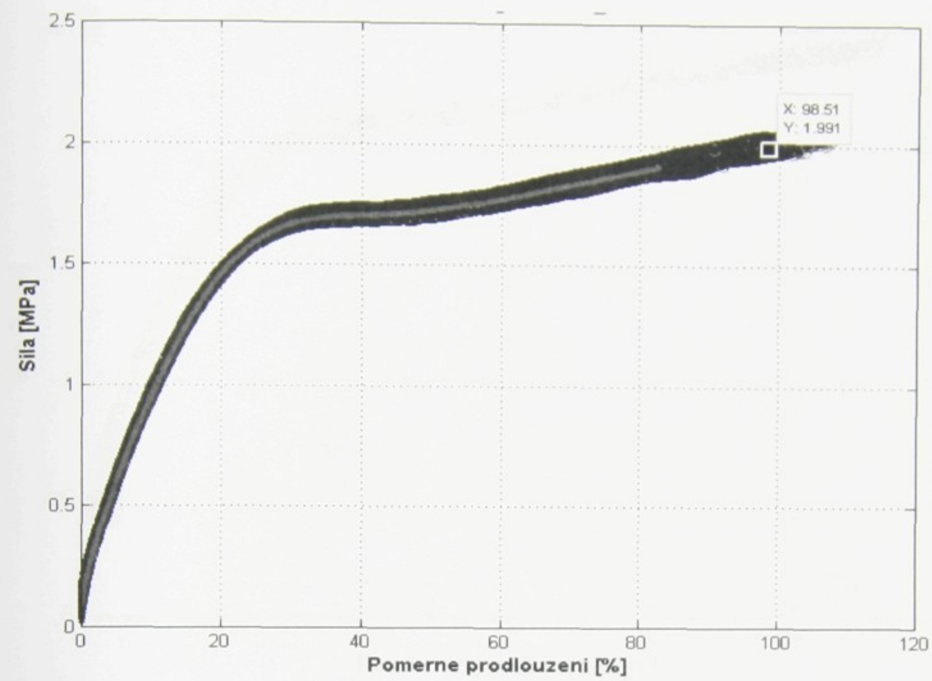

Fig 8.3.1.5: Strength at break for POP filament at 440 twist (440t/m)

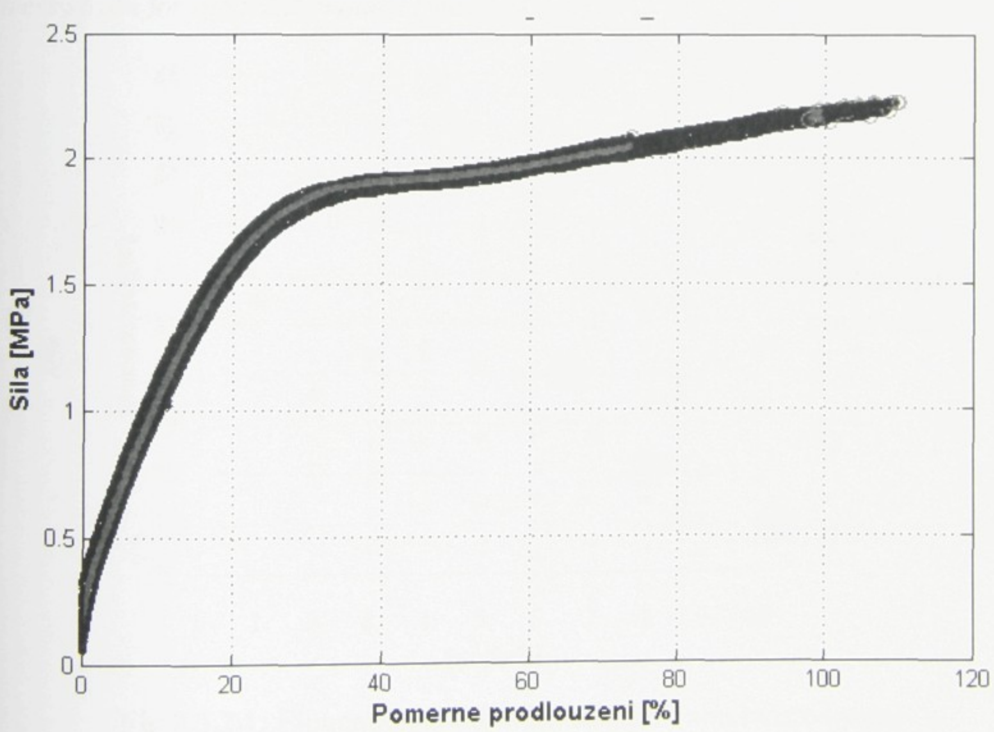

Fig 8.3.1.6: Strength at break for POP filament at 800 twist (800t/m)

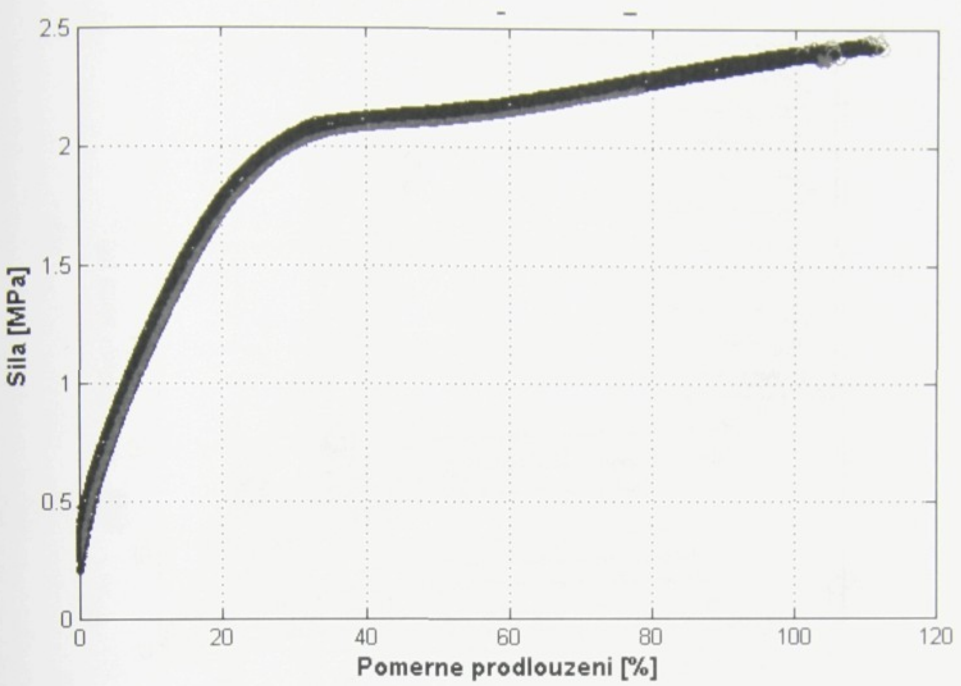

Fig 8.3.1.7: Strength at break for POP filament at 1200 twist (1200t/m)

8.3.2 Stress strain for different bundles (bundle 1 -10)

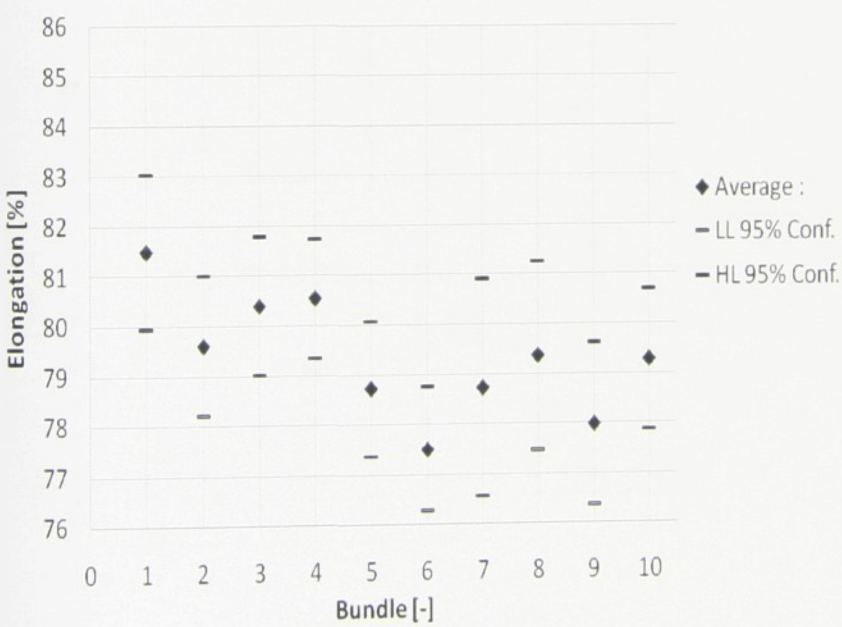

Fig 8.3.2.1: Elongation at different bundle. (non twisted yarn)

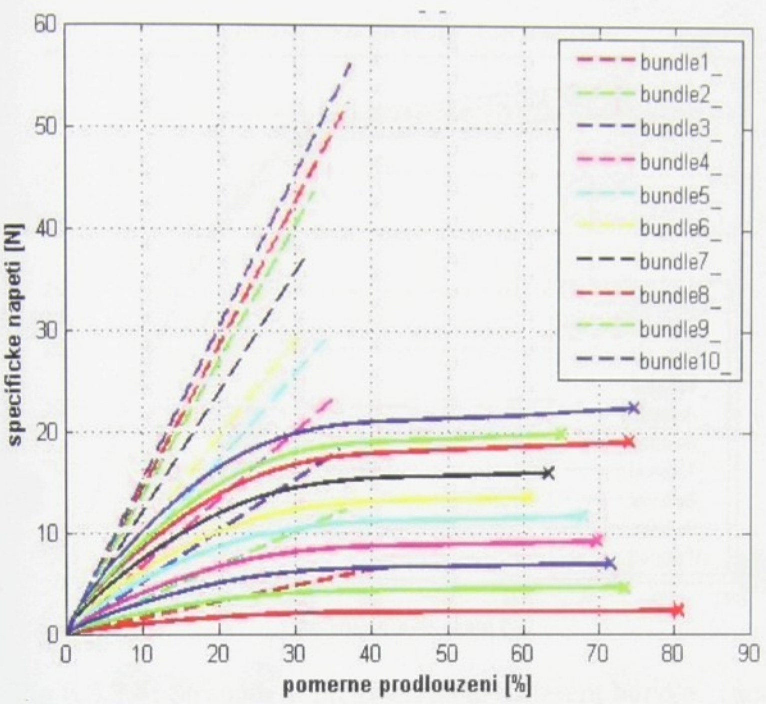

Fig 8.3.2.2: Elongation and tenacity graph at different bundle. (non twisted yarn)

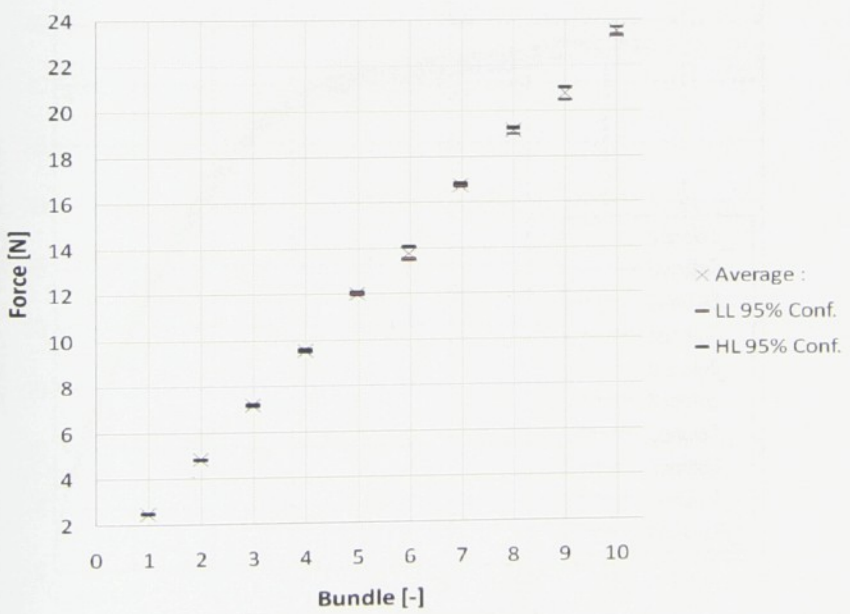

Fig 8.3.2.3: Stress strain force at different bundle. (non twisted yarn)

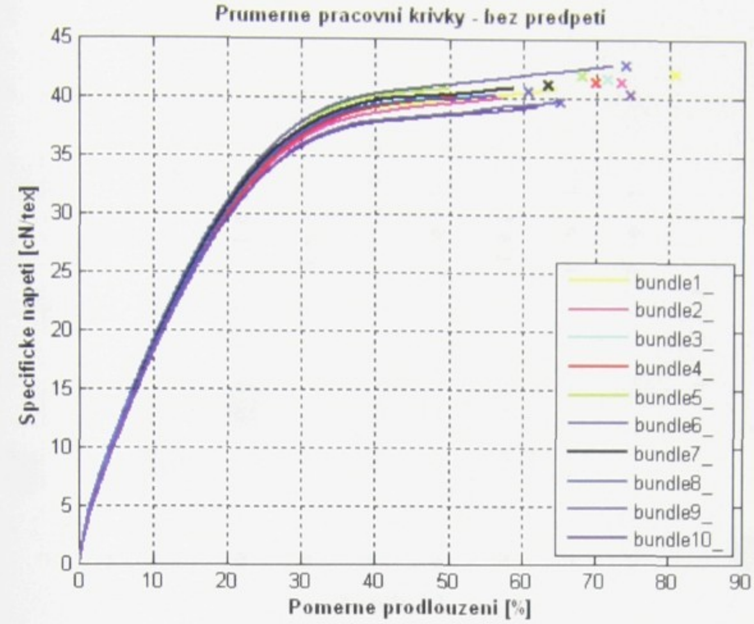

Fig 8.3.2.4: Strength at break graph at different bundle. (non twisted yarn)

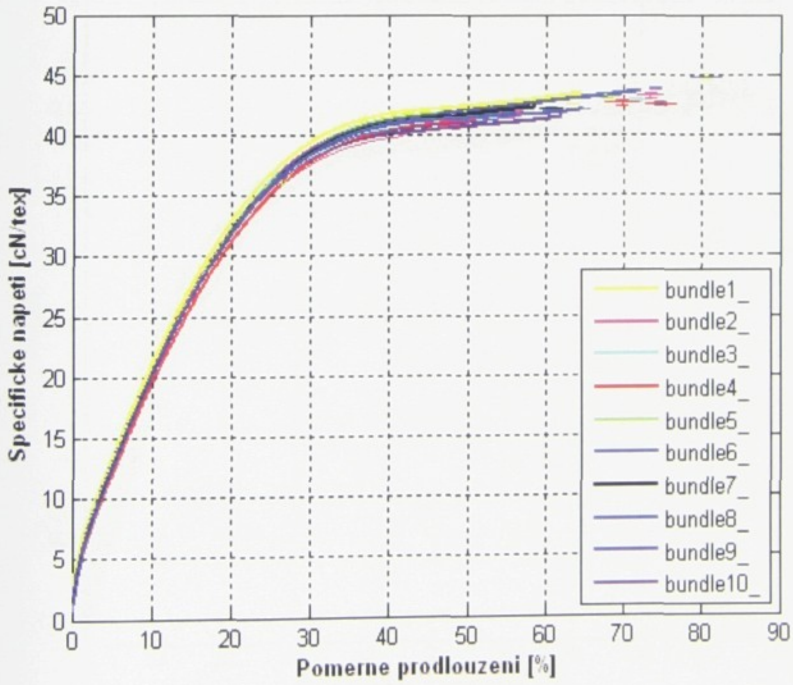

Fig 8.3.2.5: Strength at break graph at different bundle. (non twisted yarn)

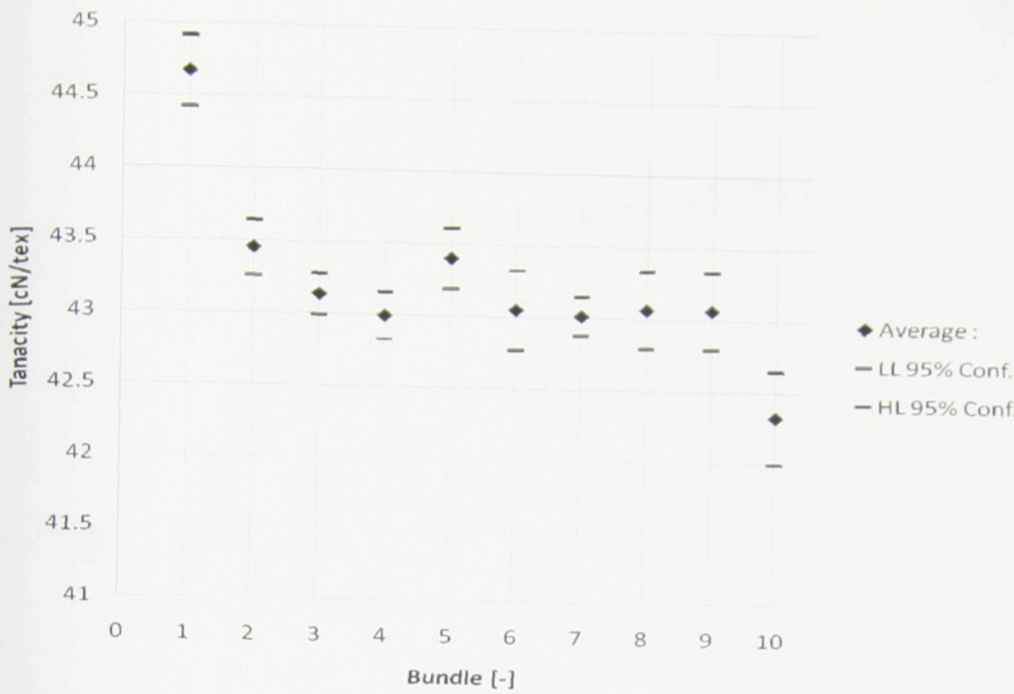

Fig 8.3.2.6: Stress strain force at different bundle. (non twisted yarn)

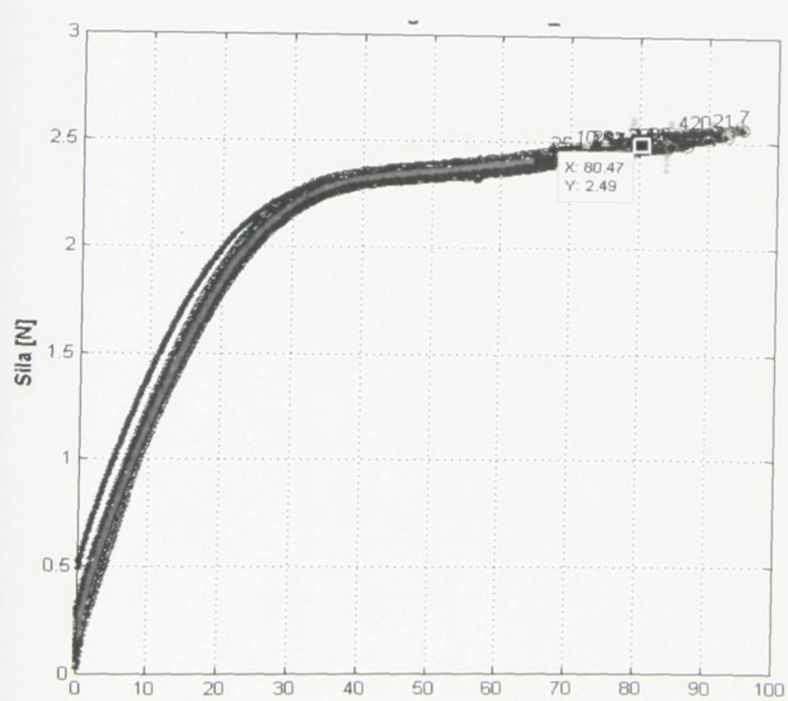

Fig 8.3.2.7: Elongation and tenacity graph for bundle 1. (non twisted yarn)

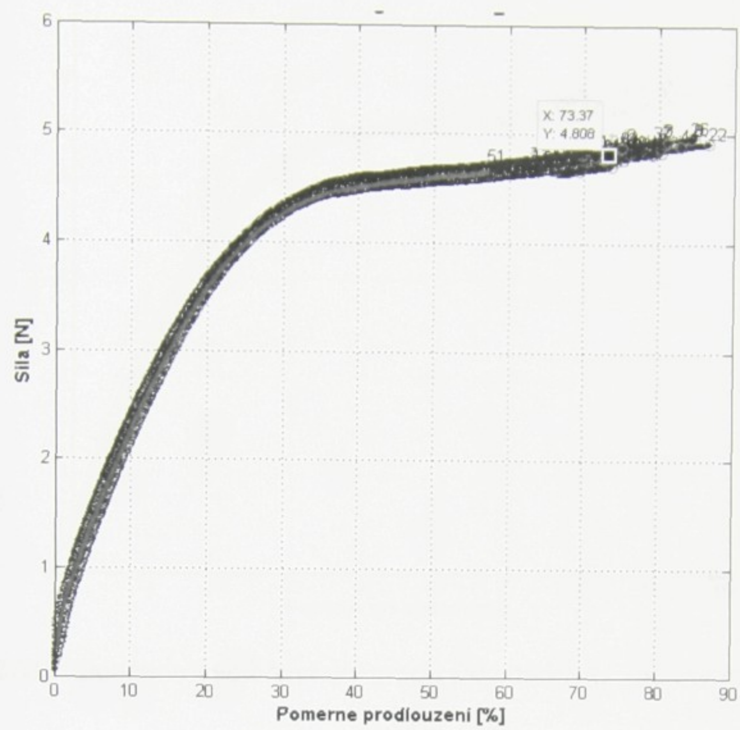

Fig 8.3.2.8: Elongation and tenacity graph for bundle 2. (non twisted yarn)

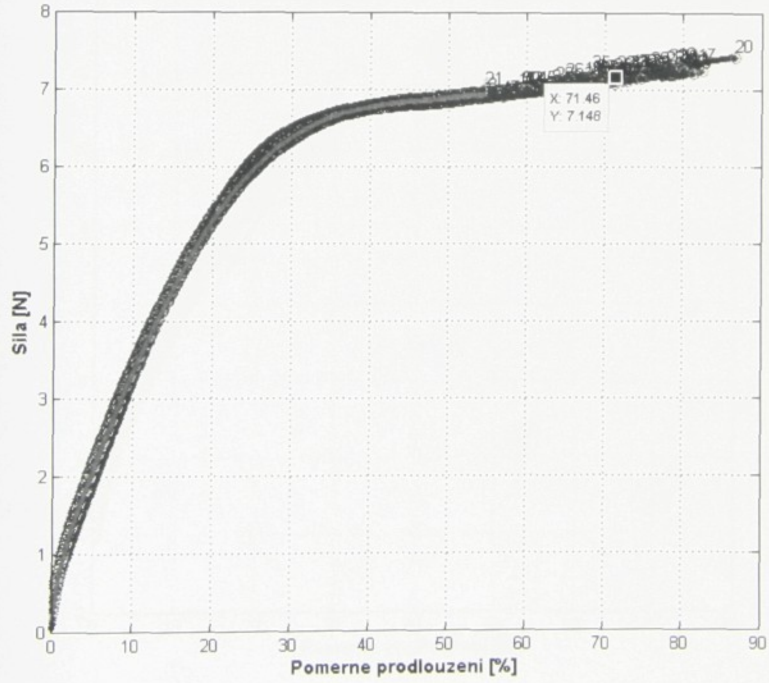

Fig 8.3.2.9: Elongation and tenacity graph for bundle 3. (non twisted yarn)

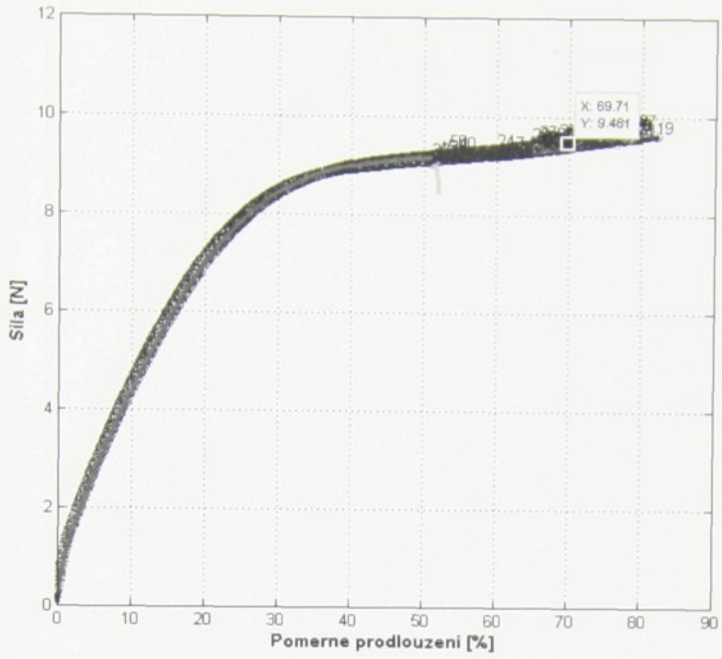

Fig 8.3.2.10: Elongation and tenacity graph for bundle 4. (non twisted yarn)

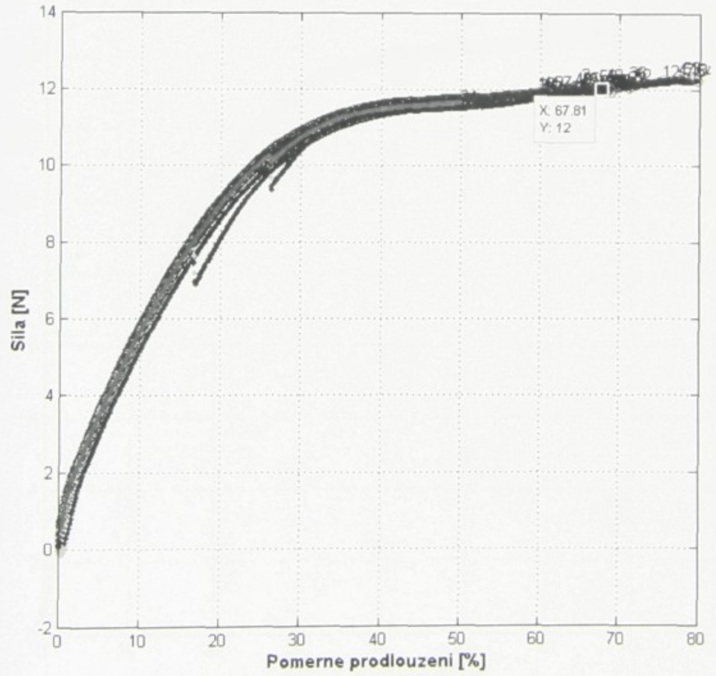

Fig 8.3.2.11: Elongation and tenacity graph for bundle 5. (non twisted yarn)

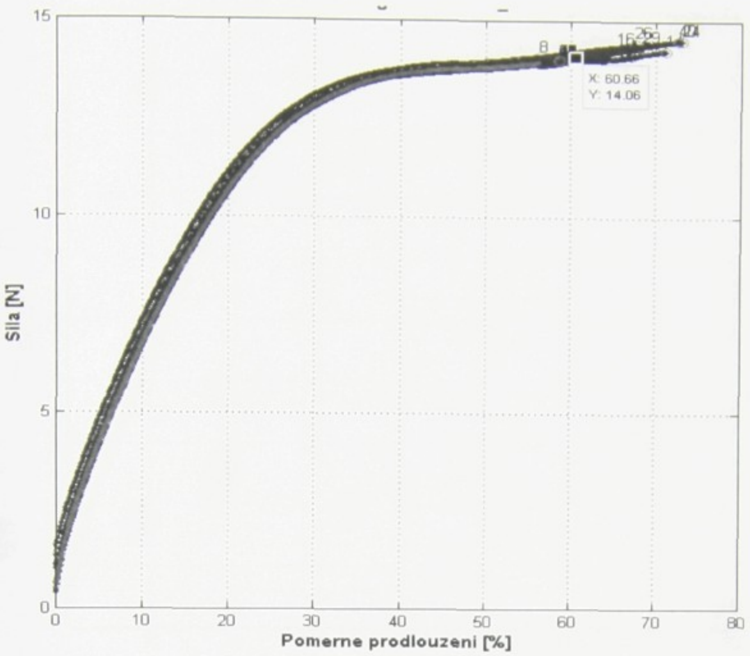

Fig 8.3.2.12: Elongation and tenacity graph for bundle 6. (non twisted yarn)

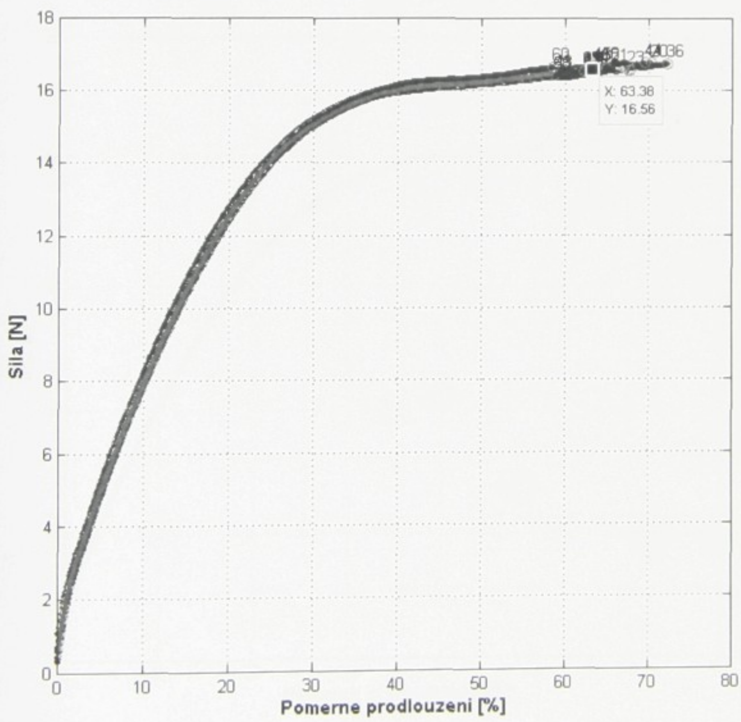

Fig 8.3.2.13: Elongation and tenacity graph for bundle 7. (non twisted yarn)

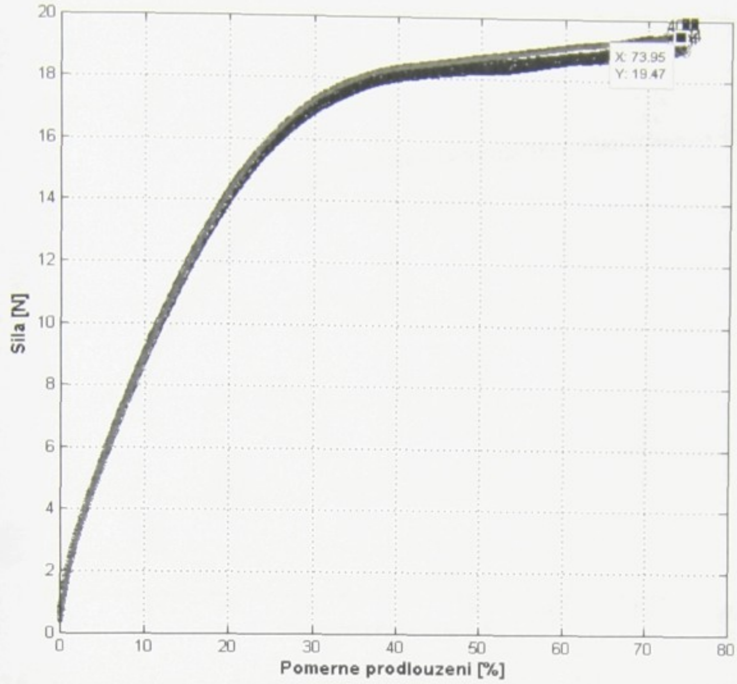

Fig 8.3.2.14: Elongation and tenacity graph for bundle 8. (non twisted yarn)

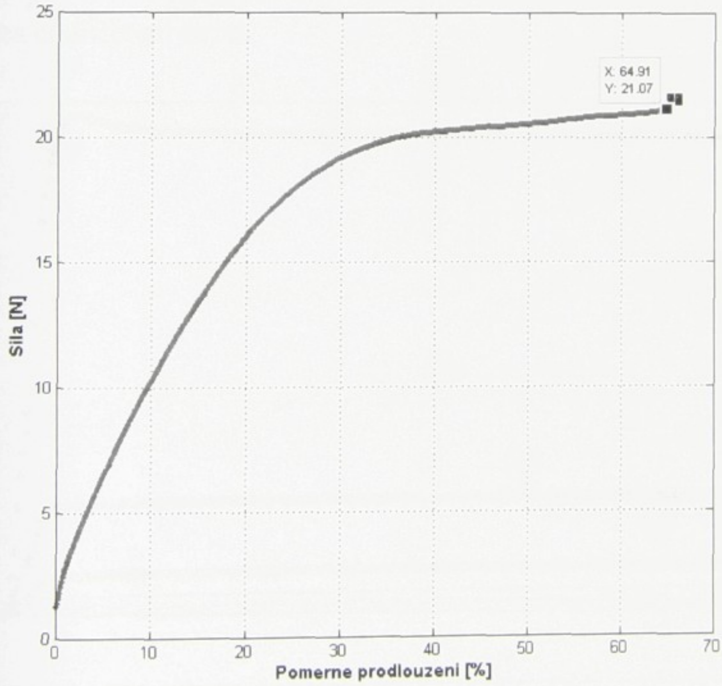

Fig 8.3.2.15: Elongation and tenacity graph for bundle 9. (non twisted yarn)

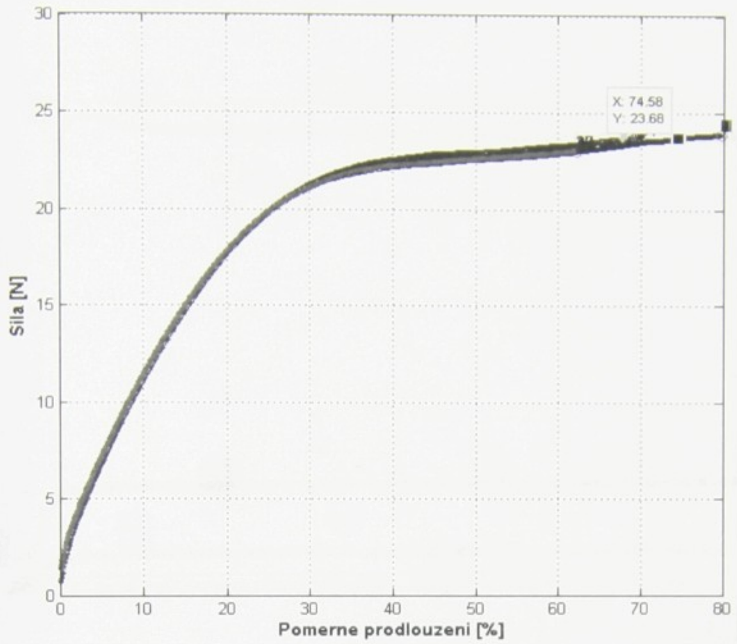

Fig 8.3.2.16: Elongation and tenacity graph for bundle 10. (non twisted yarn)

8.4 Shrinkages

8.4.1 Kinetic curves at different twist.

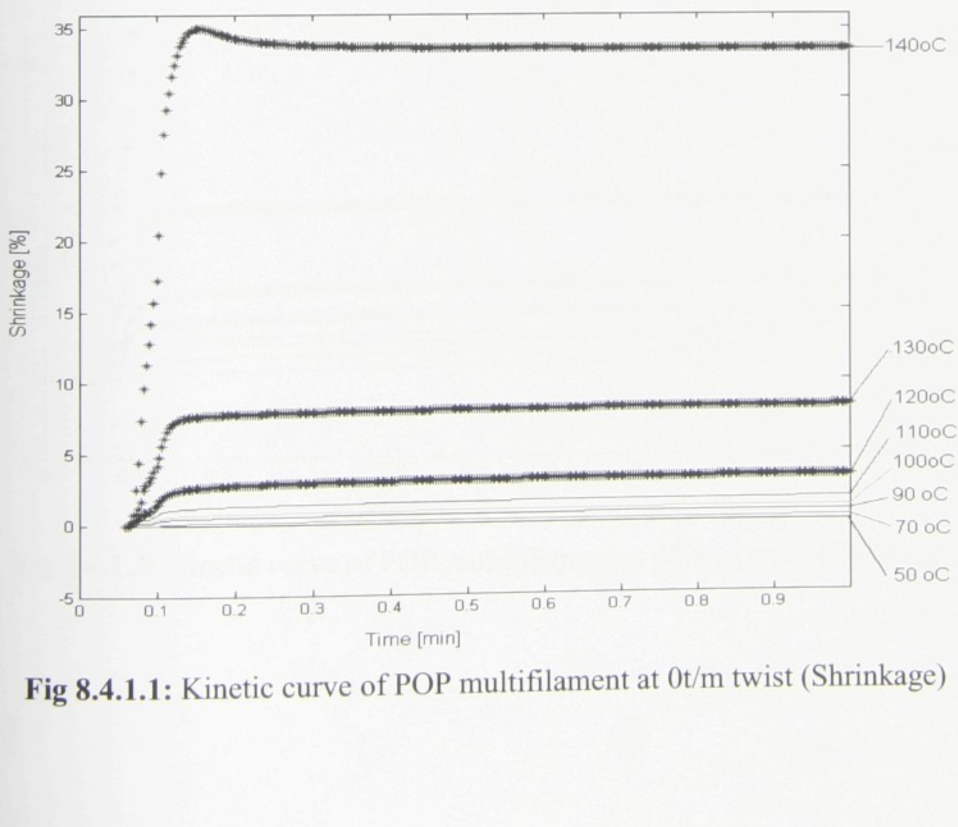

Fig 8.4.1.1: Kinetic curve of POP multifilament at 0t/m twist (Shrinkage)

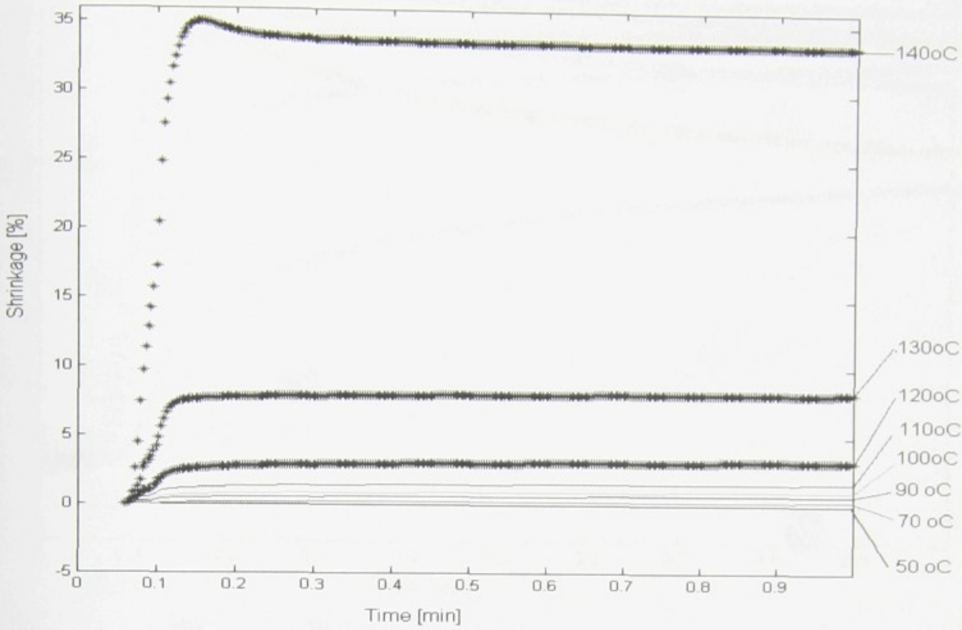

Fig 8.4.1.2: Kinetic curve of POP multifilament at 0t/m twist (Shrinkage force)

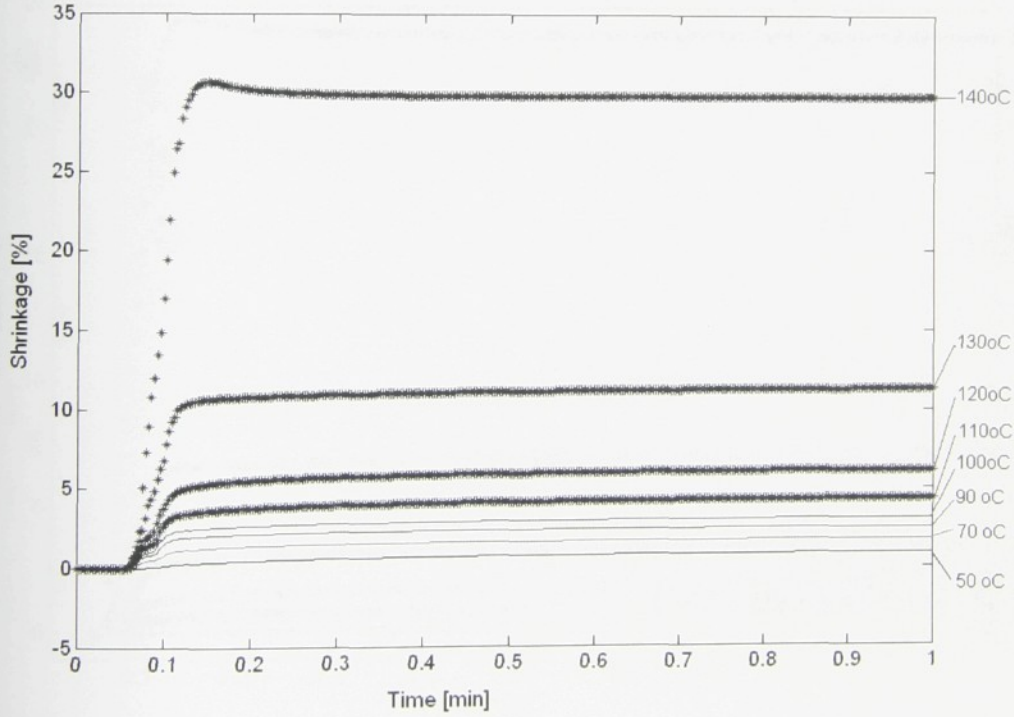

Fig 8.4.1.3: Kinetic curve of POP multifilament at 400t/m twist (Shrinkage)

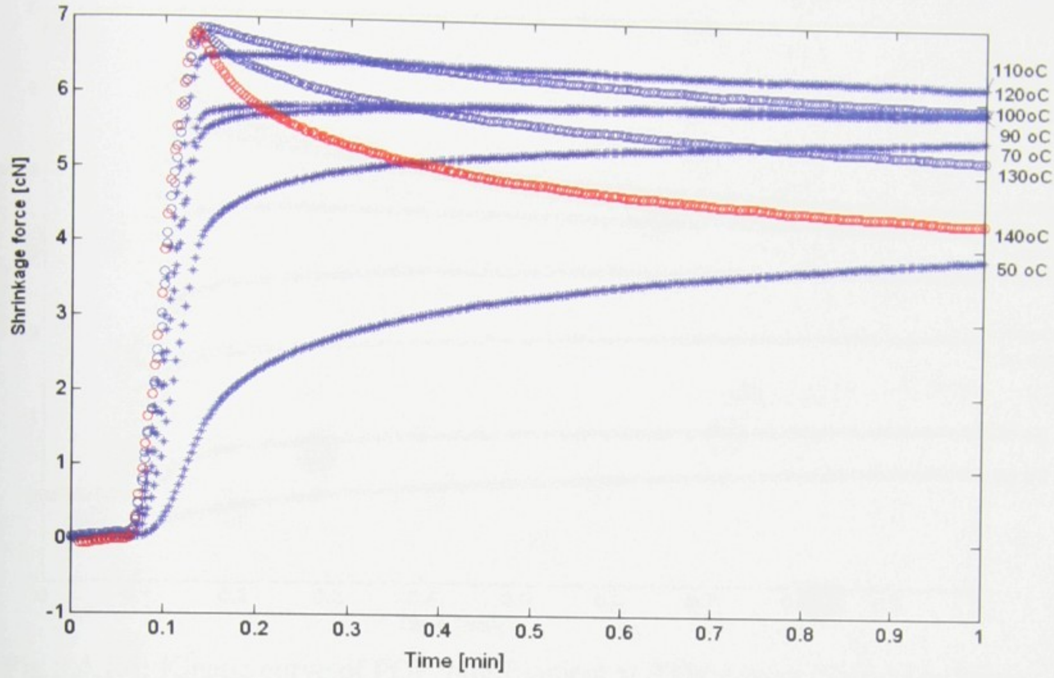

Fig 8.4.1.4: Kinetic curve of POP multifilament at 400t/m twist (Shrinkage force)

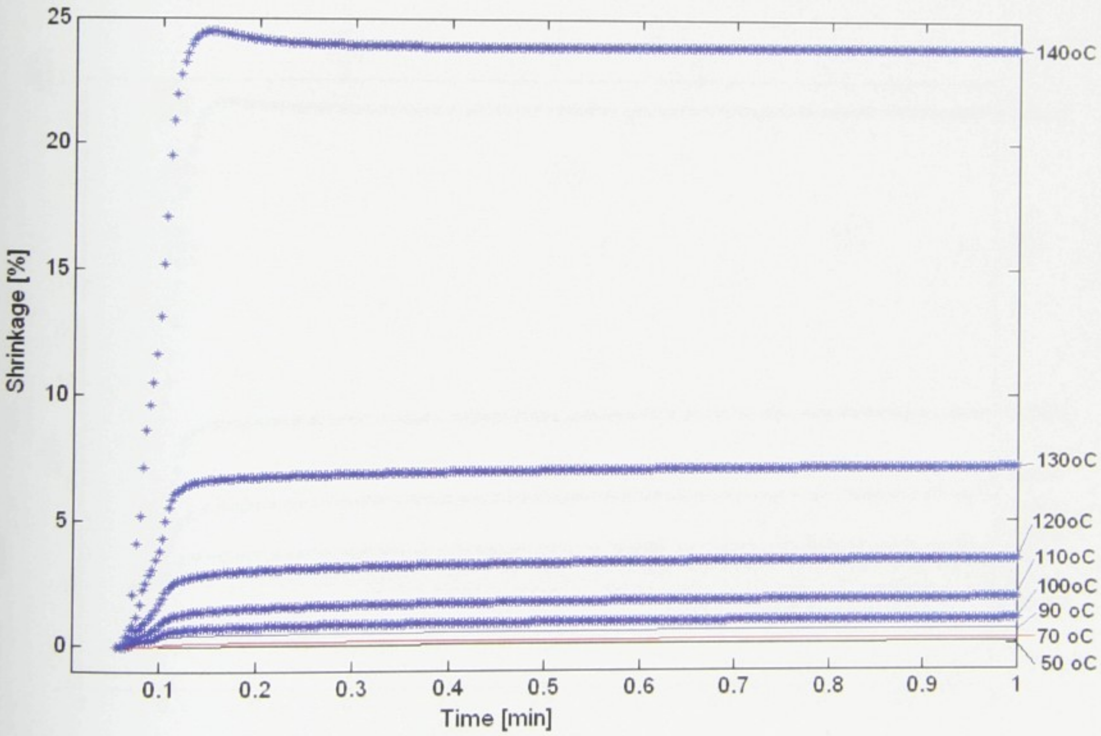

Fig 8.4.1.5: Kinetic curve of POP multifilament at 800t/m twist (Shrinkage)

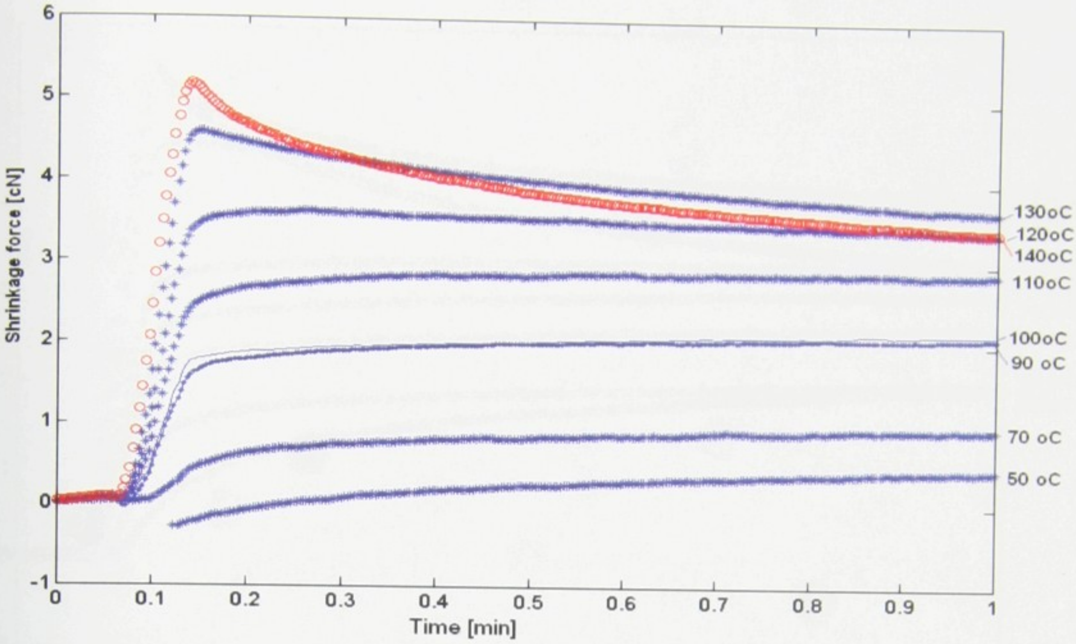

Fig 8.4.1.6: Kinetic curve of POP multifilament at 800t/m twist (Shrinkage force)

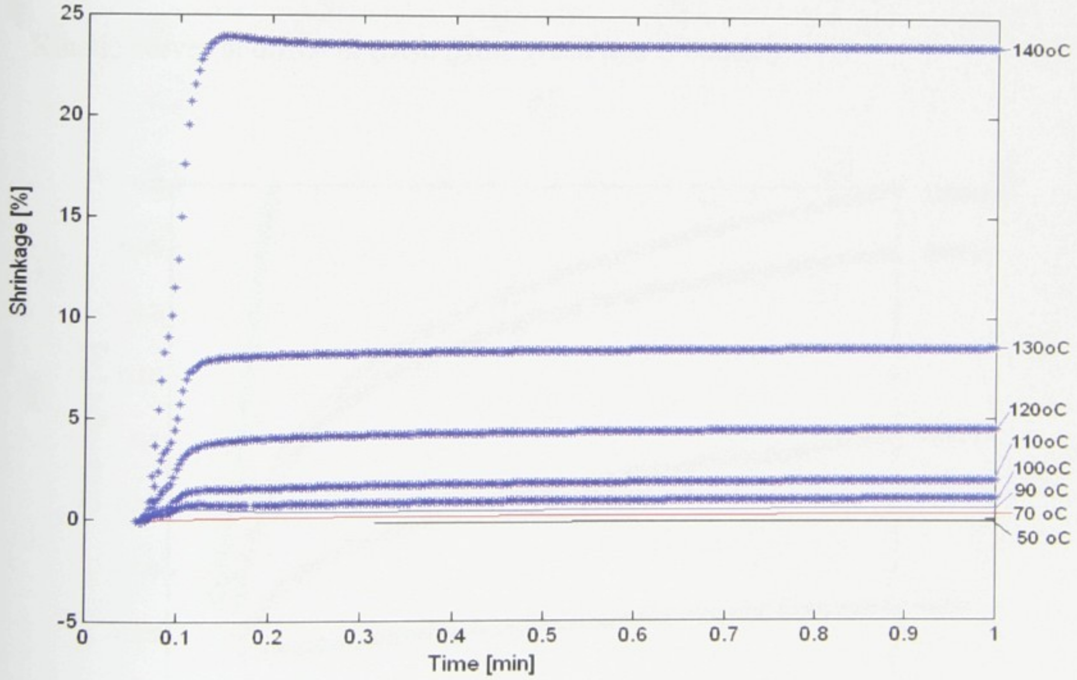

Fig 8.4.1.7: Kinetic curve of POP multifilament at 1200t/m twist (Shrinkage)

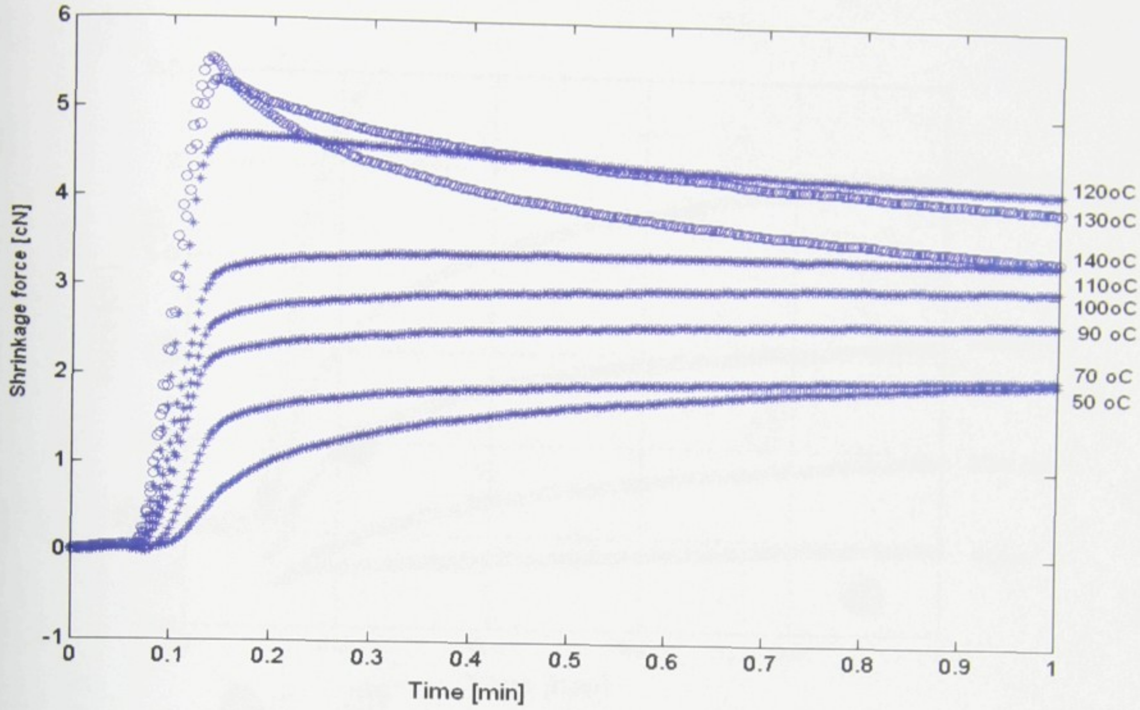

Fig 8.4.1.8: Kinetic curve of POP multifilament at 1200t/m twist (Shrinkage force)

8.4.2 Kinetic curves at different twist. *(Note green line is 400t/m)*

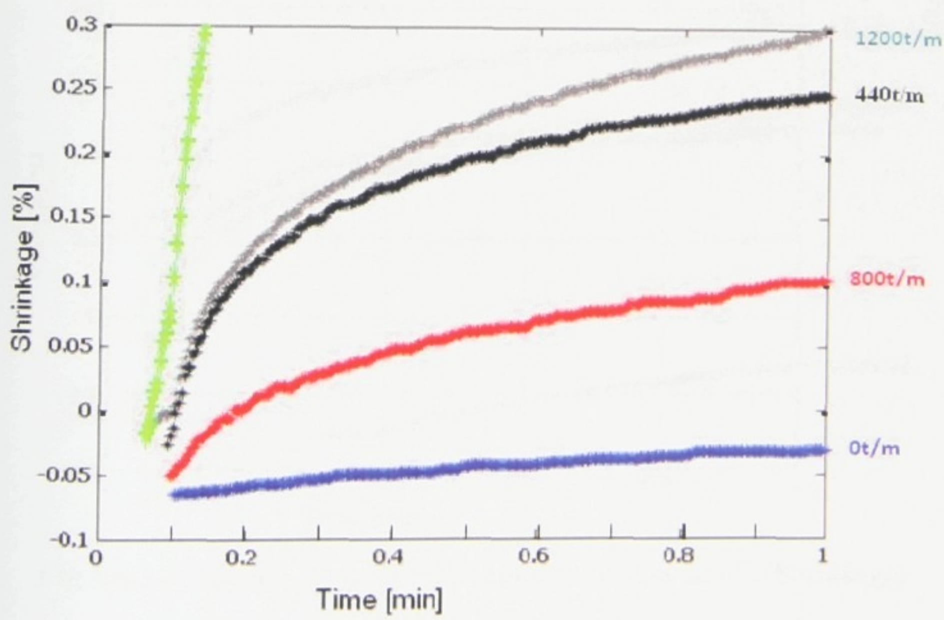

Fig 8.4.2.1: Kinetic curve of POP multifilament at 50 oC (Shrinkage)

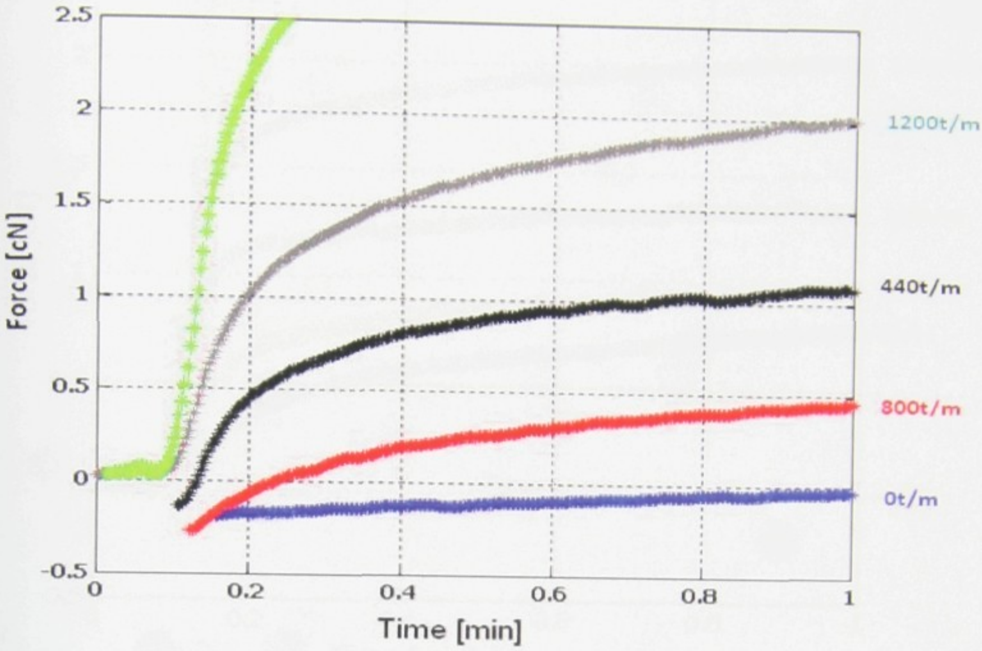

Fig 8.4.2.2: Kinetic curve of POP multifilament at 50 oC (Shrinkage force)

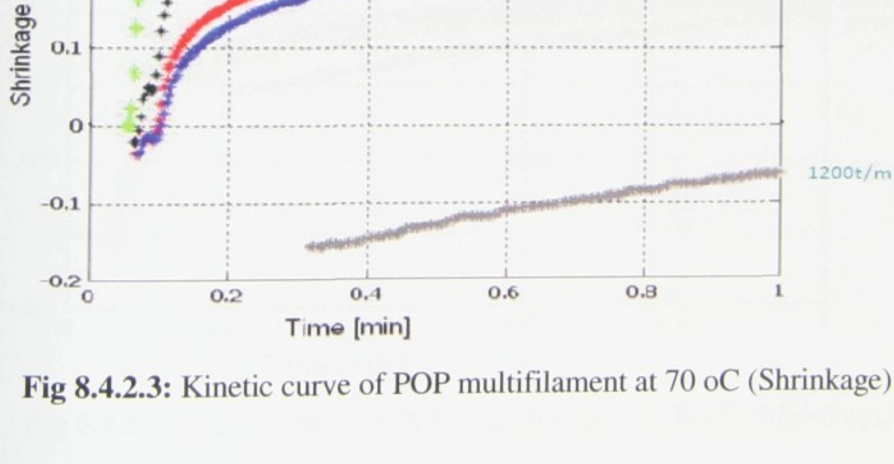

Fig 8.4.2.3: Kinetic curve of POP multifilament at 70 oC (Shrinkage)

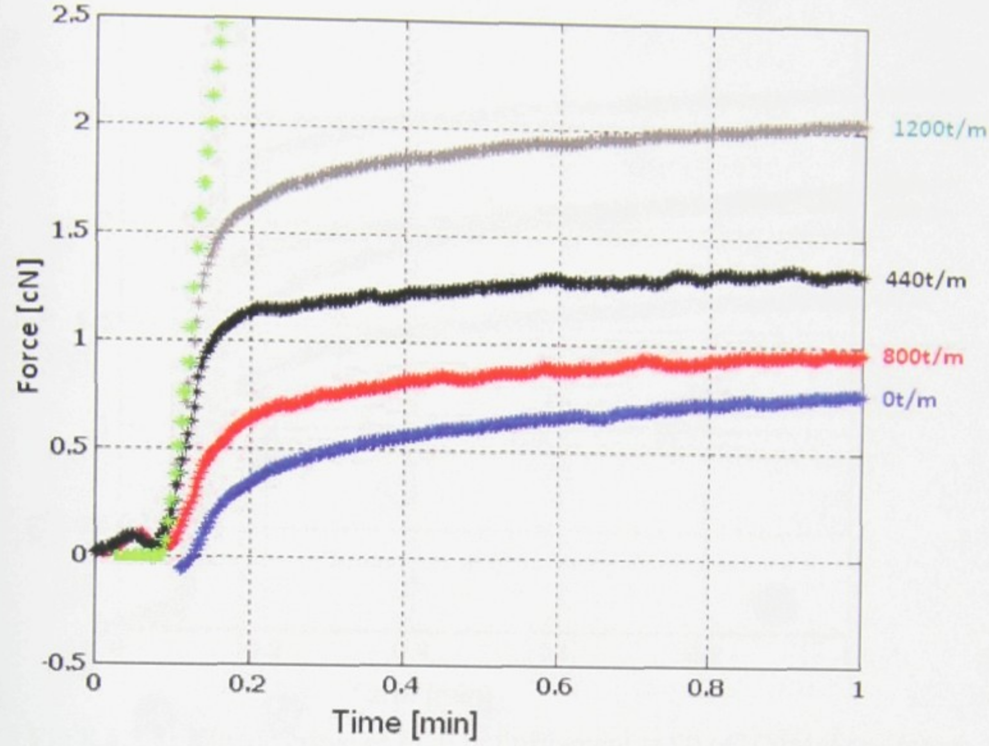

Fig 8.4.2.4: Kinetic curve of POP multifilament at 70 oC (Shrinkage force)

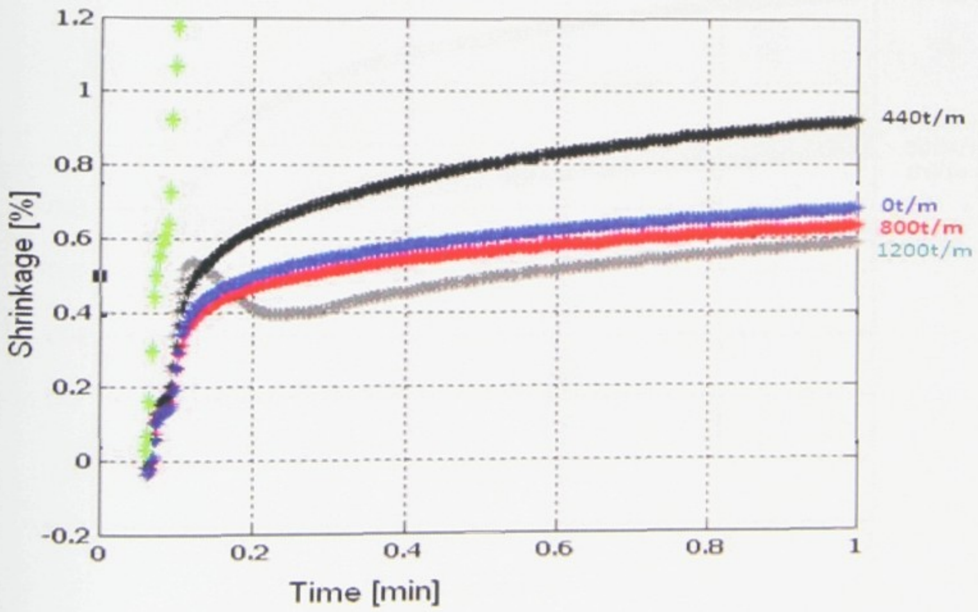

Fig 8.4.2.5: Kinetic curve of POP multifilament at 90 oC (Shrinkage)

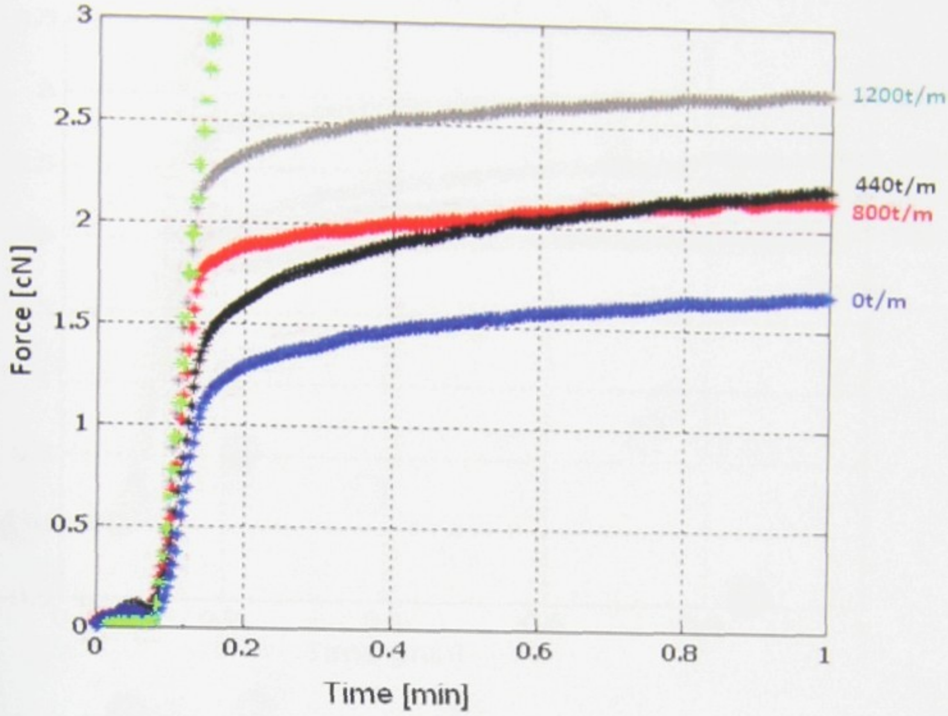

Fig 8.4.2.4: Kinetic curve of POP multifilament at 90 oC (Shrinkage force)

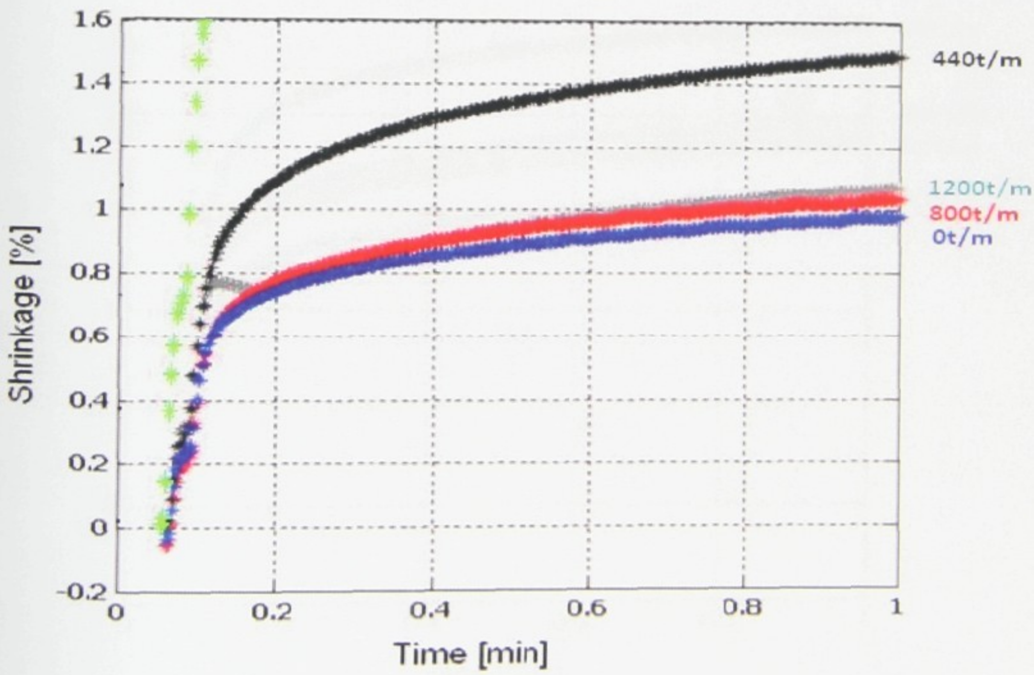

Fig 8.4.2.6: Kinetic curve of POP multifilament at 100 oC (Shrinkage force)

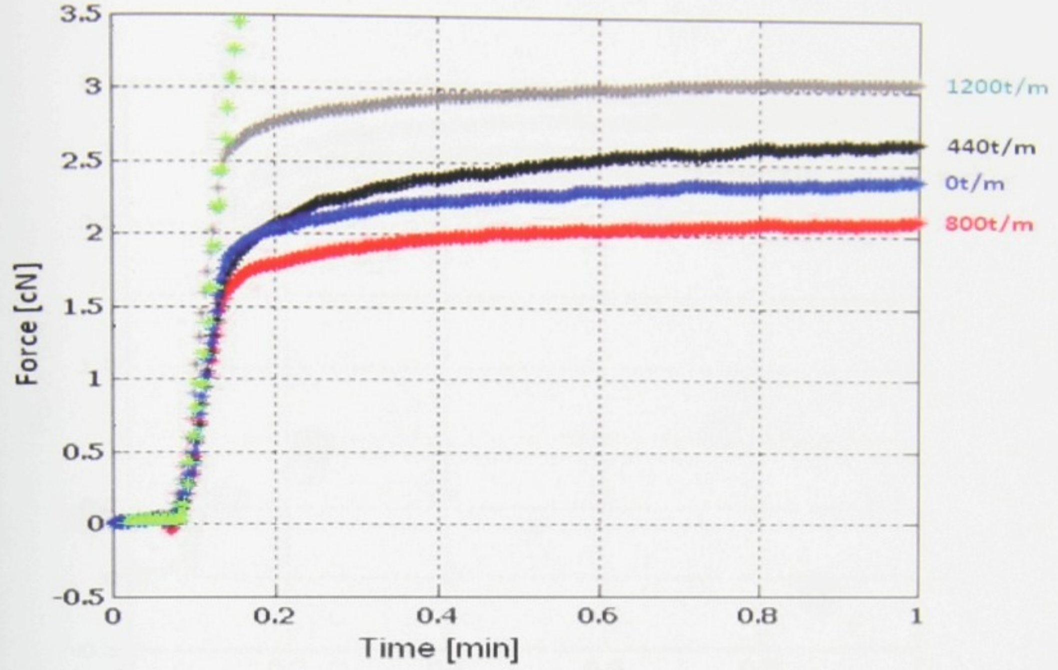

Fig 8.4.2.6: Kinetic curve of POP multifilament at 100 oC (Shrinkage force)

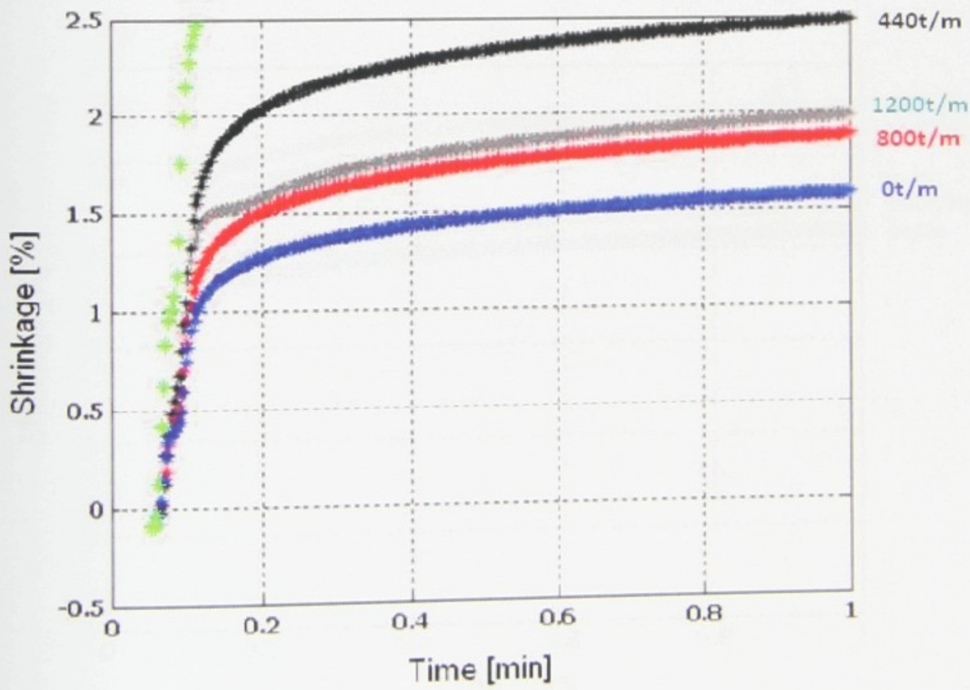

Fig 8.4.2.7: Kinetic curve of POP multifilament at 110 oC (Shrinkage)

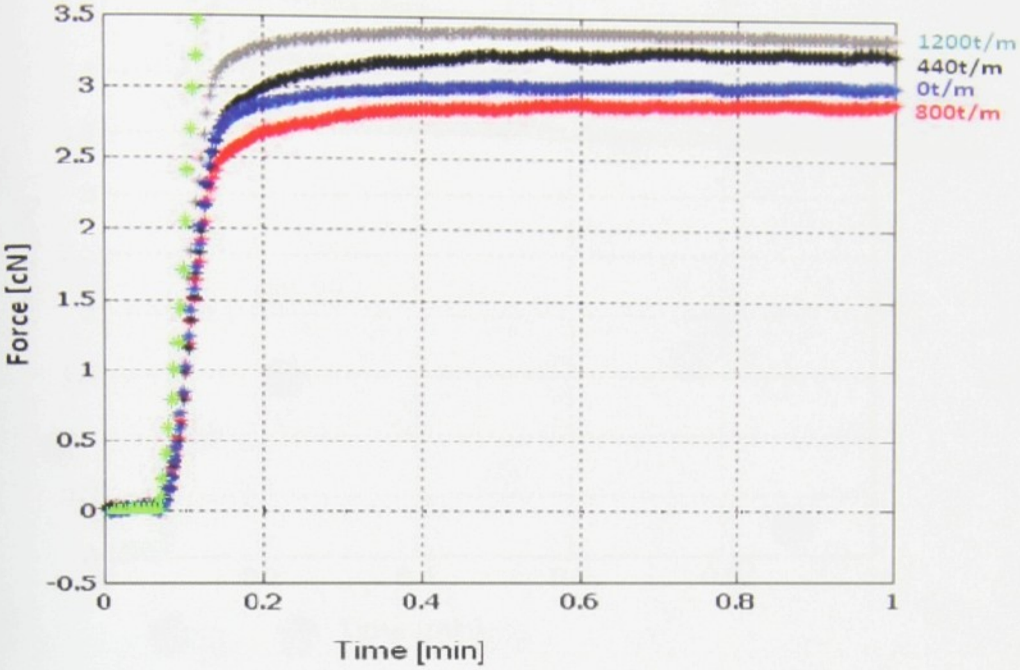

Fig 8.4.2.8: Kinetic curve of POP multifilament at 110 oC (Shrinkage force)

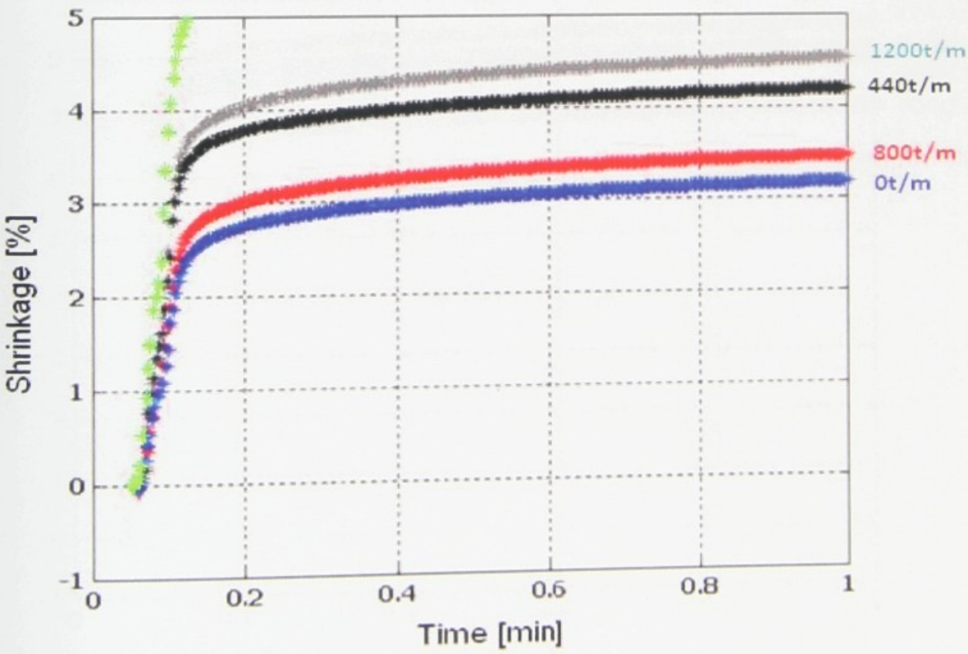

Fig 8.4.2.9: Kinetic curve of POP multifilament at 120 oC (Shrinkage)

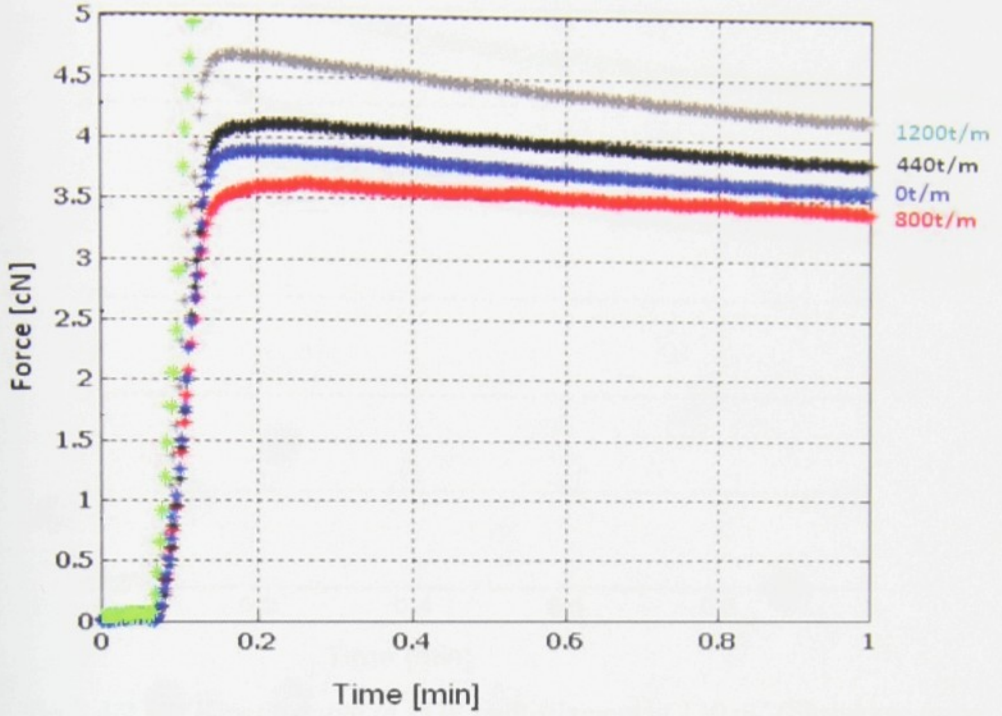

Fig 8.4.2.9: Kinetic curve of POP multifilament at 120 oC (Shrinkage)

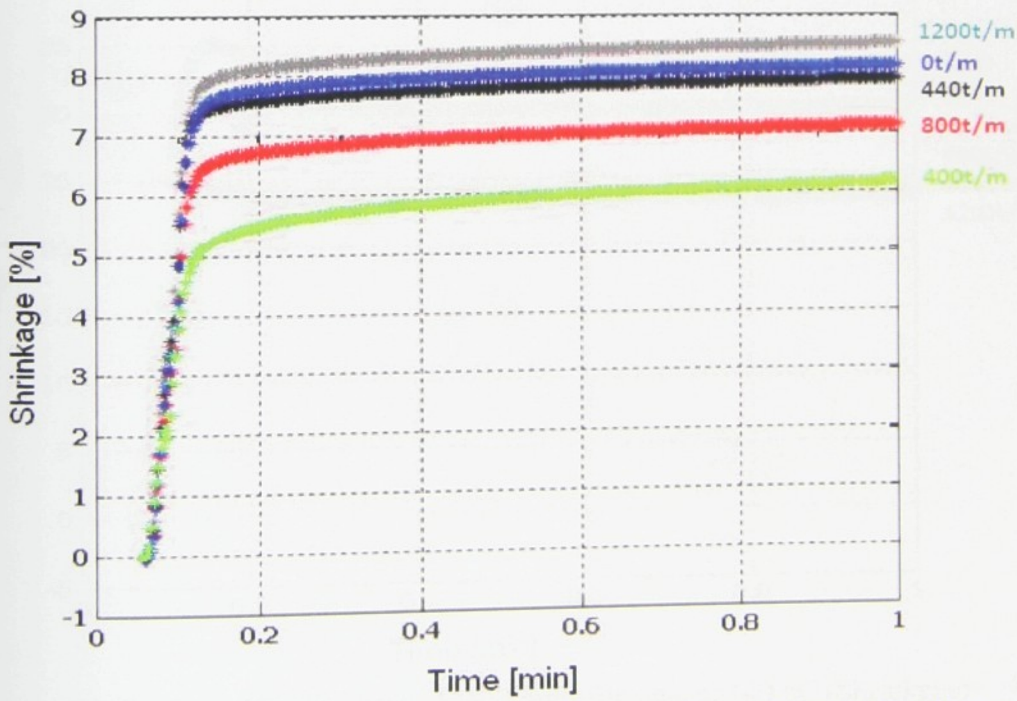

Fig 8.4.2.10: Kinetic curve of POP multifilament at 130 oC (Shrinkage force)

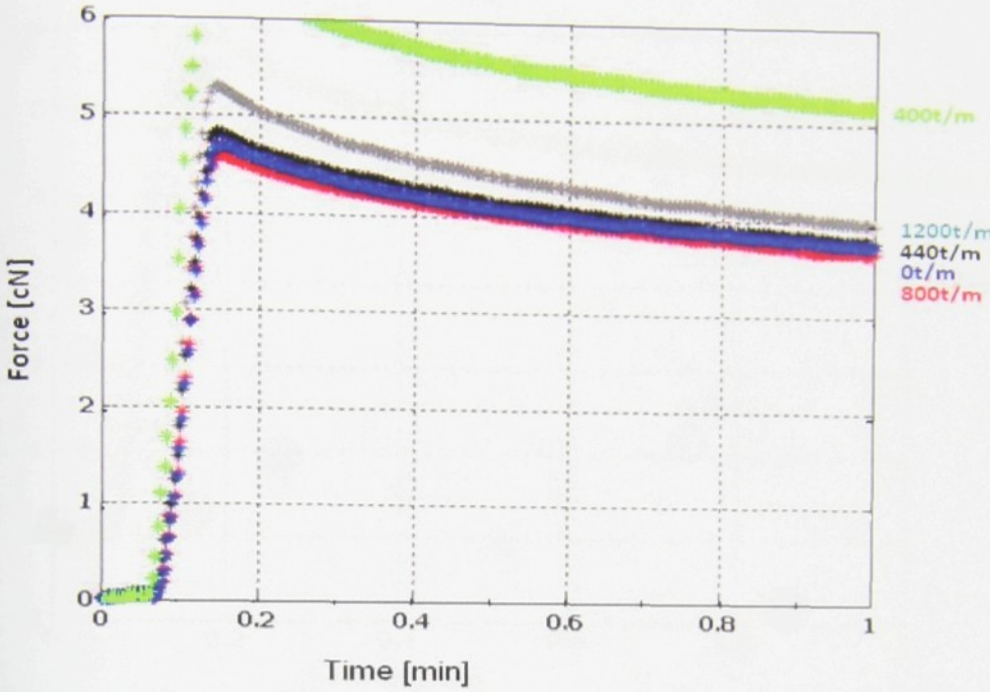

Fig 8.4.2.10: Kinetic curve of POP multifilament at 130 oC (Shrinkage force)

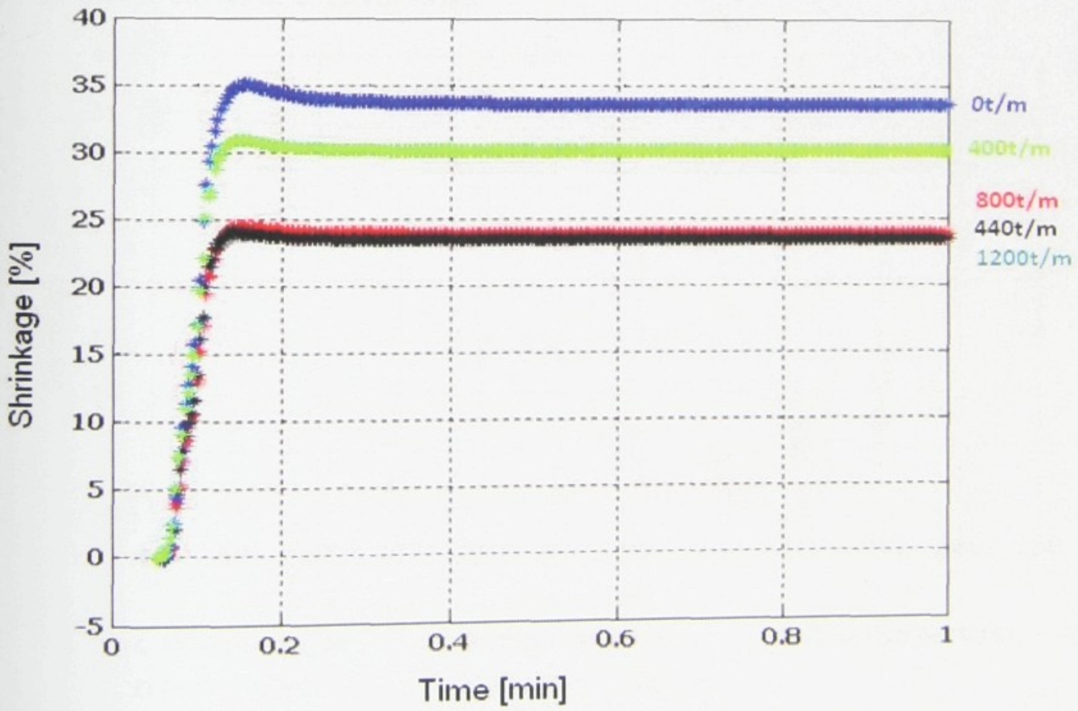

Fig 8.4.2.11: Kinetic curve of POP multifilament at 140 oC (Shrinkage)

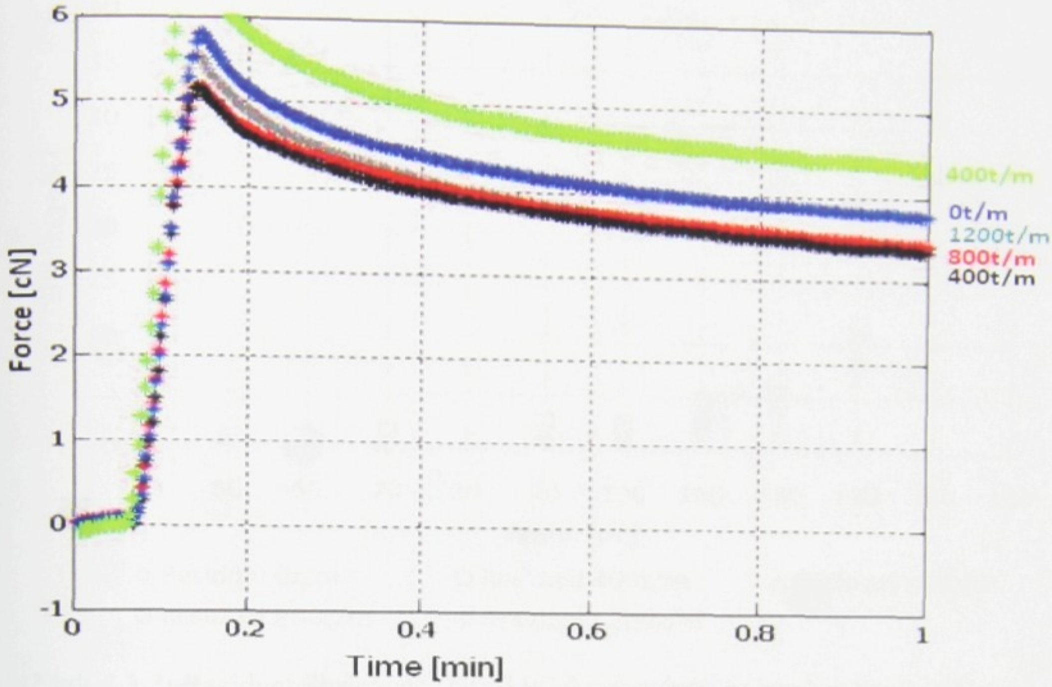

Fig 10.4.2.12: Kinetic curve of POP multifilament at 140 oC (Shrinkage force)

8.4.3 Shrinkage curves at different twist.

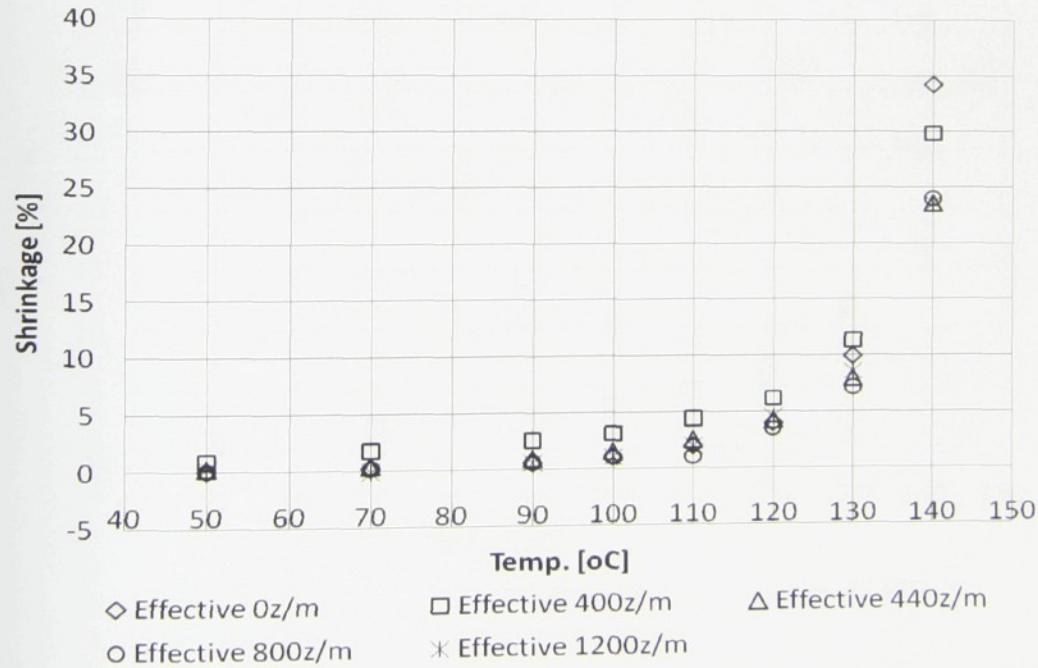

Fig8.4.3.1: Effective Shrinkage for all POP yarns (non twisted and twisted yarn)

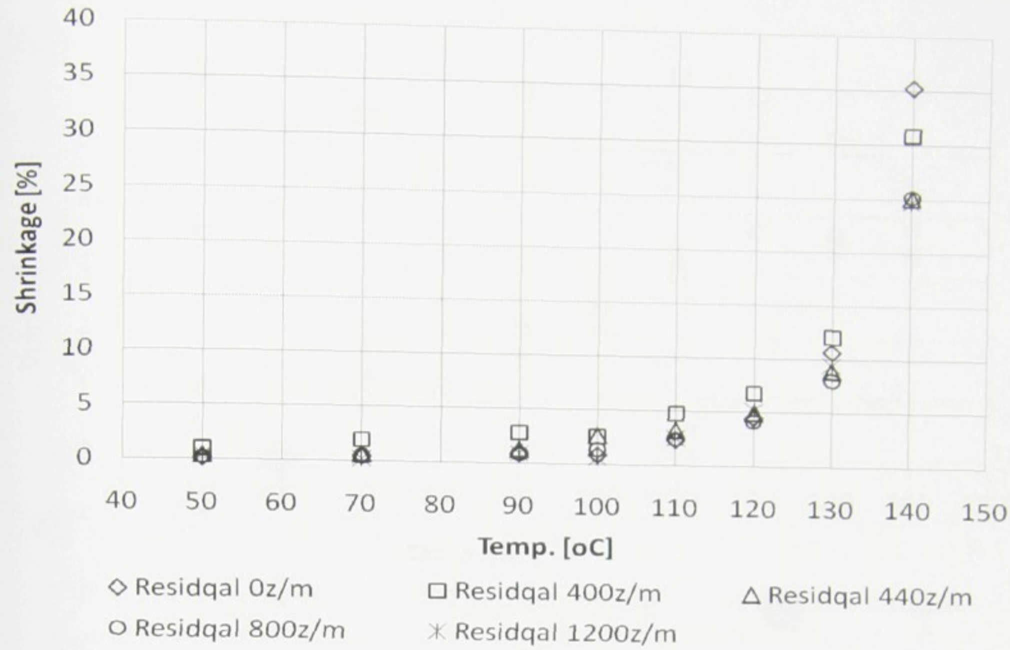

Fig8.4.3.2: Residual Shrinkage for all POP yarns (non twisted and twisted yarn)

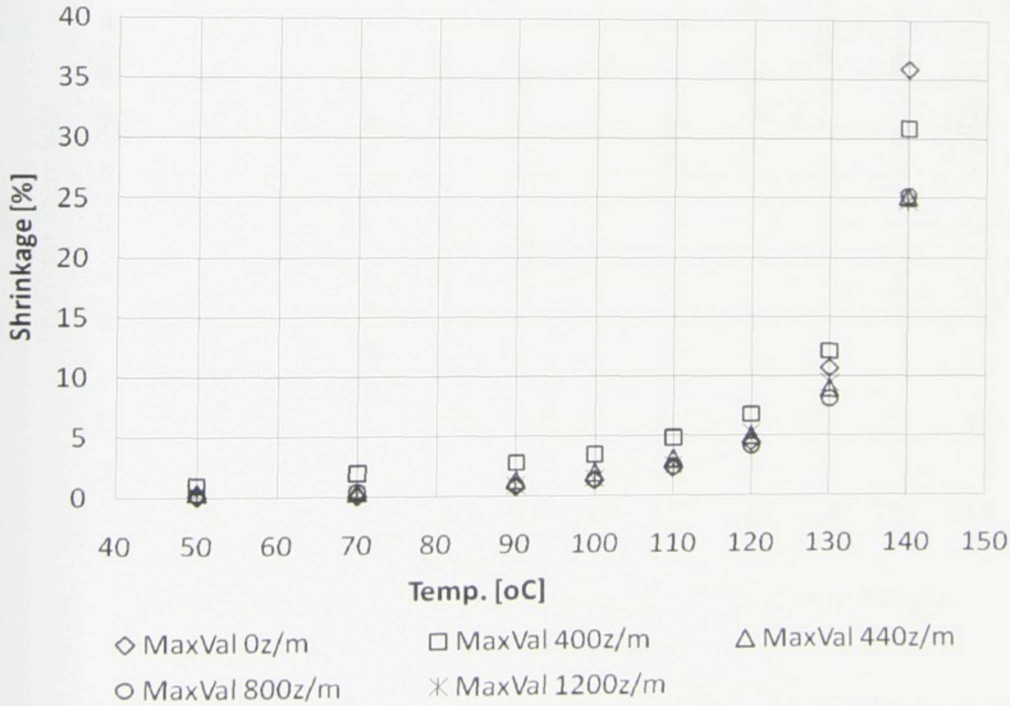

Fig8.4.3.3: MaxVal Shrinkage for all POP yarns (non twisted and twisted yarn)

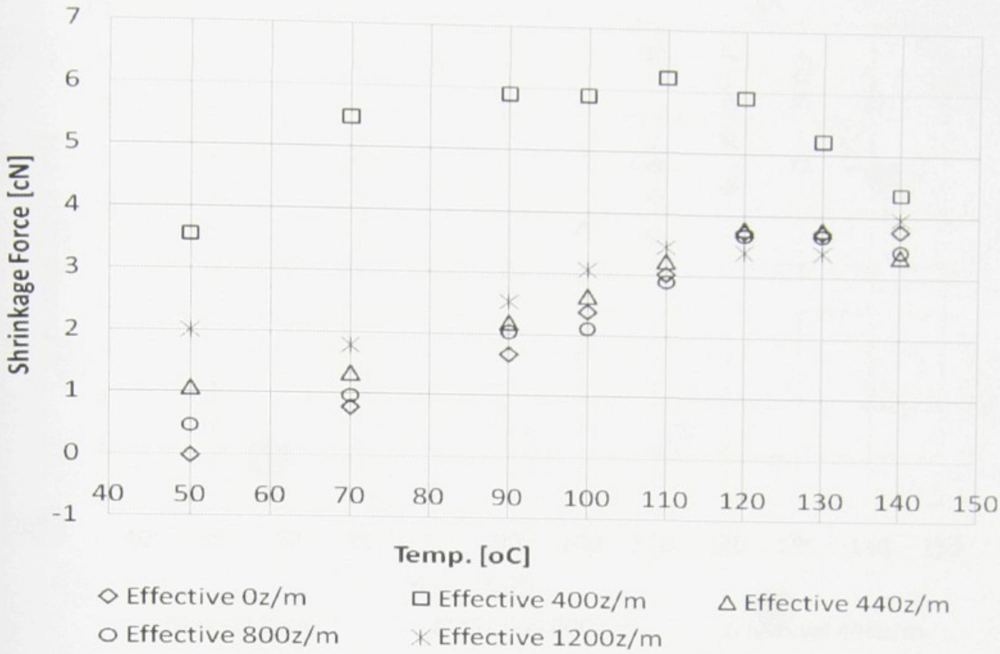

Fig8.4.3.4: Effective Shrinkage force for all POP yarns (non twisted and twisted yarn)

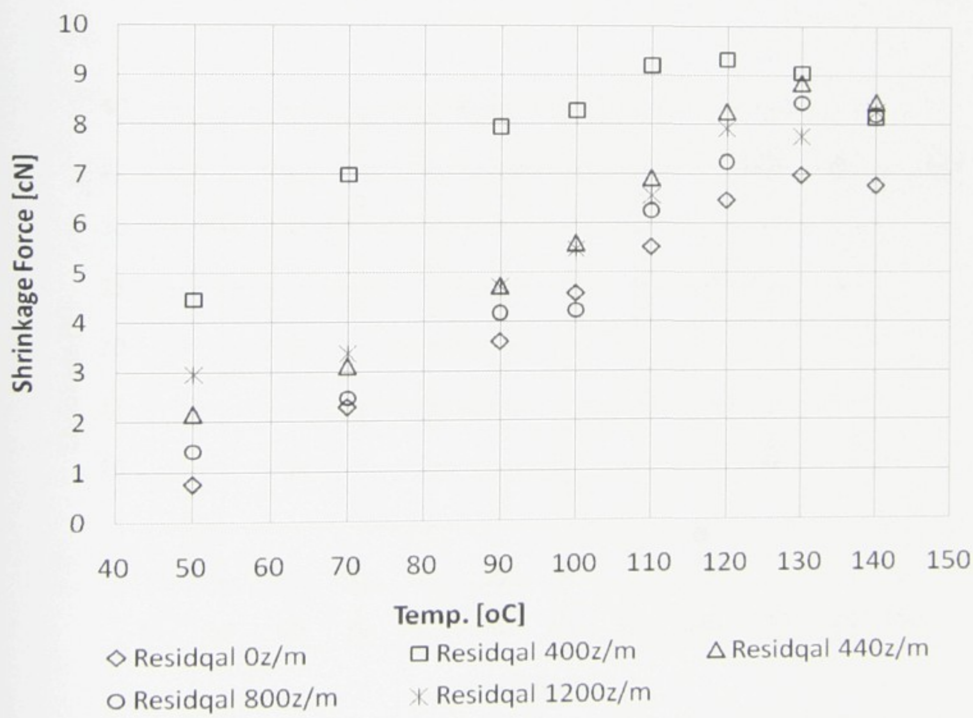

Fig8.4.3.5: Residual Shrinkage force for all POP yarns (non twisted and twisted yarn)

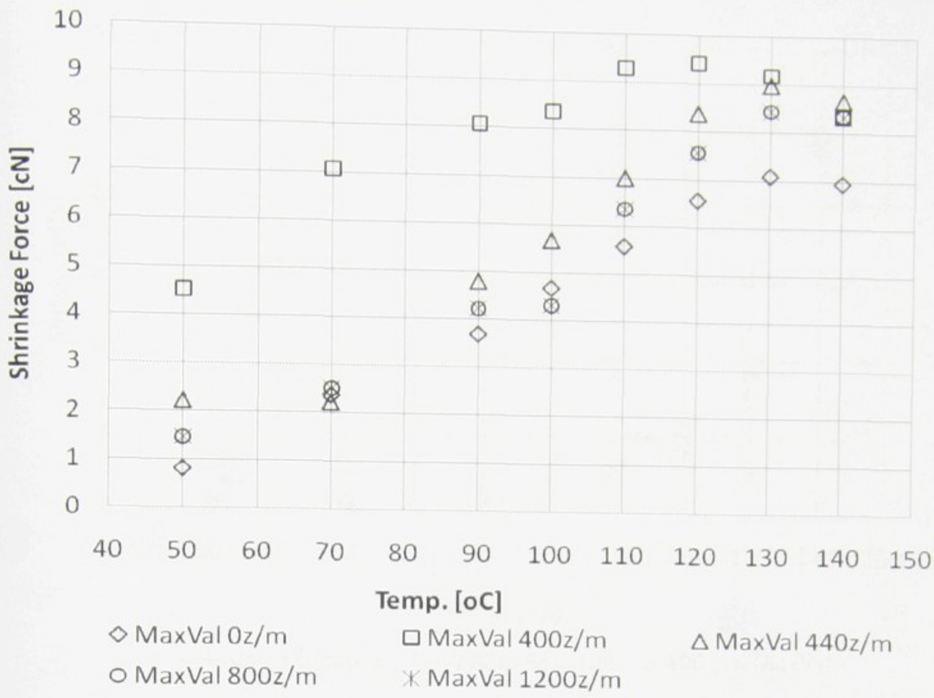

Fig8.4.3.6: Maximum Shrinkage force for all POP yarns (non twisted and twisted yarn)

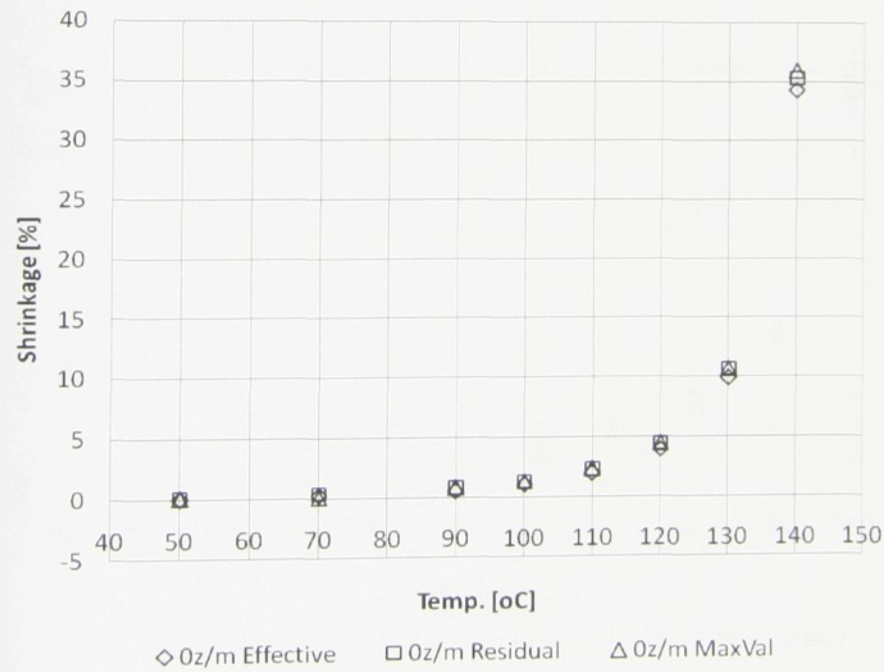

Fig8.4.3.7: Shrinkage for POP yarns at no twist

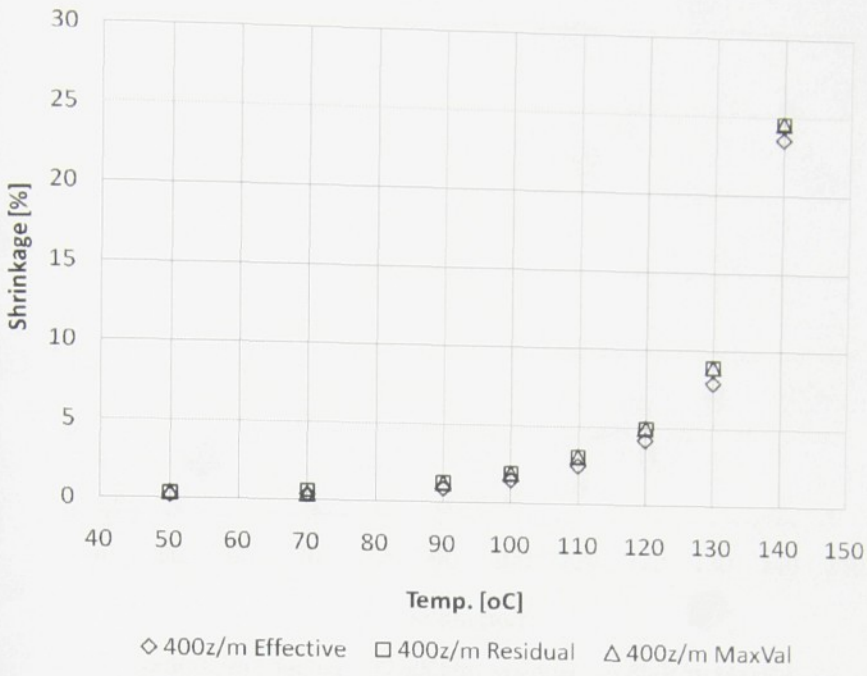

Fig8.4.3.8: Shrinkage for POP yarns at 400t/m

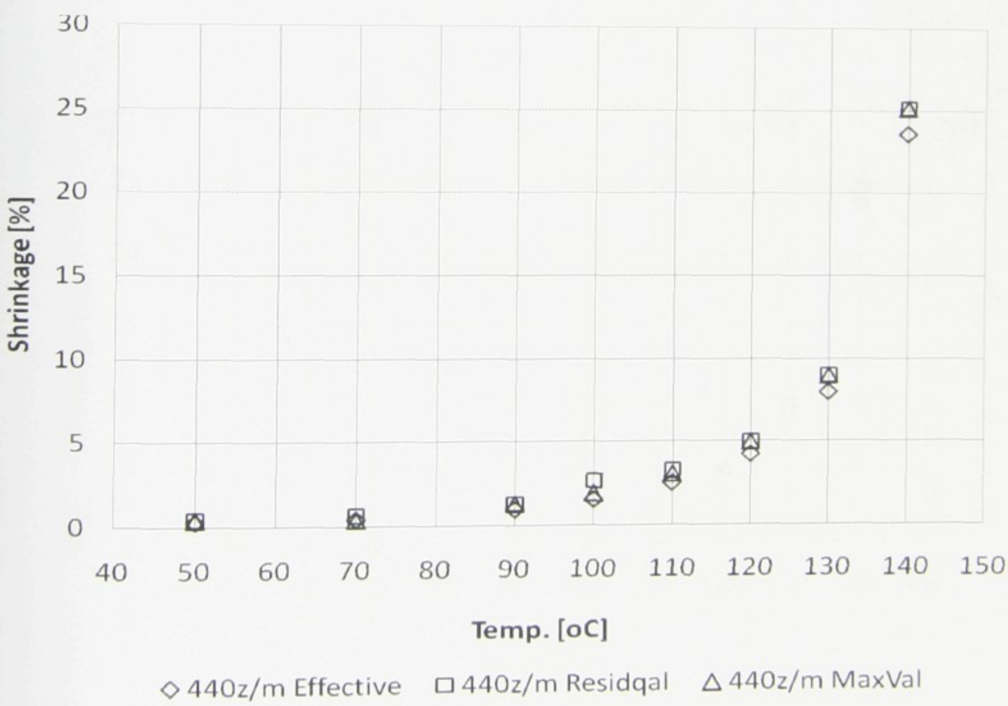

Fig8.4.3.9: Shrinkage for POP yarns at 440t/m

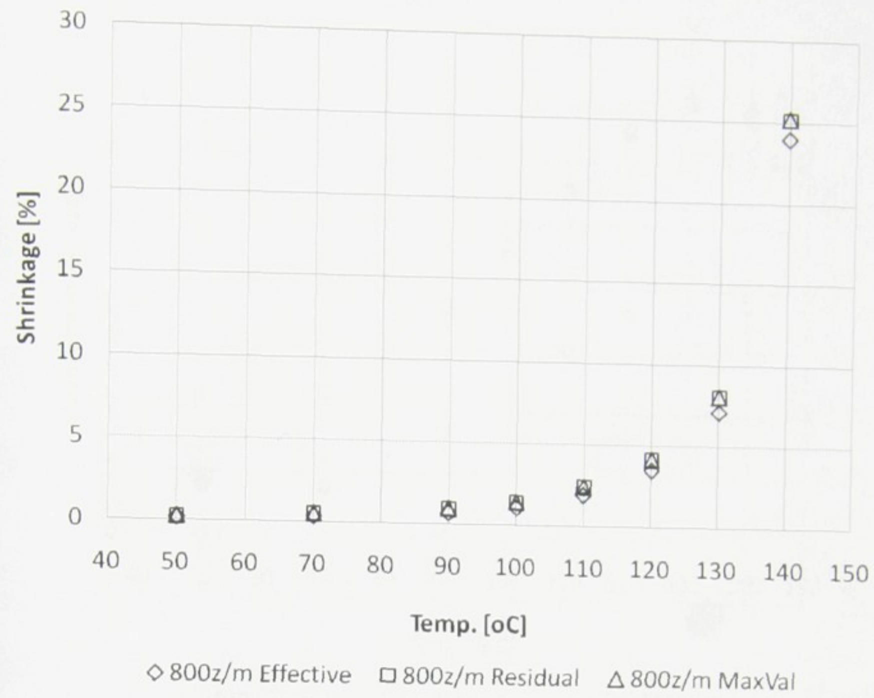

Fig8.4.3.10: Shrinkage for POP yarns at 800t/m

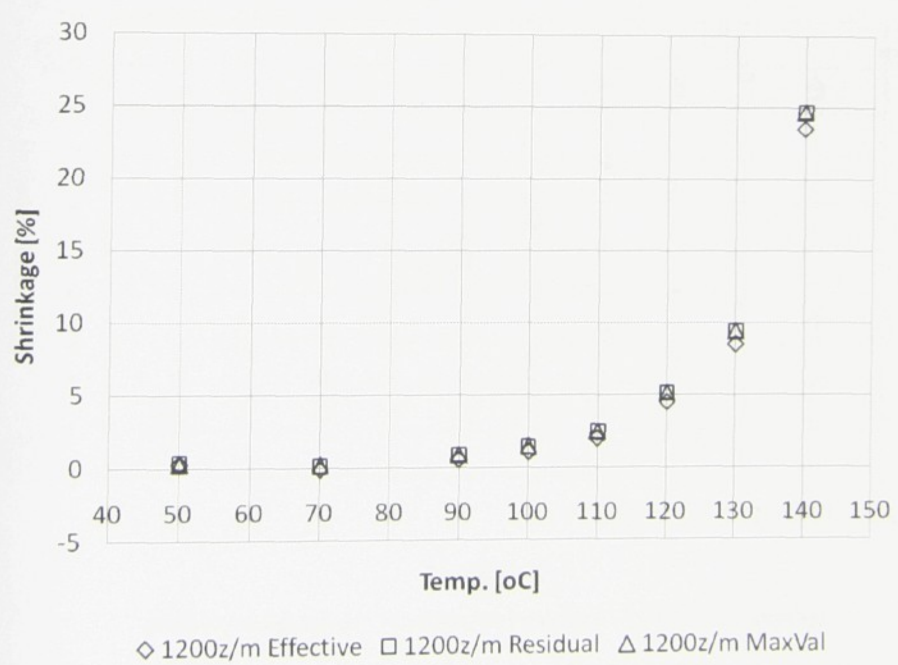

Fig8.4.3.11: Shrinkage for POP yarns at 1200t/m

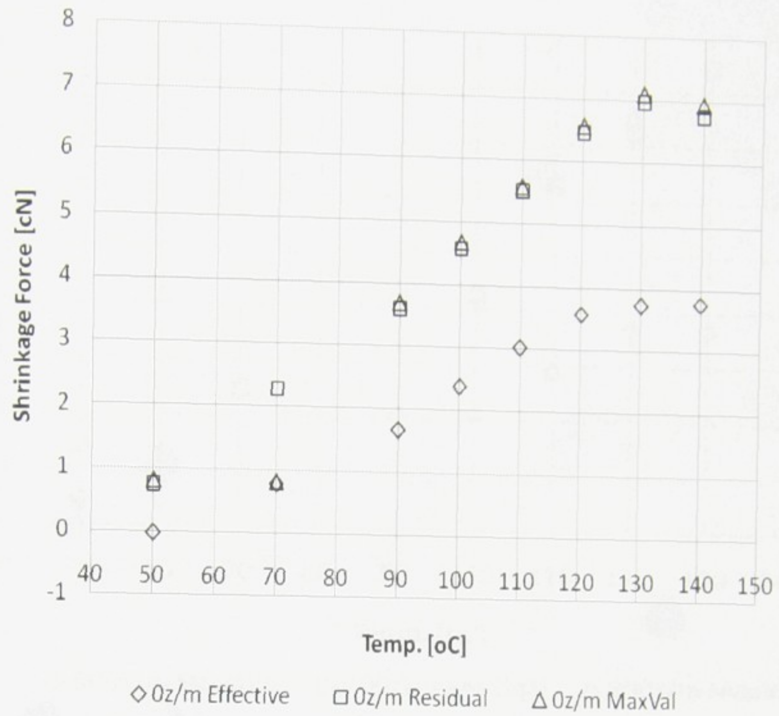

Fig8.4.3.12: Shrinkage force for POP yarns at 0t/m

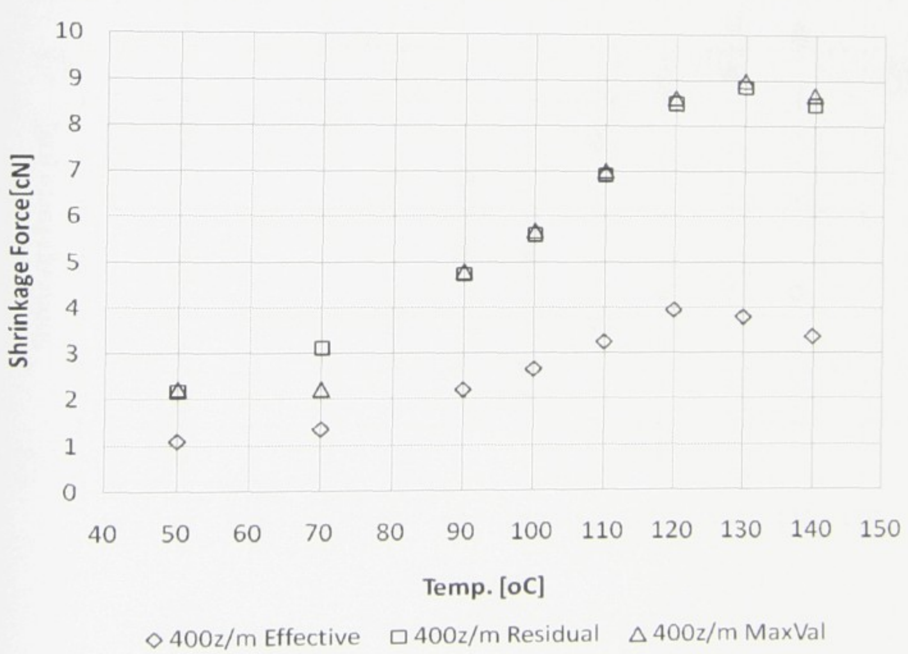

Fig8.4.3.13: Shrinkage force for POP yarns at 400t/m

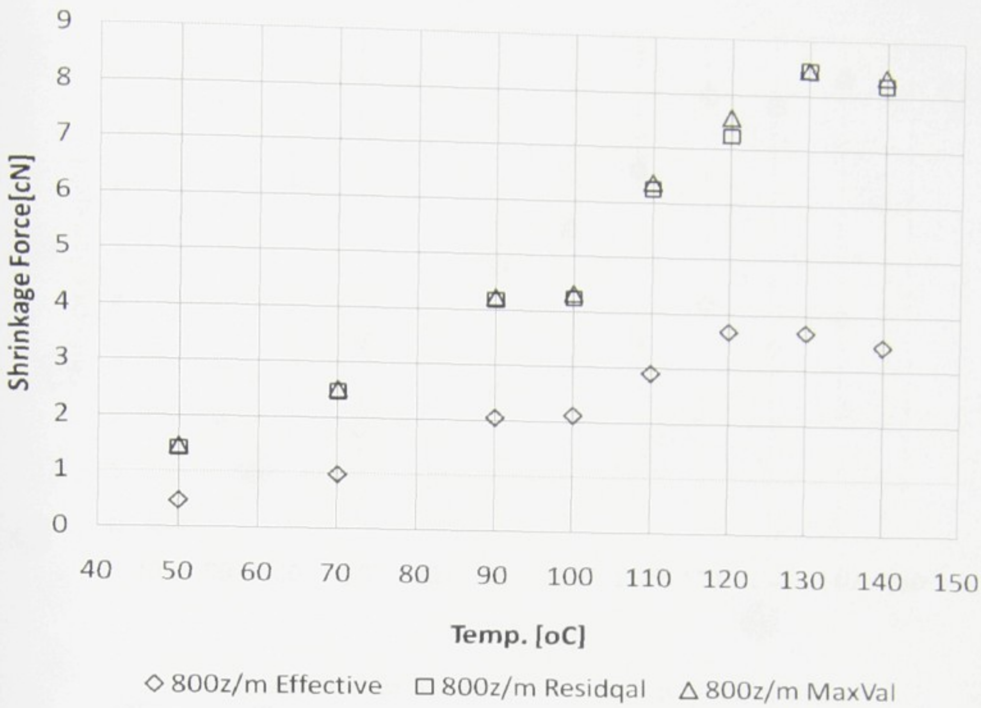

Fig8.4.3.13: Shrinkage force for POP yarns at 440t/m

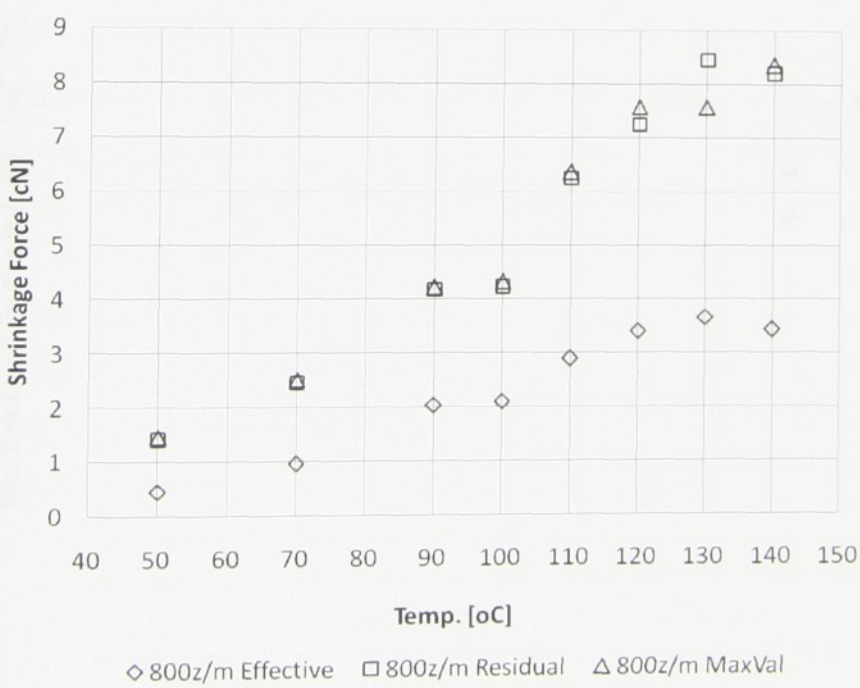

Fig8.4.3.13: Shrinkage force for POP yarns at 800t/m

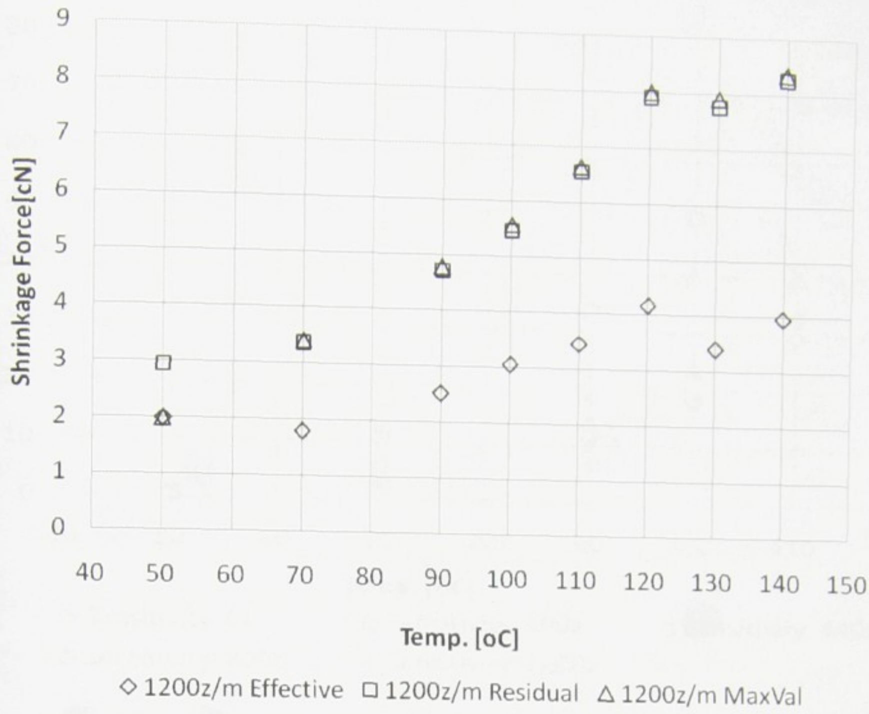

Fig8.4.3.14: Shrinkage force for POP yarns at 1200t/m

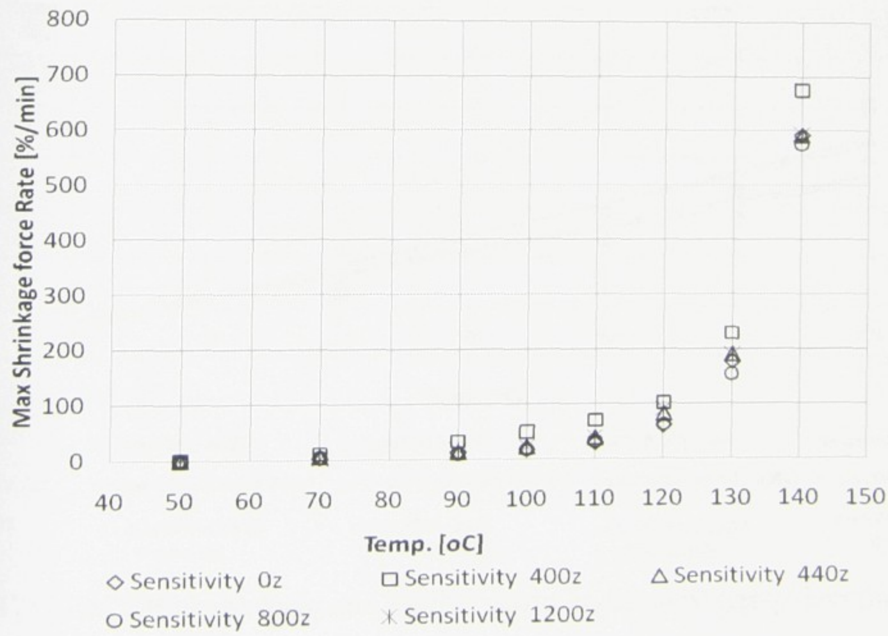

Fig8.4.3.15: Max. Shrinkage force rate for POP yarns at dif twist (0z, 400z, 800z and 1200z)

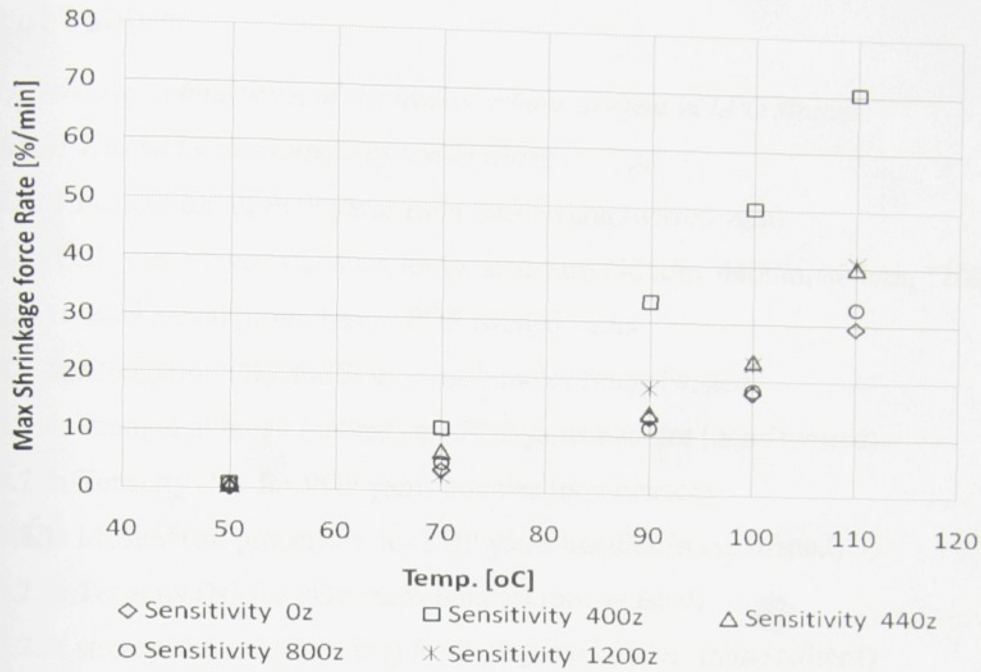

Fig8.4.3.16: Max. Shrinkage force rate for POP yarns at dif. twist (temp. less than 120°C)

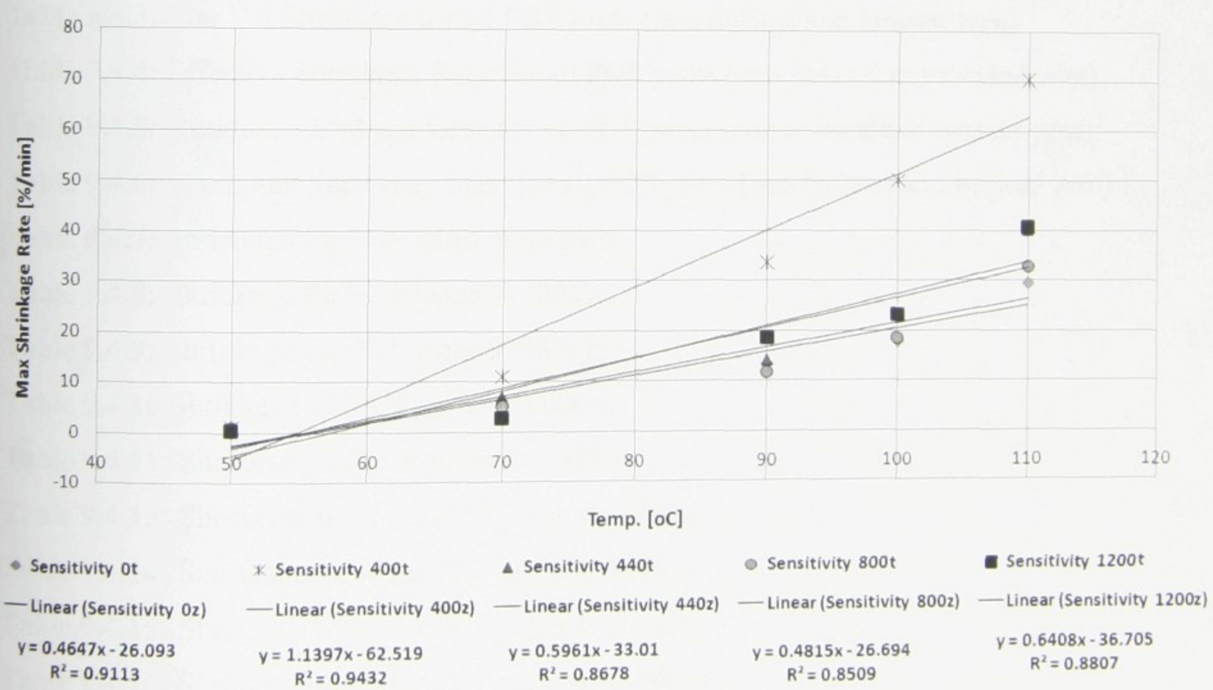

Fig8.4.3.17: Max. Shrinkage force rate for POP yarns at dif. twist (temp. less than 120°C)

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