ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

DETERMINATION OF THIXOTROPIC FLOW BEHAVIORS OF URETHANE OILS

M. Sc Thesis by

Orçun YILMAZ, Chem. Eng.

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Supervisor (Chairman): Assoc. Prof. Dr. F. Seniha GÜNER

Members of the Examining Committee Prof.Dr. İ. Ersin SERHATLI

Prof.Dr. Hasancan OKUTAN (I.T.U)

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LIST of ABBREVITIONS

Pas : Pascal
MDI **:** Diphenylmethylene diisocyanate
HDI **:** Hexamethylene diisocyanate
THF **:** Tetrahydrofuran
TI **:** Thixotropic index
PDI **:** Polydispersity index

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τ : Shear stress, Pas
$\dot{\gamma}$: Shear rate, s^{-1}
η : Viscosity, Pas

DETERMINATION OF THIXOTROPIC FLOW BEHAVIORS OF URETHANE OILS

SUMMARY

Coatings are used for protection of substrates against hostile environments and for aesthetic purposes. When a coating is formulated various flow-releted or reological characteristics that effect a application must be taken into consideration. One of the important property that must be taken into consideration is the thixotropic flow property of the coating which provide anti-sagging and anti-setting behaviour and the forces of the surface tension and the gravity, which facilite flow and leveling.

The defination of thixotropy is the time dependent fluid behavior in which the apparent viscosity degreases with the time of shearing and in which the viscosity recovers to, or close to, its original value when shearing ceases. The recovery may take place over a considerable time. This may occur with polymer systems.

There are many types of thixotropic additives. There may classify as pigmentary materials and vehicular materials. Some examples for them are: polyamide, polyurethane, polyurea, clays, pyrogenic slicas, calcium sulfonate gels, cellulose.

The most commonly use test methods are: Hysteresis Loop Method, Recovery Time Method, Rosen Method, Thixotropic Index Method.

The aim of this study is to produce the oil-based polymer giving thixotropic property to organic solvent-based surface coatings and to determine their solubilities. It was used partial glyceride mixtures prepared from triglyceride oils, and diisocyanates (HMDI and MDI) in the preparation of polyurethane. The reactions of preparation were achieved two or three steps. After determining the solubility of the produced polymers, they were mixed with alkyd resins in different ratios and determined flow properties of mixtures.

POLİÜRETAN YAĞLARININ TİKSOTROPİK AKIŞ ÖZELLİKLERİNİN BELİRLENMESİ

ÖZET

Tiksotropi akışkanlarda gözlenen zamana bağımlı olarak değişkenlik gösteren bir özelliktir. Akışkan üzerine uygulanan gerilme kuvvetleri ile birlikte akışkanın viskozitesinin zamana bağlı olarak azalması şeklinde gözlenir. Akışkan üzerine uygulanan gerilme kuvvetleri kaldırıldığında ise akışkan geri kazanım süresi sonunda ilk viskozite ve akış özelliklerini geri kazanır.

Polimerik malzemelere tiksotropik özellik kazandırmak amacıyla tiksotropik özellik taşıyan katkı maddeleri eklenir. Bu katkı maddelerini başlıca poliamidler, poliolfinler, kalsiyum sulfonat jeller, poliüretanlar ve selüloz olarak sınıflandıra biliriz.

Yüzey kaplama malzemesi olarak kullanılan polimerik malzemenin üretimi sırasında dikkat edilmesi gereken özelliklerin başında, polimerik yüzey kaplamalarının çevreye karşı dirençlerinin yanı sıra akış özellikleri ve reolojik özellikleri önemli bir yer tutar.

Üretim aşamasından sonra viskozite ve reolojik özellikleri belirlenmelidir. Bu alanda polimerik malzemenin değişik kayma hızlarında verdikleri tiksotropik özelliklerin belirlenmesi kaplama olarak kullanılmalarında kullanım kolaylıkları film özellikleri açısından önemli bir yer tutar.

Polimerik malzemeye tiksotropik özellikleri belirlemek amacıyla yapılan testleri başlıca dört ana başlık altında toplaya biliriz bunlar :
Hysteresis çevrim metodu, polimerik malzemeye uygulanabilecek en düşük kayma hızından başlayarak kayma hızının arttırılması ile polimerik malzemenin verdiği yüzey gerilmeleri belirlenir.
Geri kazanım metodu, bu metotla polimerik malzemeye uzun süre ile yüksek kayma hızı uygulanır. Bu süre sonunda kayma hızı kesilir ve maddenin ilk özelliklerini tekrar geri kazandığı süre belirlenir.
Rosen metodu, ampirik eşitliklerle tiksotropik davranış belirlenmeye çalışılır.
Tiksotropik indeks metodu, polimerik malzemenin yüksek kayma hızındaki viskozitesinin ve düşük kayma hızındaki viskozitesine bölünmesiyle elde edilir.

Bizim çalışmamızda trigliserid yağ (keten yağı), HMDI, MDI ile polimerler üretilmiştir. Üretimin ilk aşamasında keten yağı ve yağın %12 oranında gliserin kullanılarak kısmi gliserid üretilmiştir. Üretilen kısmi gliseridin hidroksil değeri 177.91 olarak bulunmuştur. Üretan yağlarının üretilmesinde hazırlanan kısmi gliserid HMDI ve MDI ile farklı oranlarda reaksiyona eklenmiştir. Üretilen üretan yağları moleküler ağırlıkları, çözünürlükleri gibi özellikleri belirlendikten sonra alkid reçinesi ile %0,5-%5 oranları arasında karıştırılarak tiksotropik ajan olarak etkinlikleri test edilmiştir. Bu amaçla Haake tarafından üretilen reo-stress 1 cihazı kullanılmıştır.

1. INTRODUCTION

Coatings are used for protection of substrates against hostile environments and for aesthetic purposes. When a coating is formulated various flow-related or reological characteristics that effect an application must be taken into consideration. One of the important properties that must be taken into consideration is the thixotropic flow property of the coating, which provide anti-sagging and anti-setting behavior and the forces of the surface tension and the gravity, which facilities flow, and leveling [1].

The popularity of polymers prepared from biological source has grown significantly over the past decade, because of environmental concerns. One of the most widely used type of biological source is triglyceride oils. They used mainly in surface coating industry for preparing of coating polymers, dispersing agents, rheology modifiers, etc. [2-5]. For example linseed and sunflower oils are widely used for production of solvent based paints, and esters of acrylic acid with fatty alcohols proves to be useful as dispersing agents for pigments in paint and varnishes, castor oil derivatives and oil-based polyurethanes can be used for thixotropic agents.

Thixotropy is a form of the reological behavior, which is particularly advantageous in decorative coatings and is now used very commonly for improving paint stability, aid application and improving film appearance. Thixotropic coatings can be changed by intervention. The viscosity of paint will decrease as a force is applied [6,7]. Chain enlargements of the polymeric chains are formed by hydrogen bonds. These hydrogen bonds are first stretched, then broken and finally reformed. As under high stress paint or thixotropic fluid appears like a solid. Under low stress or gravity, it will not flow. If we insert a brush paint changes sufficiently mobile to transfer to the brush, but not so mobile that the paint runs or splashes but it becomes like a true liquid. It spreads easily. And then when we stop brushing and the paint will behave like a solid again but this does not become immediately. If the paint behaved like, a solid immediately after brushing stopped "then brush marks would be frozen into the

film which would spoil the appearance of the painted object. On the other hand there would be no runs or sagging. If the paint film continued to behave like a liquid after brushing stopped then flow would continue the brushmarks would disappear but runs and sagging would occur in thick films leading to an unsightly appearance. In thixotropic paints there is a time dependent transition from liquid like behavior to solid like behavior long enough to allow leveling, thereby removing brush marks, but short enough to prevent.

The aim of this study is to produce the oil-based polymer giving thixotropic property to organic solvent-based surface coatings and to determine their solubilities. It was used partial glyceride mixtures prepared from triglyceride oils, and diisocyanates (HMDI and MDI) in the preparation of polyurethane. The reactions of preparation were achieved two or three steps. After determining the solubility of the produced polymers, they were mixed with alkyd resins in different ratios and determined flow properties of mixtures.

2.THEORETICAL PART

2.1.RHEOLOGY

Rheology is the science of the deformation and flow of materials in response to the stress [8]. Rheology comes from the Greek alphabet combination of the rheo means flow and logy means science [9]. Rheology extent with the response of materials to mechanical force. Response may be irreversible flow, have reversible elastic deformation, or both of them. The reological properties are necessary for understanding of rheology and the ability to measure before the control of viscous behavior. Such control is essential for the manufacture and handling of numerous polymeric materials and products, example, rubber, plastics, paints, inks, and others.

Deformation is the relative displacement of points of a body. It can be separated into two types: flow and elasticity. Flow can be defined as an irreversible deformation, the material does not revert to its original configuration when the stress is removed. It shows conversion of work to heat. Elasticity is a reversible deformation, as the they respond to external stress by deforming and returning to their original shape and applied work is largely recoverable. Both flow and elasticity are observed on viscoelastic materials [9].

Flow properties are being studied from early centuries. In the seventeenth century Hooke and Newton proposed the basic laws of elastic response and simple viscous flow, respectively. In the mid-nineteenth century with models for viscous flow in round tubes gives further advances in understanding flow properties. In 1890 there was another milestone with the introduction of the first practical rotational viscometer. In recent years the science of rheology has grown rapidly [10].

The flow properties of a liquid are defined by its resistance to flow, viscosity, and may be measured by determining the rate of flow through a capillary, the resistance to flow when the fluid is sheared between two surfaces, or the rate of motion of a bubble or ball moving through the fluid. Applying a stress and measuring the deformation or strain may study the mechanical properties of an elastic solid. Many solids, such as polymers, undergo flow in addition to recoverable elastic deformation. In addition, a number of liquids show elastic as well as flow behavior.

These materials are viscoelastic, and additional techniques beyond those indicated for solids and liquids are needed for complete characterization. Examples of such methods are the measurement of response to sinusoidal oscillatory motion; the measurement of flow with time after application of stress, creep; and the measurement of the rate and degree of recovery after removal of stress, stress relaxation.

In addition to viscometers, microscopes are often used for defining and solving flow problems. This is particularly true for formulated materials, such as paints and inks, where the use of a microscope allows the investigator to see the physical structure of the material and its effect on flow.

2.1.1 Viscosity [11]

Viscosity, which describes the physical property of a liquid to resist shear induced flow, may depend on up to six independent parameters, these parameters are: S, T, P, $\dot{\gamma}$, t, V.

$$\eta = \text{function of } S, T, P, \dot{\gamma}, t, V$$

"S" This parameter denotes the physical-chemical nature of a substance being the primary influence on viscosity, whether the liquid is water, oil, honey or a polymer melt etc.

"T" This parameter is linked to the temperature of the substance. Viscosity is heavily influenced by changes of temperature. A little changes in temperature effects the viscosity of the materials.

"P" This parameter "Pressure". Pressure compresses fluids and thus increases intermolecular resistance. Liquids are compressible under the influence of very high pressure. Increases of pressure tend to increase the viscosity.

‘’ $\dot{\gamma}$’’ Parameter "shear rate. $\dot{\gamma}$ is a decisive factor influencing the viscosity of very many liquids. Increasing shear rates may decrease or increase the viscosity.

"t" Parameter "time" denotes the phenomenon that the viscosity of some substances, usually dispersions, depends on the previous shear rate. Examples thixotropic fluids on the length of time the substance was subjected to continuous shear or was allowed to rest before being tested.

"V" Parameter "Voltage" is related to a family of suspensions characterized by the phenomenon that their flow behavior is strongly influenced by the magnitude of electrical fields acting upon them. These suspensions are called either "electro-viscous fluids" (EVF) or "electro-rheological fluids" (ERF). They contain finely dispersed dielectric particles such as aluminum silicates in electro-conductive liquids such as water, which may be polarized in an electrical field. These EVF's may have their viscosity changed instantaneously and reversibly from a low to a high viscosity level, to a dough-like material or even to a solid state as a function of electrical field changes, caused by voltage changes.

2.1.2 Aspects Of Viscometry

Isaac Newton was the first to express the basic law of viscometry describing the flow behavior of an ideal liquid (Equation: 2.1).

$$\tau = \dot{\gamma} \cdot \eta \qquad \text{Equation 2.1}$$

τ : Shear Stress $\quad \dot{\gamma}$: Shear Rate $\quad \eta$: Viscosity

For define the parameters τ, $\dot{\gamma}$, η in the equation (2.1) parallel plate model can be used. Figure 2.1

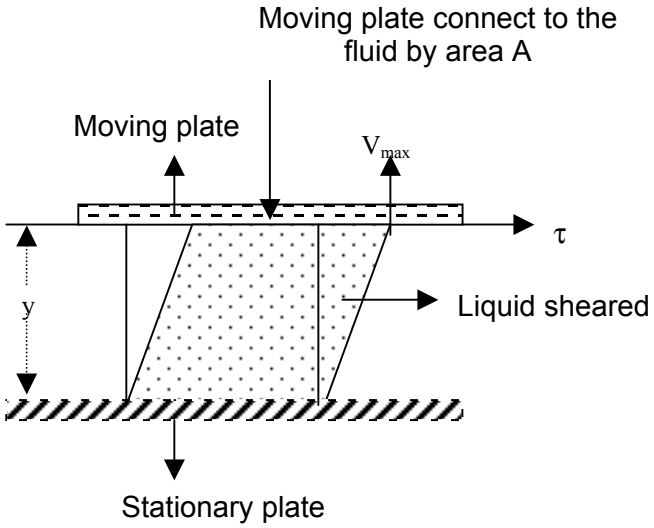


Figure 2.1 Flow between the two plates

A force F (τ) applied to an area A being the interface between the upper plate and the liquid underneath, leads to a flow in the liquid layer. The internal resistance of the liquid controls the velocity of flow that can be maintained for a given force, by it's viscosity.

$$\tau = \frac{F\,(force)}{A\,(area)} = \frac{N\,(newton)}{m^2} = \text{Pa [Pascal]} \qquad \text{Equation 2.2}$$

The shear stress τ causes the liquid to flow in a special pattern. A maximum flow speed V_{max}, is found at the upper boundary.

The speed drops across the gap size y down to $V_{min} = 0$ at the lower boundary contacting the stationary plate. Laminar flow means that infinitesimally thin liquid layers slide on top of each other. One laminar layer is then displaced with respect to the adjacent ones by a fraction of the total displacement encountered in the liquid between both plates. The speed drop across the gap size is named "shear rate" and in its general form it is mathematically defined by a differential.

$$\dot{\gamma} = \frac{dv}{dy} \qquad \dot{\gamma} = \frac{m/s}{m} = \frac{1}{s} = s^{-1} \qquad \text{Equation 2.3}$$

In case of the two parallel plates with a linear speed drop across the gap the differential in the equation reduces to:

$$\dot{\gamma} = \frac{V_{max}}{y}\ [s^{-1}] \qquad \text{Equation 2.4}$$

2.1.3 Newtonian Liquids

Newton assumed that the graphical equivalent of his equation $\tau = \dot{\gamma} \cdot \eta$ for an ideal liquid would be a straight line starting at the origin of the flow curve and would climb with a slope of an angle α. Any point on this line defines pairs of values for τ and $\dot{\gamma}$. Dividing one by the other gives a value of η. This value can also be defined as the tangent of the angle α.

Because the flow curve for an ideal liquid is straight. The ratio of all pairs of τ and $\dot{\gamma}$, these values belonging to this line is constant. This means that η is not affected by changes in shear rate. All liquids for which this statement is true are called Newtonian liquids. Like the liquids water, mineral oils, bitumen, molasses, etc. Flow curves for Newtonian fluids are:

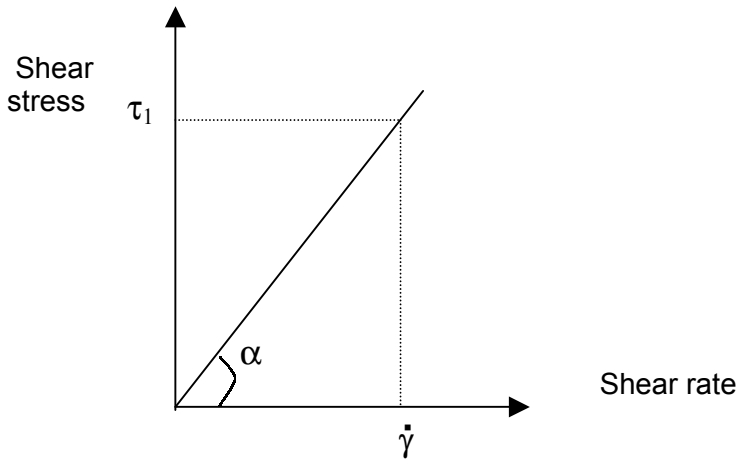


Figure 2.2 Flow curve of Newtonian fluid

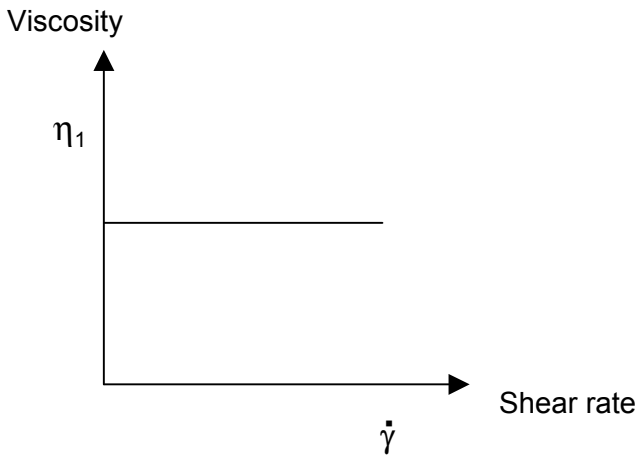


Figure 2.3 Viscosity curve of a Newtonian liquid

2.1.4 Non-Newtonian Liquids [12]

All other liquids not exhibiting this "ideal" flow behavior are called Non-Newtonian Liquids.

Most common flow and viscosity curves are shown at Figure 2.4 and 2.5

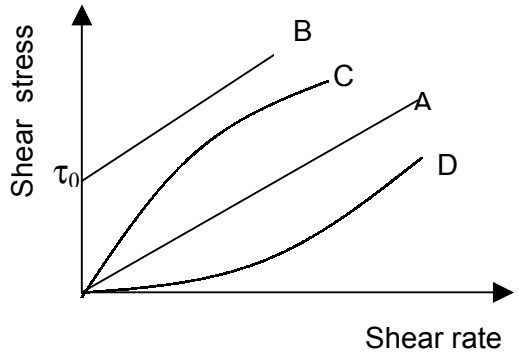


Figure 2.4 Flow curves for non-Newtonian fluids

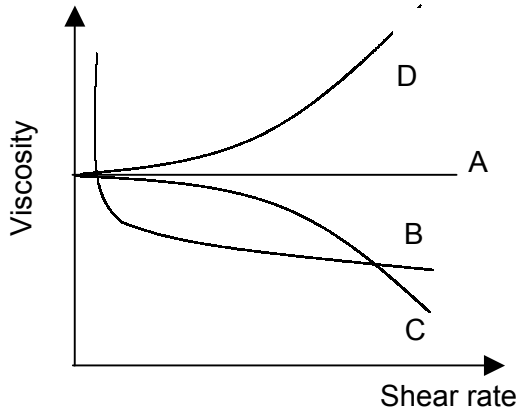


Figure 2.5 Viscosity curves for non-Newtonian fluids

A. Newtonian fluid.

B. Bingham plastics.

Describes pseudoplastic liquids, which additionally feature a yield point. Typical substances showing yield points include oil well drilling mud, greases, lipstick masses, toothpastes and natural rubber polymers.

C. Pseudoplastic Liquids

Pseudoplastic materials increase in shear rate their viscosity degreases. These fluids, which become thinner as the shear rate increases. Very many substances such as emulsions, suspensions, or dispersions of high technical and commercial importance belong to this group.

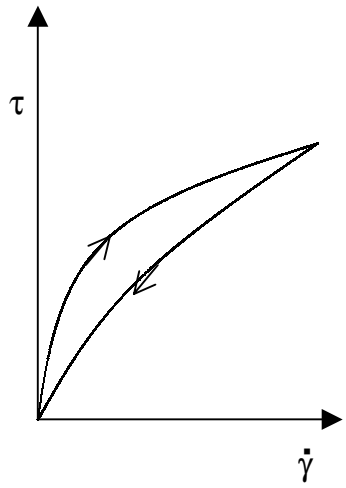
D. Dilatant fluid.

This type of a material characterized by a shear rate dependent viscosity (dilatant substances) or liquids, which under certain conditions of stress or shear rate show a dilatant, flow behavior. Dilatant fluids increase their viscosity whenever shear rates increase.

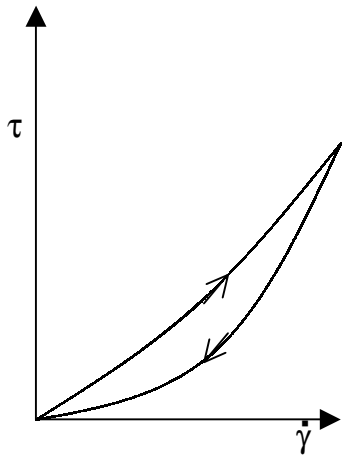
2.1.5 Time Dependence Flow Properties

The curves at the Figure 2.4 and Figure 2.5 are not dependent the history of the fluid. Curves are always same under the different shear rates. But a thixotropic liquid is defined by it's potential to have it's gel structure reformed. Whenever the substance is allowed to rest for an extended period of time. The change of a gel to a sol and of a sol to a gel is reproducible any number of times. Thixotropic fluids viscosity degrease by increase on shear rate.

Rheopeciive liquids, they shows negative thixotropy also called antithixotropy, is a rheological phenomenon characterized by a flow-induced increase of a viscosity [13]. When these liquids are allowed to rest they will recover the original viscosity level. Rheopective liquids can cycle infinitely between the shear-time related viscosity increase and the rest-time related decrease of viscosity. Rheopexy and thixotropy are opposite flow properties. Thixotropy is a very common behavior for many liquids whereas true rheopexy is very rare indeed.



Thixotropic Flow



Rheopectic Flow

Figure 2.6 Flow curves for thixotropic and rheopectic flow

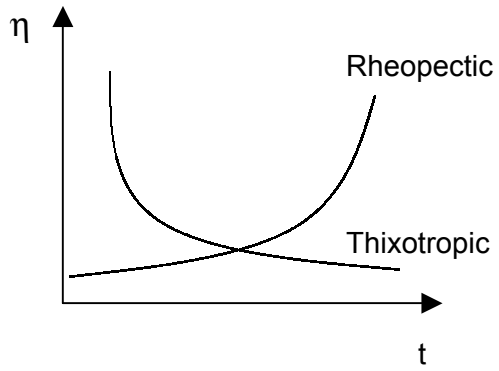


Figure 2.7 Viscosity curves for thixotropic and rheopectic flow

2.1.5.1 Thixotropy

The definition of thixotropy is the time dependent fluid behavior in which the apparent viscosity degreases with the time of shearing and in which the viscosity recovers to, or close to, its original value when shearing ceases. The recovery may take place over a considerable time. This may occur with polymer systems [14].

Thixotropy term comes from Greek alphabet and union of thixis meaning of stirring or shake and trepo meaning of turning and changing [15].

In 1923, Schalek and Szegvari found that aqueous iron oxide "gels have the property of becoming completely liquid through shaking, and after a rest time they recover their original sol and the change of state process could be repeated a number of times without any visible change in the system [16]. After that first paper that properly described phenomenon was published by Peterfi [17]. After that at 1935 Freundlich had published a book called ‘’Thixotropie’’, which described the flow properties of aluminum hydroxide gels [18].

One of the first definitions of thixotropy was given by Freundlich and Rawitzer who stated that "By thixotropy is meant the phenomena of concentrated gels ... which solidify to gels which may again be liquefied to sols [19]. However, Pryce-Jones soon afterwards stated that the true meaning of thixotropy was "an increase of viscosity in a state of rest and a decrease of viscosity when submitted to a constant shearing stress" [20].

At present, there exists a rather general agreement to call thixotropy the continuous decrease of apparent viscosity with time under shear and subsequent recovery of at rest for a sufficiently long time before the experiment is done [15,21].

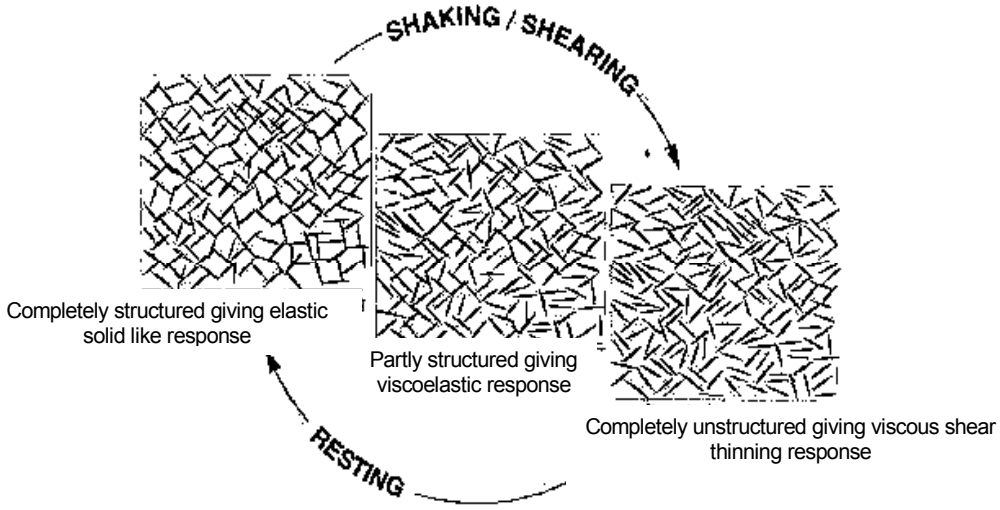


Figure 2.8. Breakdown of a 3D structure

Other definitions for thixotropy are:

Oxford Encyclopedic Dictionary of Physics, -"Thixotropy: Certain materials behave as solids under very small applied stresses but under greater stresses become liquids. When the stresses are removed the material settles back into its original consistency. This property is particularly associated with certain colloids which form gels when left to stand but which become sols when stirred or shaken, due to a redistribution of the solid phase " [22].

Chambers Dictionary of Science and Technology-"Rheological property of fluids and plastic solids characterized by a high viscosity at low stress, but a decreased viscosity when an increased stress is applied. A useful property of paints, because it makes for a thick film which is nevertheless easily worked "[23].

McGraw-Hill Dictionary of Scientific and Technical Terms-"Property of certain gels which liquify when subjected to vibratory forces, such as ultrasonic waves or even shaking, and then solidify again when left standing. Thixotropic clay: a clay which weakens when disturbed and increases in strength upon standing " [24].

Van Nostrand's Scientific Encyclopedia -"A thixotropic fluid is a fluid whose viscosity is a function not only of the shearing stress, but also of the previous history of motion within the fluid. The viscosity usually decreases with the length of time the

fluid has been in motion. Such systems commonly are concentrated solutions of substances of high molecular weight, or colloidal suspensions" [25].

Oxford Concise Science Dictionary -"More common, however, is the opposite effect in which the viscosity depends not only on the viscosity gradient but also on the time for which it has been applied. These liquids are said to exhibit thixotropy. The faster a thixotropic liquid moves the less viscous it becomes. This property is used in nondrip paints (which are more viscous on the brush than on the wall) and lubricating oils (which become thinner when the parts they are lubricating start to move)" [26].

Chambers 20th Century Dictionary -"Thixotropy: the property of gels of showing a temporary reduction in viscosity when shaken or stirred" [27].

Definitions given in more specialized dictionaries emphasize- the time aspect of thixotropy:

Polymer Technology Dictionary -"Thixotropy. A term used in rheology which means that the viscosity of a material decreases significantly with the time of shearing and then, increases significantly when the force inducing the flow is removed" [28].

Polymer Science Dictionary -"Time-dependent fluid behavior in which the apparent viscosity decreases with the time of shearing and in which the viscosity recovers to, or close to, its original value when shearing ceases. The recovery may take place over a considerable time. This may sometimes occur with polymer systems, when molecular disentanglement increases with time of shearing [29].

A fluid, which is thixotropic, is characterized by the fallowing five topic [10]:

1. Structure develops while the fluid is at rest.

2. The structure can be destroyed by the application of shear or force.

3. The process of destroying and rebuilding of the structure is reversible and occur isothermally.

4. In laminar shear flow, under conditions of constant shear rate, the fluid behaves as fallows:

    - The shear stress degreases with time if the fluid was previously at rest or was sheared under conditions of lower shear rate

- The shear stress increases with time if the fluid was previously sheared under conditions of higher shear rate

- No matter what were the previous shear conditions, if an applied shear rate maintained constant for a sufficiently long time, shear stress approaches an equilibrium value dependent only on the shear rate.

5. The response of shear stress to a suddenly change of shear rate is immediate.

2.1.5.2 Testes For Thixotropy

When we place a thixotropic material into a viscometer and apply a constant shear rate, the measured viscosity will decrease with time, but it will eventually steady out to a constant value. Then if we switch off the shear and allow the material to rest for a long time (without drying or any other artifacts such as sedimentation and switch the shear on again, the measured viscosity will be initially higher, but it will then again decrease and end up at the same value as that which was seen after the original long-term shearing. However, the level for the original value will not necessarily be the same, because that will depend on how carefully or vigorously the material was initially loaded into the viscometer and how long it was left to rest before shearing.

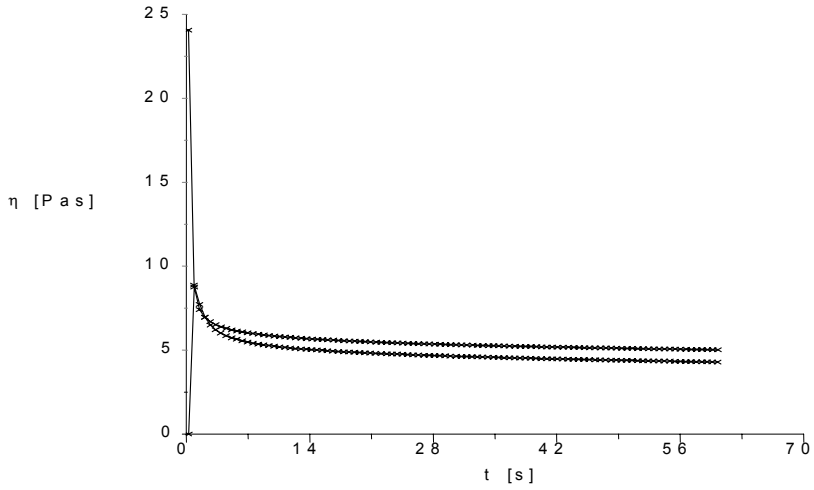


Figure 2.9. Shearing of a thixotropic fluid after short (4 hour) and long (24 hour) rest times

Experimental techniques for such thixotropic fluids are more difficult than for time-independent fluids. For example, the simple act of filling the viscometer will disturb the time-dependent structure and a long resting time may be necessary before valid measurements can be made. Most commonly test techniques for thixotropic fluids are:

1. Hysteresis Loop Method

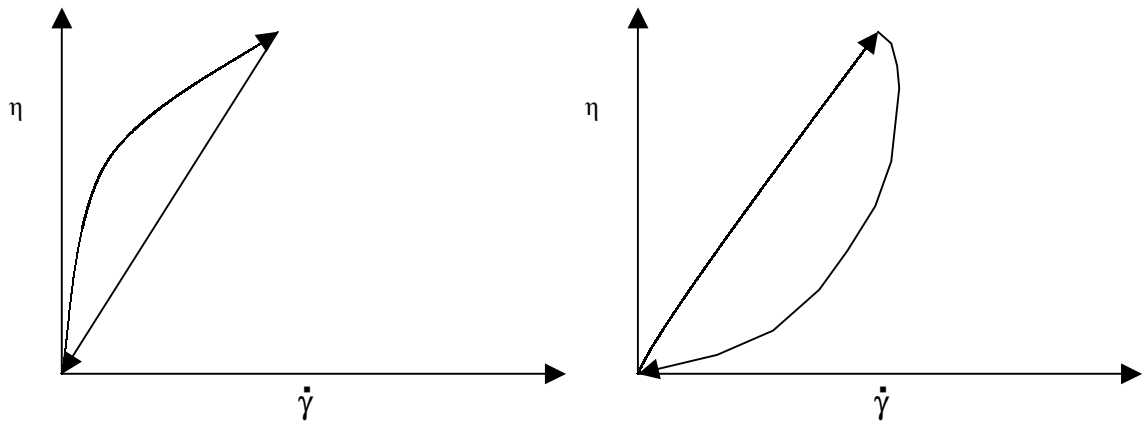
2. Recovery Time Method

3. Rosen Method

4.Thixotropic Index Method

2.1.5.2.1 Hysteresis Loop Method

One of the favorite ways of measuring thixotropy is to perform a loop test; that is to say, to linearly increase the shear rate (or sometimes shear stress) from zero to a maximum value, and then to return at the same rate to zero. The procedure is repeated until the highest shear rate is reached and the system is then sheared to its equilibrium stress. After reaching equilibrium the shear rate is reduced stepwise and the shear stress is measured again at each point until the lowest shear rate is reached. The shear stress is then plotted versus the shear rate. Examples of Thixotropic and Rheopectic curves can be seen in Figure 2.10 [14].



Thixotropic Reopextic

Figure2.10. Thixotropic and reopextic behavior.

The Hysteresis Loop method may be determined by using a 'three-point system". In this technique, fluids are classified according to three parameters: apparent viscosity, shear sensitivity and extent of Thixotropic behavior. Three parameters A, B and C are determined from the plot of apparent viscosity vs. shear rate.

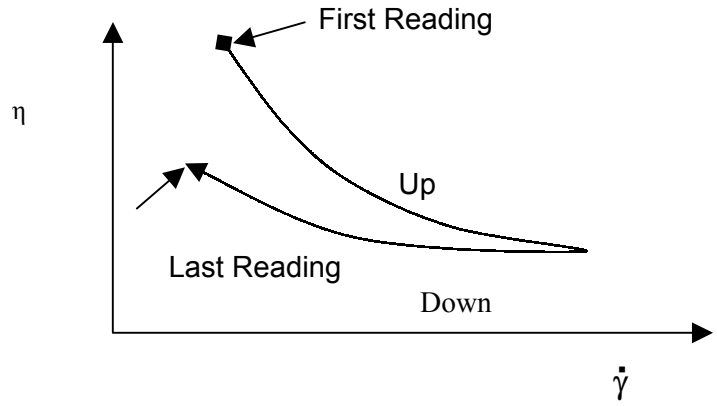


Figure 2.11. Three point system for thixotropic fluids

The A value is the Thixotropy-free viscosity at the lowest shear rate and is the last viscosity reading on the "down" curve. It provides an apparent viscosity value after a standard shearing procedure. The B value represents an index of Pseudoplasticity.

$$B = \frac{A\ (\text{value of vicosity})}{\text{viscosity at the highest shear rate}} \qquad \text{Equation 2.5}$$

The C value represents an index of thixotropy under a set of standardized conditions. It represents the fraction of recoverable viscosity after an arbitrarily chosen recovery time:

$$C = \frac{(\text{viscosity after t min recovery time}) - A\ (\text{viscosity})}{A\ (\text{viscosity})} \qquad \text{Equation 2.6}$$

The C value does not represent the ultimate state of thixotropy but only the extent present under the standardized conditions. The standard time may be chosen according to the patience of the investigator [30].

2.1.5.2.2. Recovery Time Method [30]

Another method useful in studying thixotropy is to shear the sample for a long time at a high shear rate. The shear rate is then immediately dropped to a very low value recovery of shear stress with time is observed.

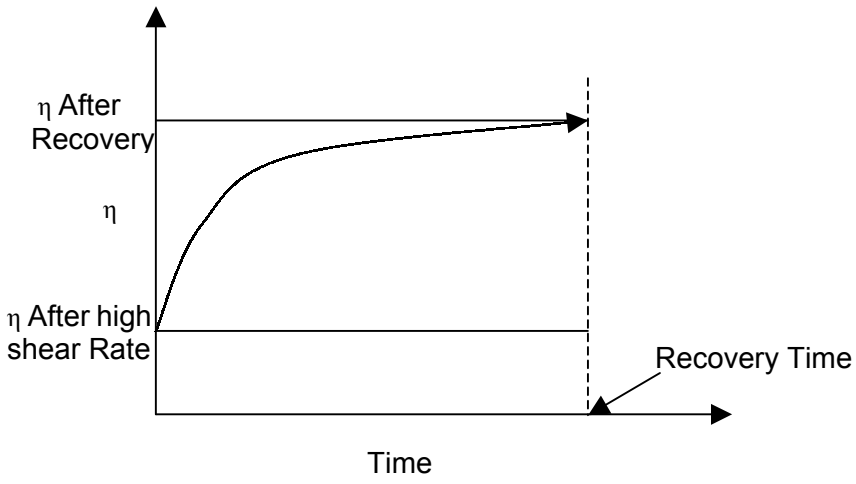


Figure 2.12. Stress recovery for a thixotropic fluid

A thixotropic index is suggested by Patton is:

$$I = \frac{\dot{\tau}_{0,01}\ \text{(before shearing)}}{\tau_{0,01}\text{(after shearing)}} \qquad \text{Equation 2.7}$$

Where $\tau_{0,01}$, is the shear stress at a shear rate of 0.01 1/s. These values are obtained using the spring relaxation technique.

Weltmann proposed a method which involves shearing the sample at a constant rate for a short time, t, then reducing the shear rate for a short time, t, then reducing the shear rate to zero, in steps and plotting shear rate versus shear rate.

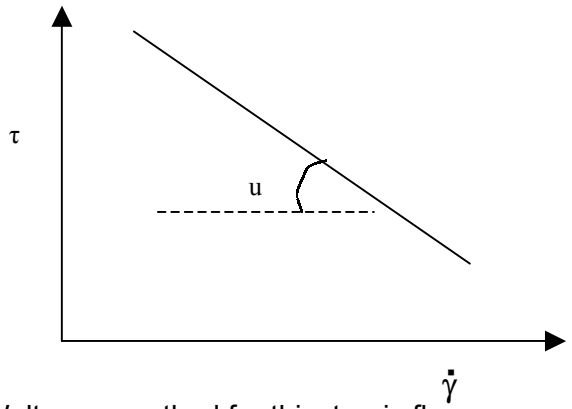


Figure 2.13 Weltmann method for thixotropic flow

A straight line is obtained and the slope is the plastic viscosity u. By repeating this procedure for various shearing times, a series of plastic viscosity values are obtained. A plot of u versus In t results in a straight line of slope B where:

$$B=\frac{u_1-u_2}{\ln\frac{\tau_2}{\tau_1}}$$ Equation 2.8

2.1.5.2.3. Rosen Method

Another method, which is useful in correlating Thixotropic data, is an empirical equation of the form:

$$\eta = A\,(\gamma)^{B}\,(t)^{C}$$ Equation 2.9

Where A, B and C are constants. The value B is an index of Pseudplastity, while the value C is an index of Thixotropy. As B increases, the fluid becomes more shear-sensitive, and C increases, the fluid becomes more time dependent. To evaluate A, B and C the sample is sheared at a constant shear rate, γ, and viscosity readings are plotted as a function of time. Then the process is repeated with a number of times with a new sample and different values of shear rate.

Then according to the experiments viscosity and time graph is performed. A serious of vertical lines is erected on the time axis as shown in Figure below.

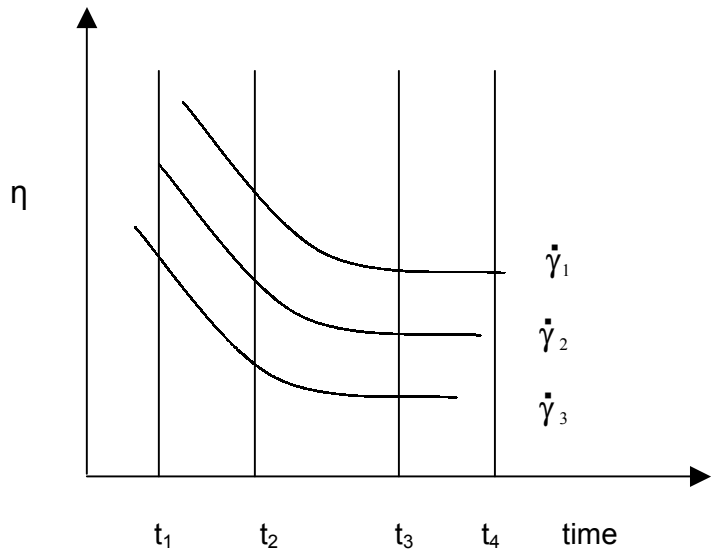


Figure 2.14. Time and shear rate changes

Then $K = A\,(t)^{C}$ equation 2.9 becomes

$$\eta = K\,\dot{\gamma}^{B}$$ Equation 2.10

By taking logarithms of the equation 2.10, equation 2.11 is obtained.

$$\text{Ln}(\eta) = \text{ln}(K) + B\,\text{ln}(\dot{\gamma}) \qquad \text{Equation 2.11}$$

As a plot of ln (viscosity) versus ln (time) constants K values are found

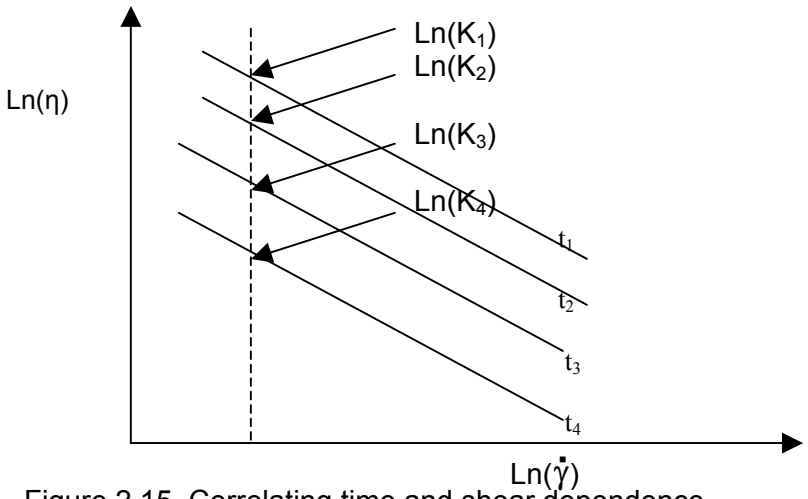


Figure 2.15. Correlating time and shear dependence

A series of intercept points and the corresponding time values determined are from Figure 2.15. Taking logarithms of equation $K = A\,(t)^{C}$

$$\text{Ln}\,K = \text{ln}\,A + C\,\text{ln}\,(t) \qquad \text{Equation 2.12}$$

An ln plot of the intercepts K versus time (t), result a straight-line slope C and intercepts ln (A).

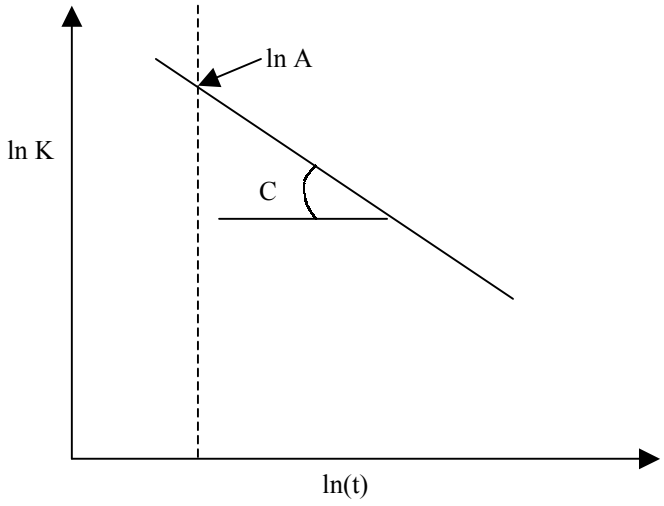


Figure 2.16 Correlating shear and time dependence

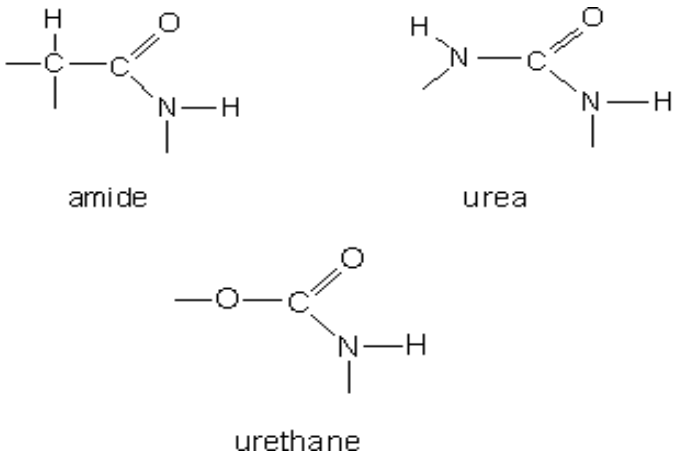
2.1.5.2.4.Thixotropic Index Method

Thixotropic index is an indication of thixotropic efficiency and it is obtained by dividing the low speed viscosity by the high-speed viscosity. On the other words thixotropic index calculate by dividing viscosity value obtain at lower shear rate to viscosity value obtain at higher shear rate. As thixotropic index value increases, the polymer mixture yields to a more thixotropic phase [6].

$$TI\ (\text{Thixotropic index}) = \left(\frac{\eta_{Low\gamma}}{\eta_{High\,\gamma}} \right) \qquad \text{Equation 2.13}$$

2.1.5.3 Thixotropic Additives

The three basic building blocks causing thixotropy are the amide, the urethane and the urea group.



The reaction of ethylene diamine and dimeric fatty acids is the traditional technology of thixotropic alkyd resins. The amide bonds in these resins, lead shear thinning and thixotropy. This ‘amide’ -systems are often combined with isocyanates and mono-amines resulting in a mixture of urethane- and urea- based thixotropic resins. Figure 2.17.

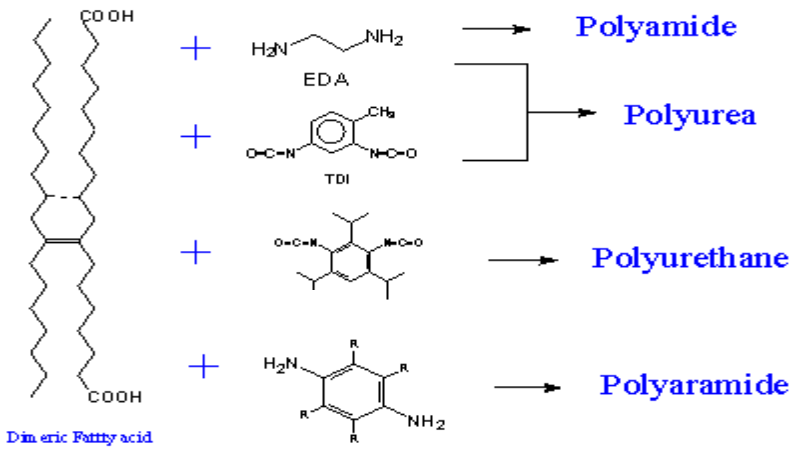


Figure 2.17 Scheme of some thixotropic resins

The urea blocks cause formation of tough gels having excellent thixotropic behavior in polar solvents and more stability at higher temperatures but having problems during paint production [31].

Then another formation was determined, it was found the aramide-based products of the reaction of polyaramides with dimeric fatty acids had shown better gel-forming properties then urethane- and urea- based thixotropic resins

In a pair of aramide molecules the most probable conformation is formed showing strong association forces between the hydrogen from the oxygen atom and the nitrogen atom of the neighboring amide group. Figure 2.18.

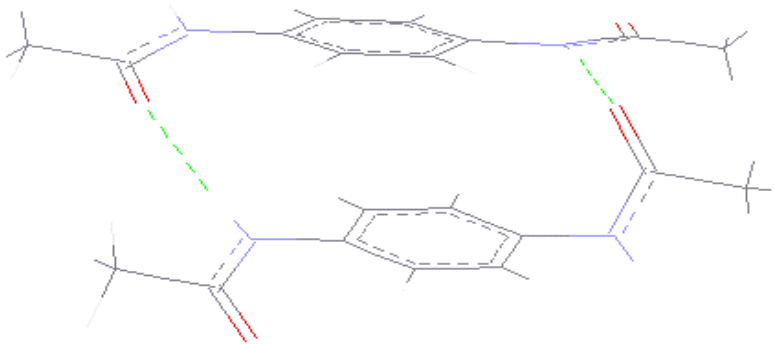


Figure 2.18 Forces between the hydrogen from the oxygen atom and the nitrogen atom

The other thixotropic additives are [4]:

Clays

They also have hydroxyl groups and these hydroxyl groups inter-associates via free water molecules, which may act as bridges.

Pyrogenic slicas

They are commonly used as solvents and thickeners in water-borne coatings. During dispersion, aggregates and agglomerates of these materials are broken up to produce chain-like structures of individual particles bearing pendant hydroxyl groups. Right after the shear force is cut out, association of these chains with hydrogen bonds occur, leading to tightening, anti-settling, sag control situation which is shear sensitive. These silica based thixotropes are more efficient when multi-functional polyols such as ethylene glycol and glycerol are added to the chain like structure through hydrogen bonding.

Calcium sulfonate gels

The over-based calcium sulfonate derivatives are also used as thixotropic agents for solvent-borne coatings. These materials are essentially fine crystals of calcium carbonate with hydrocarbon tails, ionically bound to the calcium carbonate via a sulfonate group. This type of thixotropes incorporates structure by an inter-reaction between the resin, solvents, and pigments in the wet film and the hydrocarbon tails of the sulfonate.

Cellulose

The resin or binder is not part of the continuous phase in latex paints. It exists in the form of discrete particles of polymer dispersed in a continuous phase, specifically, water. The viscosity of the continuous phase and the paint is largely independent of the molecular weight of the binder, because the resinous binder is not solubilized in the water. As a result, thixotropic properties occur to the coating.

2.2. POLYURETHANES

Polymers, which are known as polyurethanes combine materials that incorporate the carbamate (urethane) functional group as well as other functional groups, like ester, ether, amide, and urea.

They are cracterizied by $-\left(\begin{matrix}O\\ \|\\ NH-C-O\end{matrix}\right)-$ group [32] :

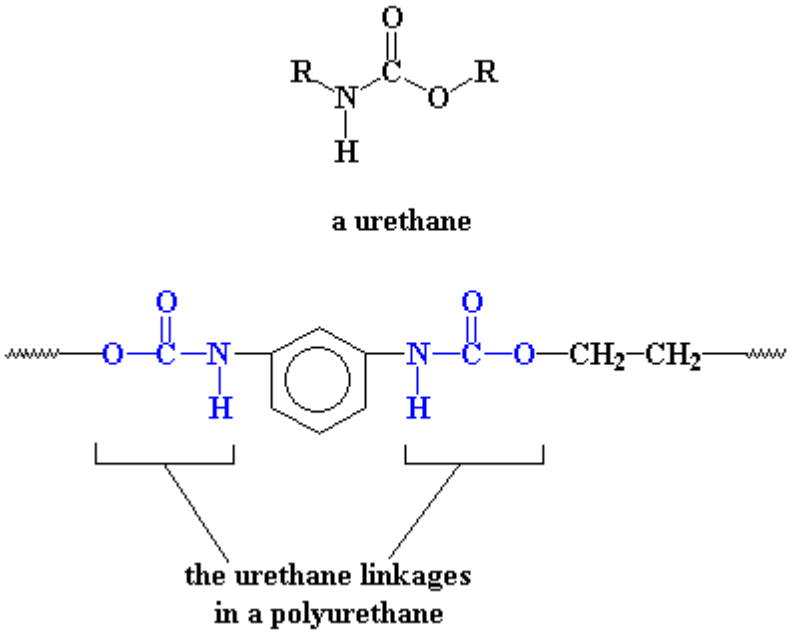


Figure 2.19 A simple polyurethane

The name polyurethane was derived from ethyl carbamate, known as urethane. These polymers were discovered at 1937 by Otto Bayer and co-workers [33]. They are generally produced by the reaction of a polyfunctional isocyanate with a polyol Reaction between the isocyanates and the hydroxyl group is [34]:

$$R-N=C=O \quad + \quad R'-OH \longrightarrow R-NH-\underset{\underset{O}{\|}}{C}-O-R' \qquad (2.14)$$

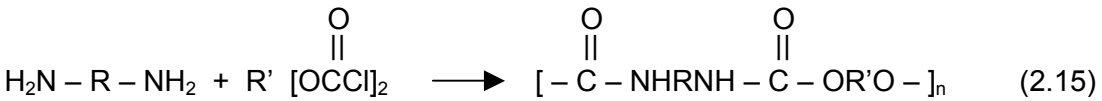
Only groups which include two functional group use linear polyurethanes are form. Since the functionality of the hydroxyl-containing reactant or the isocyanate can be adjusted, so that a wide variety of branched or cross-linked polymers can be formed.

The hydroxyl-containing component covers a wide range of molecular weights and types, including polyester and polyether polyols. The polyfunctional isocyanates can be aromatic, aliphatic, cycloatphatic, or polycyclic in structure and can be used directly as produced or modified. This selection combination of reactants leads to the wide range of physical properties and also allows polyurethanes to play an important role in the world market for quality products from synthetic polymers.

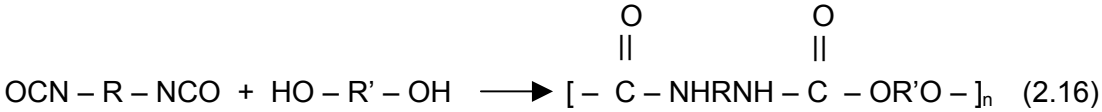
The development of polyurethanes was actively pursued in Germany from the time of the early reports in the 1930s, through World War, to the present day. It was, in fact, by a vigorous research program in the laboratories of I. G. Farbenindustrie and its successor, Bayer AG, which led to the production of rigid foams, adhesives, and coatings. Although there was also early interest in polyurethane chemistry in U.S. companies one of this companies is DuPont and other U.S. companies are produce polyurethane, also in the UK at ICA, and in other locations, the large growth of the polyurethane industry in the United States awaited the transfer in the 1950s of the Bayer technology for flexible foams. From this point, in rapid succession, came the technological achievements that have allowed the manufacture of a broad spectrum of foams, both flexible and rigid, elastomers, coatings, adhesives, and bindem [35].

After the 1950's at the low temperature reactions between the diamines and bicycloformats are also studied and there are lot of patents are published. These reactions can be seen on the equation (2.15).

The recent growth in the commercial importance of polyurethane products formed by reaction of diisocyanates and diols [36] (reaction is shown on equation 2.16 [37]) by reaction injection molding (RIM) has provided the impetus for the basic studies of relationships between molecular structure and bulk properties.



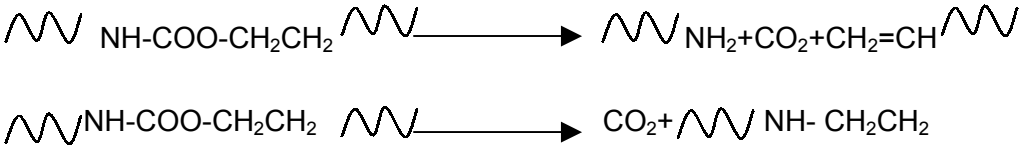
$$H_2N - R - NH_2 + R'\ [OCCl]_2 \longrightarrow [- C(=O) - NHRNH - C(=O) - OR'O -]_n \qquad (2.15)$$



$$OCN - R - NCO + HO - R' - OH \longrightarrow [- C(=O) - NHRNH - C(=O) - OR'O -]_n \qquad (2.16)$$

Also as the reactions decomposition of the polyurethanes back to the isocyanate monomers and alcohol groups. The helping of catalyst and the stoichiometry mostly control the reactions. The most common catalyst for polyurethane reactions are stannous and other metal carboxylates as well as tertiary amines. Proper choice of

the specific catalyst results in differences in the relative amount of each reaction. Temperature also affects the reaction. Polyurethane polymerization reaction temperature are moderate but no usually not higher than 100,120 °C because of the polyurethane under go several kinds of degradation reactions such as [38] :

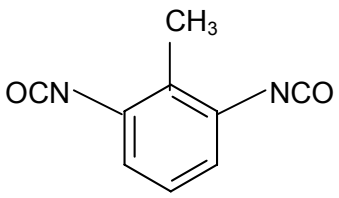


2.2.1 Raw Materials Using Preparation Of Polyurethanes

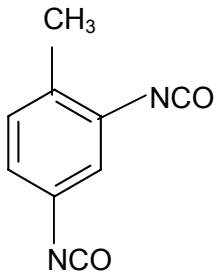
Most common raw materials using synthesis of polyurethanes are isocyanate compounds. They are classified as aromatic and aliphatic isocyanates.

$$OCN - (CH_2)_6 - NCO$$

(1,6 hexamethylene diisocyanate)

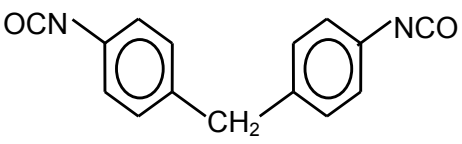


2,6 isomer



2,4 isomer

Toluene diisocyanate structure – 2,6 and 2,4 isomers



diphenylmethylene diisocyanate

The other raw materials are polyols, polyethers and polyesters.

2.2.2 Property And Structure Relations of Polyurethane [39]

Polyurethanes not only contain urethane group they also including multiplicity of other groups such as urea, ester and ether as well as aromatic rings and these groups are effected the properties of the polyurethane polymer. Because of this it is very hard to study property structure relationships in polyurethanes. But property-structure relationship in polymers may be applied to polyurethanes. These general considerations are:

2.2.2.1 Molecular Weight:

Most properties of a polymer change as the molecular weight increase to the limiting value and then relatively constant as the increase of the molecular weight. Properties such as tensile strength, melting point, elongation, elasticity and glass-transitions temperature increase as the molecular weight increase. But solubility of polymers degrease as the increase molecular weight.

2.2.2.2 Intermolecular Forces

Intermolecular forces include hydrogen bonding, polarizability, dipole moment, and van der Walls forces. The bonds are making by these forces are much weaker then primary chemical bonds and these bonds are effected by temperature and stress. The effectiveness of these bonds are reduced by factors like repulsion of like charges, bulky side chains or groups.

2.2.2.3. Stiffness Of Chain

Chain units with limited rotation tend to stiffen polyurethane chains. Flexibility favors softness, low melting points, low glass transition temperatures and elasticity.

2.2.2.4. Crystallization

An increase in crystallization generally leads to reduction in solubility, elasticity, and flexibility and increase in tensile strength, melting point and hardness in polyurethanes.

2.2.2.5. Crosslinking

Increasing greatly the degree of crosslinking of a polyurethane increase the rigidity, softening point and modulus of amorphous polymer and reduces elongation and swelling by solvents.

3. EXPERIMENTAL PART

3.1 Materials And Chemicals

Oil compound:

In the experimental work as oil component linseed oil is used. Properties of the linseed oil are given in Table 3.1.

Table 3.1 Properties of linseed oil [40].

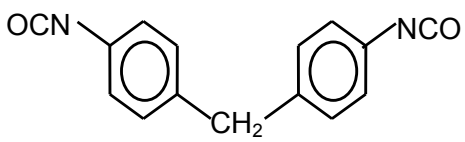
Refractive index, n_D^{20}	1,4812
Acid value	1,1
Saponification value	197
Iodine value [2]	166,8
Oil acid composition.	
$C_{16:0}$	11
$C_{16:1}$	3,2
$C_{18:0}$	11,6
$C_{18:1}$	31,6
$C_{18:2}$	21,4
$C_{18:3}$	20
Other	1,2

Isocyanate compound:

In the experimental work hexamethyle diisocyanate (HMDI), (Merck),

$O = C = N – (CH_2)_6 – N = C = O$

And diphenylmethylene diisocyanate (MDI) (Merck) were used.



Alkyd resin:

Alkyd resin that has an oil length of 62 and an acid value 5 mg KOH/g, which is supplied by Sentapol AG, was used.

Polyamide:

UniRez®521, which was used as a comparative sample in the thixotropic test, was produced by Arizona Chemicals and was supplied by Sentapol AG.

Some properties for uniRez®521 are

Acid value	6
Amine value	6
Softening temperature	110-120 °C

Solvents:

In the preparation of polymers xylene (Merck) was used as a solvent without purification and THF (Merck) was used on determination of molecular weight of polymers.

3.2 Experimental Set-Up

The polymerization reactions were carried out in a 250 ml four-necked flask equipped with a stirrer, a thermometer, a nitrogen inlet tube, a heater, motor and connection tools. This experimental set-up is shown in Figure 3.1.

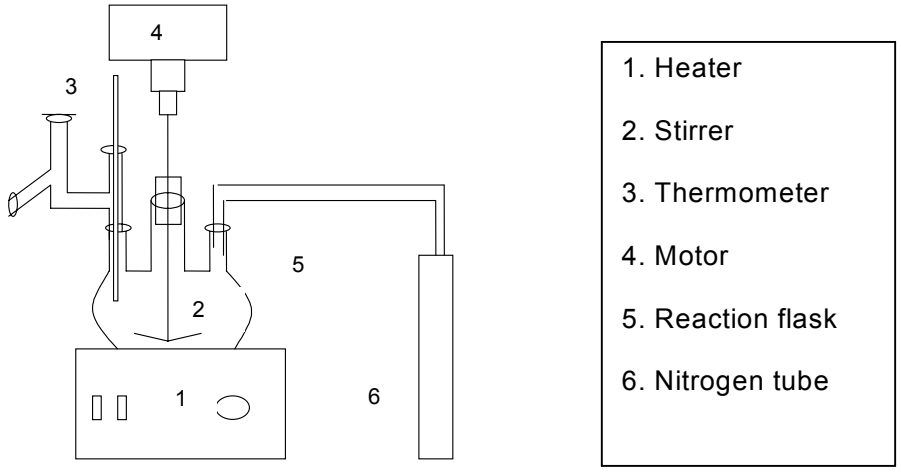


Figure 3.1 Experimental set-up

3.3 Polymer Preparation

First partial glyceride mixture was prepared from linseed oil and glycerol and then this mixture was used for the preparation of polymers.

3.3.1 Preparation of Partial Glyceride Mixture (PG) [42]

Linseed oil and glycerol (12% g of the oil) were placed into the reaction flask and heated. When the temperature reached 218°C, $Ca(OH)_2$ (0.1% of the oil) was added as a catalyst. The temperature was set at 232°C and maintained for 45 min. The reaction was achieved under the nitrogen atmosphere. After cooling the reaction mixture, it was mixed with diethyl ether and washed first with dilute hydrochloric acid and then with distilled water to remove the catalyst and free glycerol. The ethereal solution was then dried over Na_2SO_4 and the solvent was removed.

3.3.2 Preparation of Polyurethane Sample [43]

PG and dry xylene were taken into reaction flask and stirred on the atmosphere conditions for an half an hour. Then the reaction mixture was heated to 40-45°C, and an equivalent amount of isocyanate component was added slowly over a 30 min period. Lead naphthenate as a 24% solution in white spirit was added in the amount of 0.02% of the oil portion. The temperature was set at 90-95 °C and maintained. The reaction was achieved under the nitrogen atmosphere.

In the reaction of two different isocyanate component, second isocyanate component was added the reaction flask after finish the first isocyanate reaction.

Reaction was controlled by IR spectrometry.

3.4 Characterization Methods

3.4.1 Infra Red Spectroscopy (FTIR)

Polymer reactions are controlled by IR spectra that were run on a Mattson 1000 spectrometer as films on sodium chloride discs.

3.4.2 Gel Permeation Chromatography (GPC)

GPC chromatograms were obtained by using an Agilent 1100 instrument equipped with a differential refractometer by using tetrahydrofuran (THF) as the solvent at a

flow rate 1 mL/min. Molecular weights were determined using polystyrene standards.

3.4.3 Analytical Methods [40]

For the functional group analyses hydroxyl value, acid values, and isocyanate content were determined by using wet methods.

Acid Value:

As the acid value of a PG that is the number of mg potassium hydroxide required to neutralize 1 g of PG. For this experiment approximately 1 g sample is dissolved by 30 ml toluene- alcohol solution and the titration by KOH dissolved in alcohol and calculation made by equation:

$$\text{Acid value} = \frac{56{,}1 \,.\, N \,.\, V}{W}$$

N: Normality of potassium hydroxide

V: Volume of potassium hydroxide used (in ml)

W: Weight of sample (in g)

Hydroxyl Value:

Hydroxyl value is the number of mg of potassium hydroxide required to neutralize the amount of acetic acid capable of combining by acetylating with 1 g of sample. Calculation made by equation:

$$\text{Hydroxyl value} = \left(\frac{56.1 * N * (V_2 - V_1)}{W} \right) + \text{Acid Value}$$

3.5 Determination of Solubility [43]

The solubility in xylene, chloroform, *m*-cresol, n-butanol, formic acid, acetone and white sprite of the polymers was evaluated through visual examination. For this purpose, approximately 20 mg of polymer was added to 1 ml of selected solvent.

3.6 Determine The Thixotropic Flow Behavior Of Polymers

Thixotropic alkyd resin was prepared from a soybean oil alkyd and the polymer that was prepared in this study. 0.5%, 2.5%, 3.5%, 5% weight percentage of the polymer was added to the alkyd and the mixture was heated and stirred at 190-195°C until the resin product become clear. A thixotropic alkyd solution of 60% by weight concentration was prepared by dissolution of the resin in white spirit. For comparing the results, thixotropic alkyd was prepared by using commercial thixotropic agent, uni Rez®521, in the same procedure.

Rheological measurements were carried out with a Model Rheo Stress 1 Haake viscometer (Figure 3.2). The maximum shear rate was applied as 100 s^{-1}.

The required amount of sample was loaded into the cup. After immersing the rotor into the sample at a constant rate, the sample was allowed to remain at rest for a defined time before starting the experiment. The time required for remaining at rest was experimentally determined.

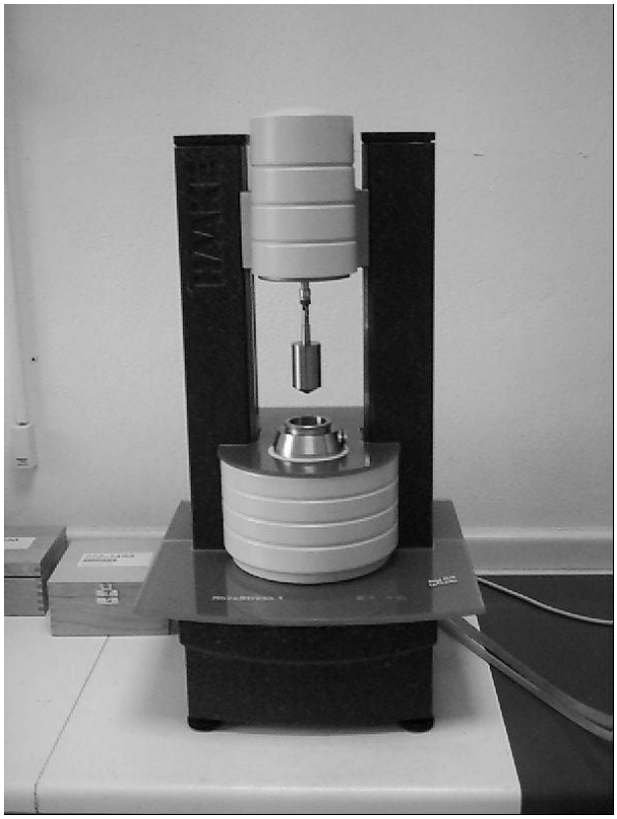


Figure 3.2 Model Rheo Stress 1 Haake viscometer

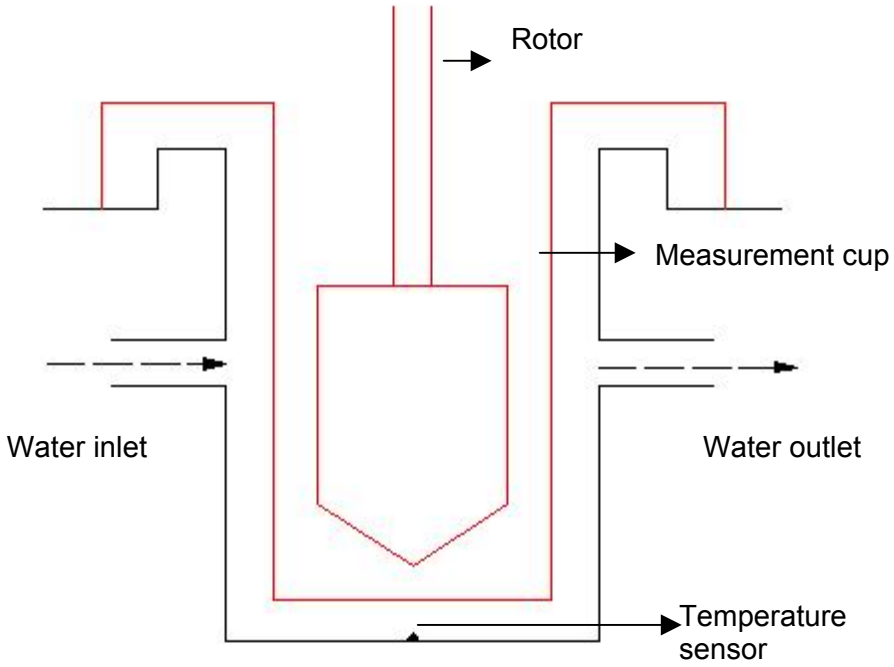
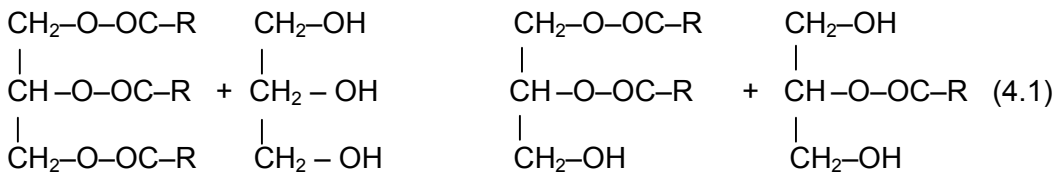


Figure 3.3 Heating system for Model Rheo Stress 1 Haake viscometer

4. RESULTS AND DISCUSSION

4.1 Preparation of Polymers

The PG reaction equation is given below by equation 4.1,



Linseed oil Glycerin Partial glyceride mixture

Hydroxyl value of the partial glyceride mixture was found 177,91 mg KOH/g and acid value was found 1,89 mg KOH/g.

For the preparation of PU_1, mixture of PG is reacted with the equivalent amount of HMDI. For the preparation of other polymers HMDI and MDI was used. In the reactions of PU_4 and PU_5 gelation was observed Reactions are given schematically on Figure 4.1.

The reactions were controlled by IR measurements. On Figures 4.2, 4.3 and 4.4 the IR spectra of both the initial reaction mixture and the final product are shown. The spectra of the final product does not have an absorption peak at 2250cm^{-1}, which appears in the initial mixture, assigned to the N=C=O group.

Table 4.1 Isocyanate ratios of the polymers

CODE	Isocyanate Components	
	HMDI	MDI
PU_1	1	0
PU_2	0,75	0,25
PU_3	0,50	0,50
PU_4	0,25	0,75
PU_5	0	1

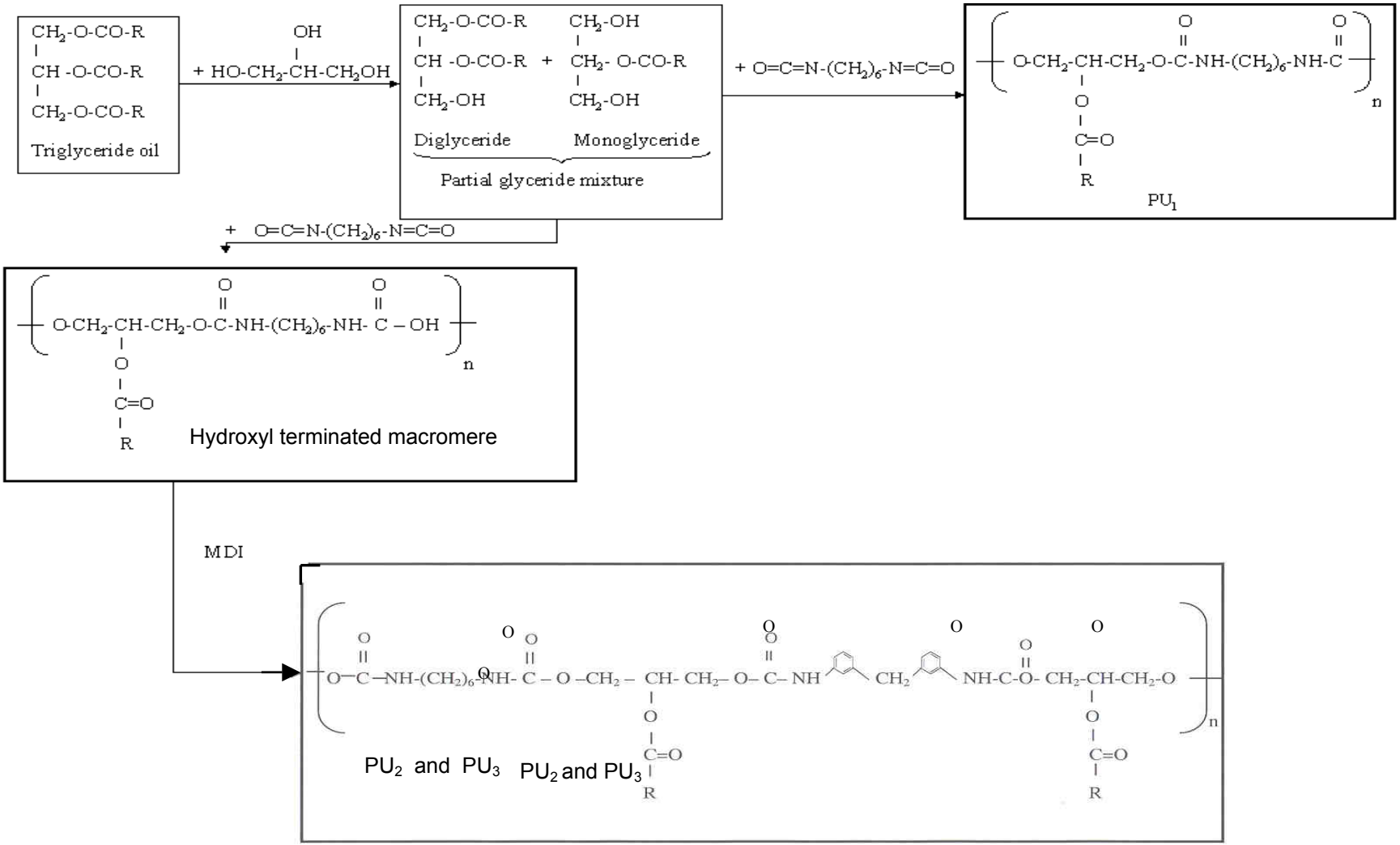


Figure 4.1 Schematically reactions equations for polymers

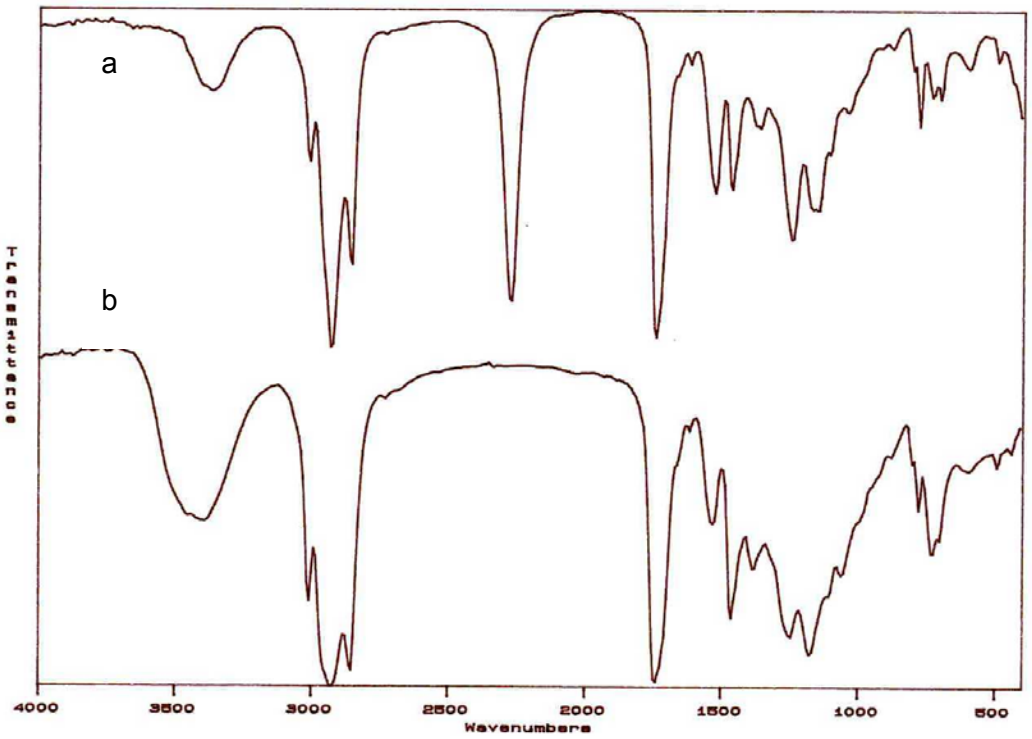


Figure 4.2 IR spectrum for PU_1
a Beginning of reaction
b Finish of reaction

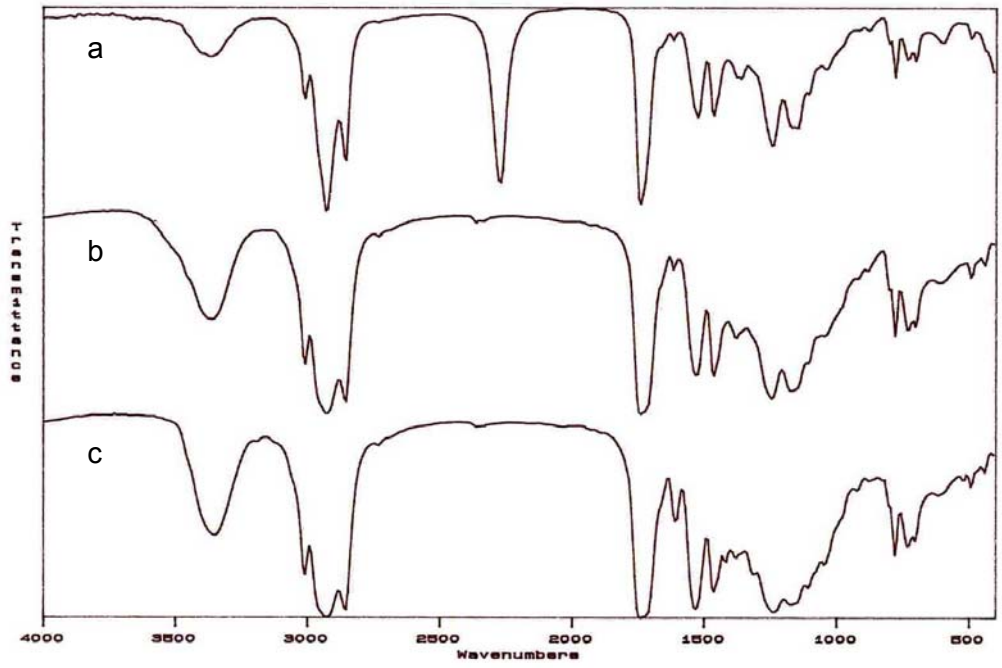


Figure 4.3 IR spectrum for PU_2
a Start of reaction
b Finish of reaction with HMDI
c Finish of reaction with MDI

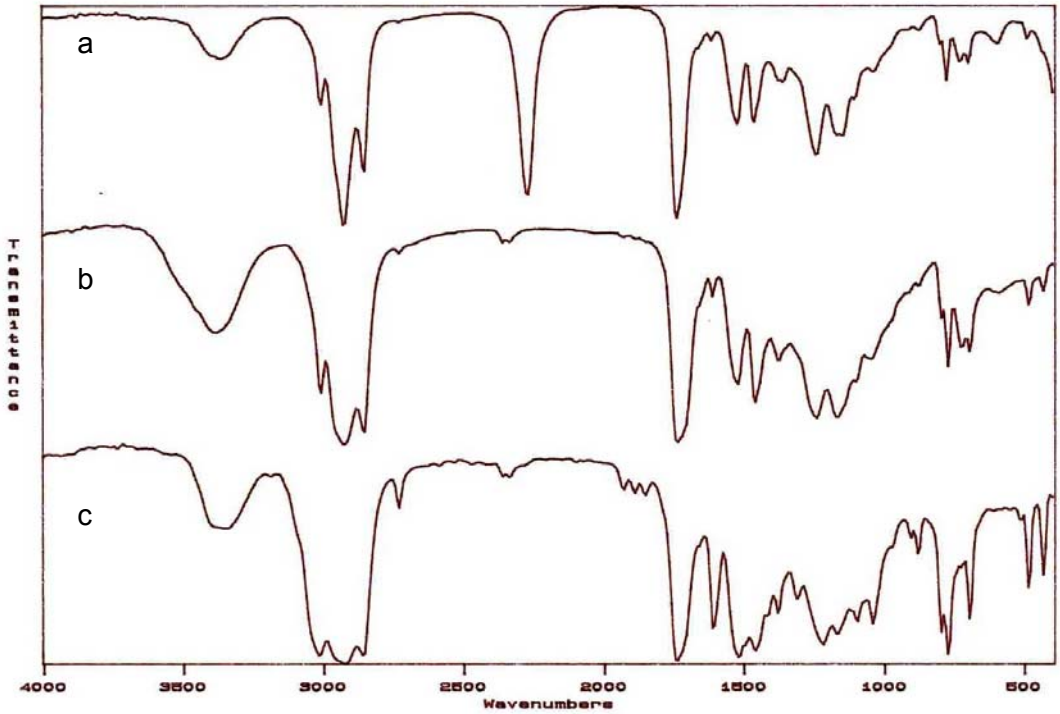


Figure 4.4 IR spectrum for PU_3
a Start of reaction
b Finish of reaction with HMDI
c Finish of reaction with MDI

4.2 Molecular Weights of The Polymers

Molecular weights of polymers obtained were given on Table 4.2.

Table 4.2 Molecular weight of polymers

Polymer	M_w	PDI
PU_1	2563	1,18
PU_2	6338	1,47
PU_3	8465	1,49
PU_4	Gelation	
PU_5	Gelation	
UniRez®521	916	1
	1831	1
	2661	1

4.3 Solution Characterization of The Polymers

The results are summarized in Table 4.3. As shown from the table, formic acid and n-butanol did not dissolve the polymers, xylene is a good solvent for all polymers

Table 4.3 Solubilities of polymers in different solvent

Polymers	**PU_1**			**PU_2**			**PU_3**			**uniRez® 521**		
Temperature (°C)	**25**	**50**	**70**	**25**	**50**	**70**	**25**	**50**	**70**	**25**	**50**	**70**
Xylene	+	+	+	+	+	+	+	+	+	+	+	+
Acetone	+	+	+	+	+	+	-	-	-	-	-	-
White spirit	-	+	+	-	-	+	-	-	+	-	-	+
m-cresol	+	+	+	-	+	+	-	-	+	+	+	+
Chloroform	+	+	+	-	+	+	-	+	+	+	+	+
n-butanol	-	-	-	-	-	-	-	-	-	-	-	-
Formic acid	-	-	-	-	-	-	-	-	-	-	-	-

4.4 Determination of Thixotropic Flow Properties of Polymers

4.4.1. Determination of Recovery Time

To determine the thixotropic flow properties, polymers were stirred with alkyd resin. The ratio of Uni-Rez®521 to alkyd resin is 2,5 as the same as industrial use and the ratio is not changed.

After beginning the thixotropic tests, recovery time was determined. For these tests Uni-Rez®521 was used. A new thixotropic mixture was used for each test. Graphics of these tests results were given on Figures 4.5,4.6 and 4.7.

All thixotropic mixture had a rest for 16 hours in room conditions addition for this thixotropic mixtures had a rest for 4 hours in reometer (Figure 4.5). Tests were done by Hysteresis loop method. All tests were repeated at least two times with new thixotropic polymer mixture. The same results were expected but areas were not same. Experiments continued with changed of rest time in reometer to 8 (Figure 4.6)

and 12 (Figure 4.7) hour, best results and also nearly same results are obtained at 8 and 12-hours tests.

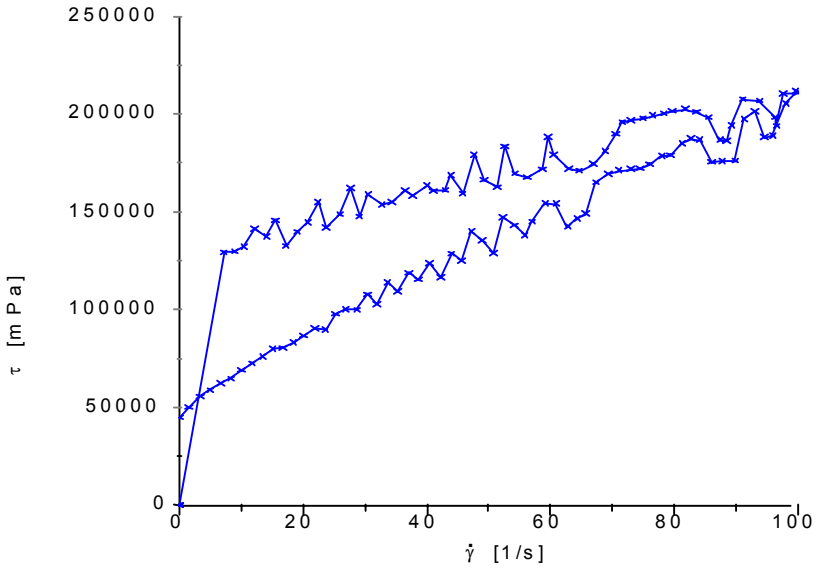


Figure 4.5 Flow curve for thixotropic mixture with a rest time for 4 hours

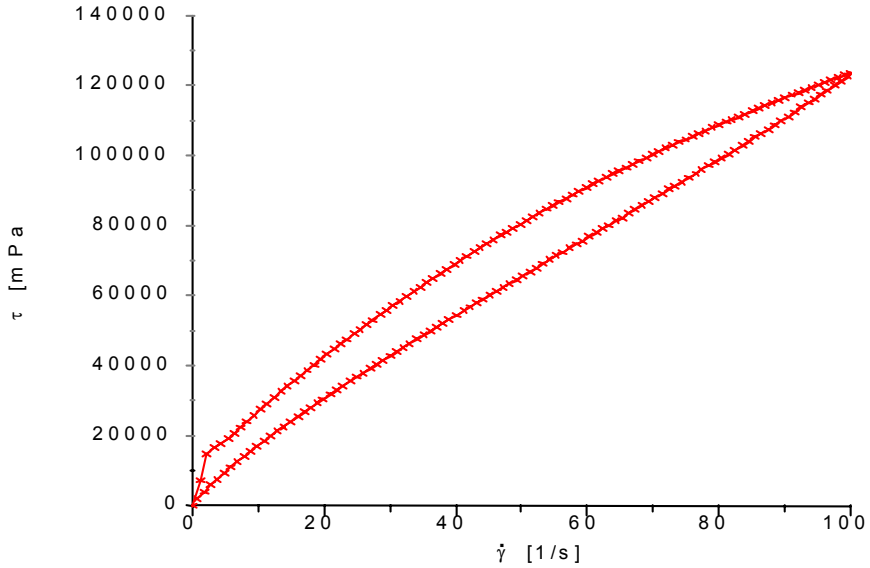


Figure 4.6 Flow curve for thixotropic mixture with a rest time for 8 hours

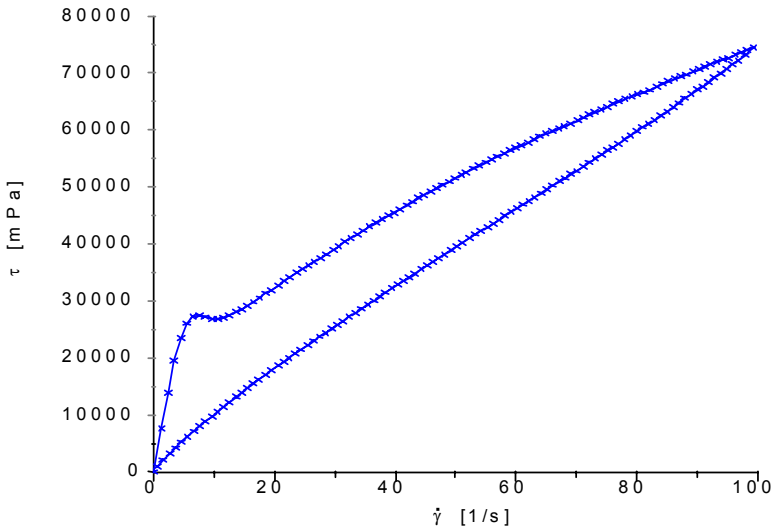


Figure 4.7 Flow curve for thixotropic mixture with a rest time for 12 hours

Also these tests were done at constant shear rate.

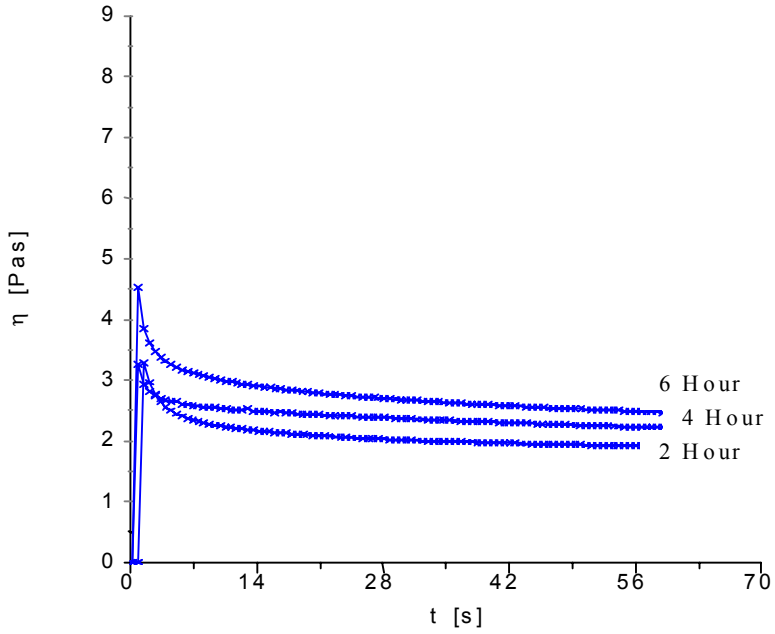


Figure 4.8 Viscosity time graphs for thixotropic mixture for different rest time

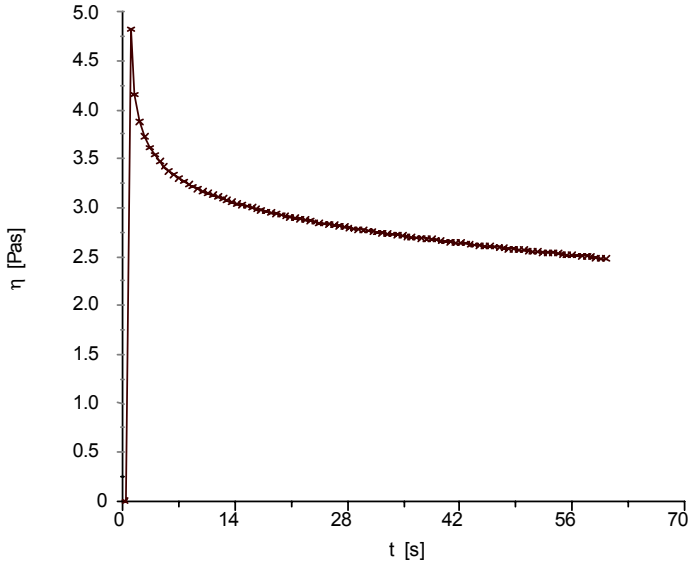


Figure 4.9 Viscosity time graphs for thixotropic mixture for 8 hour

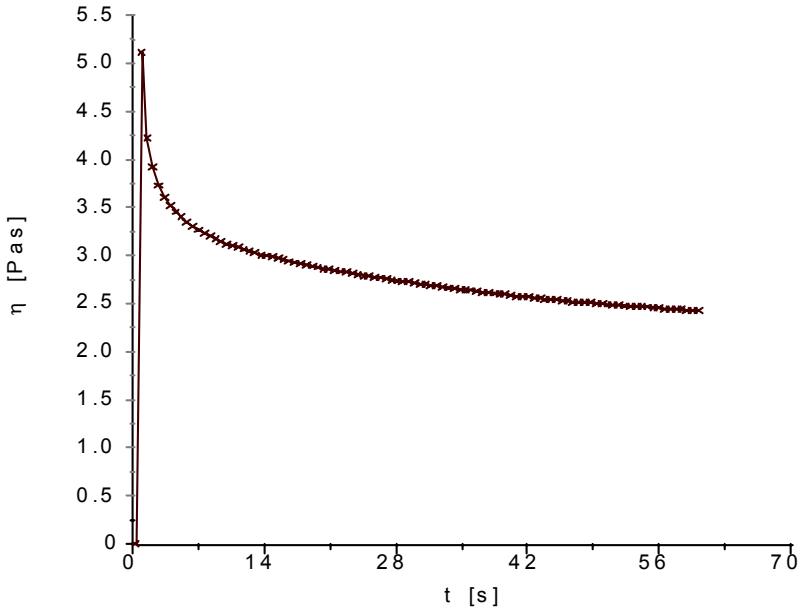


Figure 4.10 Viscosity time graphs for thixotropic mixture for 12 hour

At these tests, different results were obtained after changed rest time in reometer 2, 4 and 6 hours (Figure 4.8) and these results can not obtained again by used new thixotropic polymer mixture. But after 8 (Figure 4.9) and 12 (Figure 4.10) hours rest times in reometer, nearly same results were obtained and also same results were obtained when new thixotropic mixtures were used. By the help of both tests recovery time for alkyd resin was obtained. Then the all other experiments were done at after 8 hour rest time in reometer.

4.4.2 Thixotropic Tests

4.4.2.1 Hysterisis Loop Method

For determination of thixotropic flow behavior hysterisis loop method was used. This method bases on linearly increase of the shear rate from zero to maximum value and then return at the same rate to zero. The area between the curves is a degree of thixotropy. In this study maximum shear rate applied to polymer was 100 1/s. Shear stress measured was plotted versus shear rate.

Thixotropic agent added samples were prepared according to the industrial application.

Alkyd resin 58.5%

UniRez®521 1.5%

Solvent (white spirit) 40%.

In Figure 4.11 thixotropic test results of alkyd added without thixotropic agent were given at three temperature. As expected, a hysterisis loop was not obtained for the samples without thixotropic agent. As shown in Figures 4.12, 4.13 and 4.14 hysterisis loop was obtained for each temperature in the case of alkyd resin with uniRez®521 which was used as a comparative sample in the thixotropic tests.

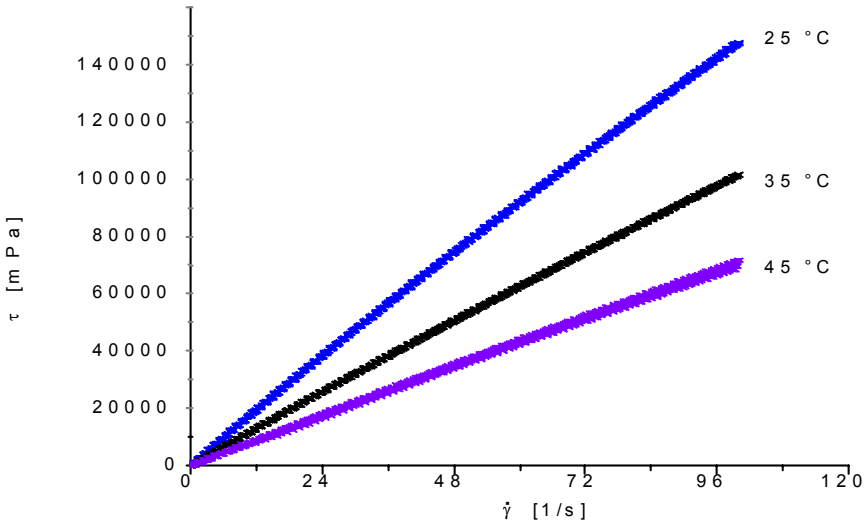


Figure 4.11 Hysteresis Loop Method results for alkyd resin at 25°C, 35°C and 45°C

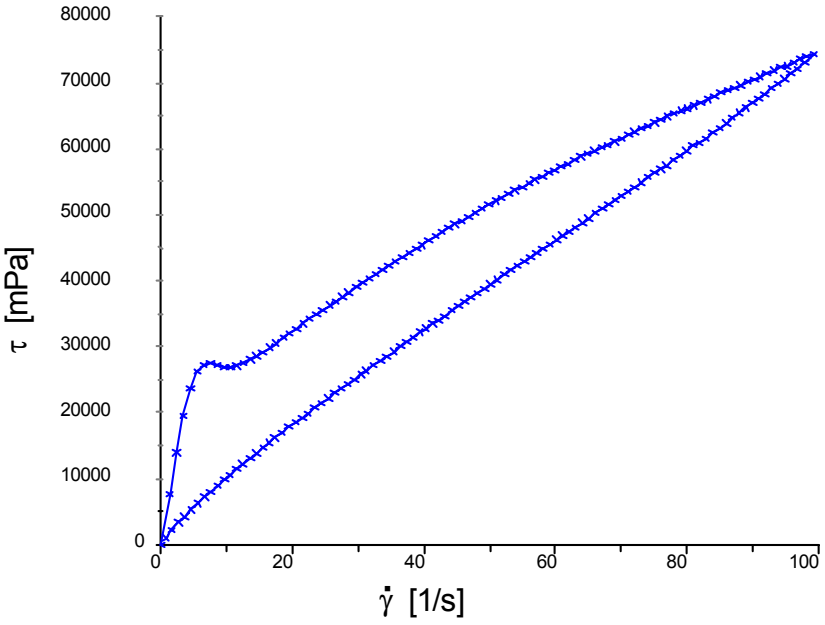


Figure 4.12 Shear rate-shear stress graph for uniRez®521 at 25°C

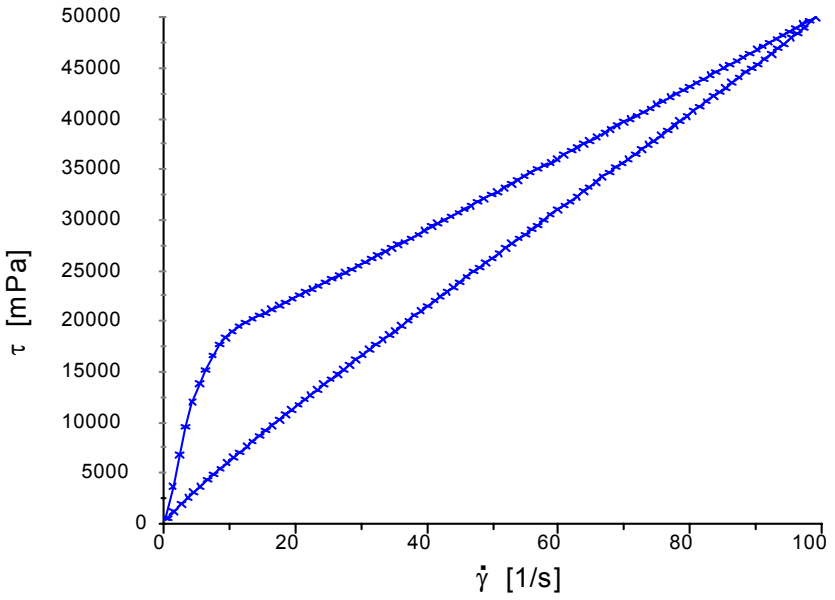


Figure 4.13 Shear rate-shear stress graph for uniRez®521 at 35°C

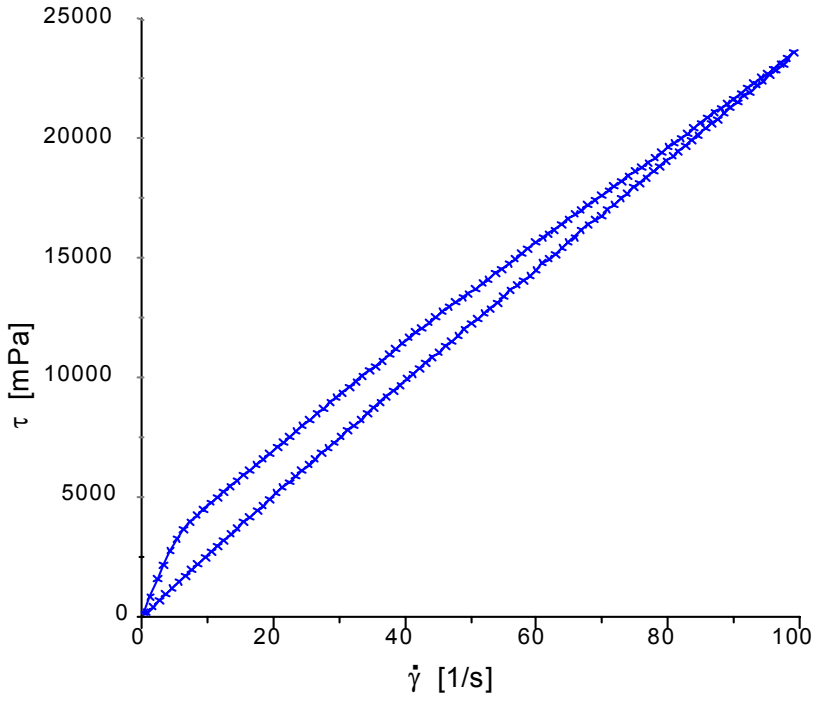


Figure 4.14 Shear rate- shear stress graph for uniRez®521 at 45°C

For determination of the effect of polyurethane amount on thixotropic behavior, polyurethane prepared in this study was added to alkyd resin in different ratios between 0,5-5 %. All mixtures were tested at the range of 25-45°C. The flow curves are given in appendix A.

4.4.2.2 Thixotropic Index Method

For all samples prepared, hysterisis loop area not big enough as compared with uniRez®521 added sample. For this reason, thixotropic index (TI) was determined for each sample. Also for thixotropic index method uniRez®521 was used as a comparative sample because of commonly use in industry.

For calculation TI equation 4.2 was used. The results were given on table 4.4 - 4.6 and viscosity time curves were given on appendix B.

$$TI = \left(\frac{\eta_{\gamma=10\,1/s}}{\eta_{\gamma=100\,1/s}} \right) \qquad \text{Equation 4.2}$$

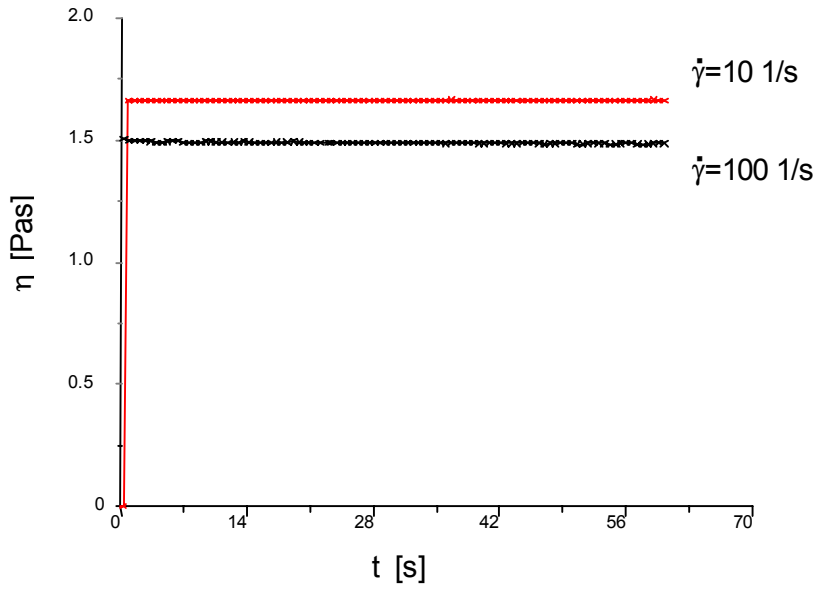


Figure 4.15 Viscosity - time curve for alkyd resin

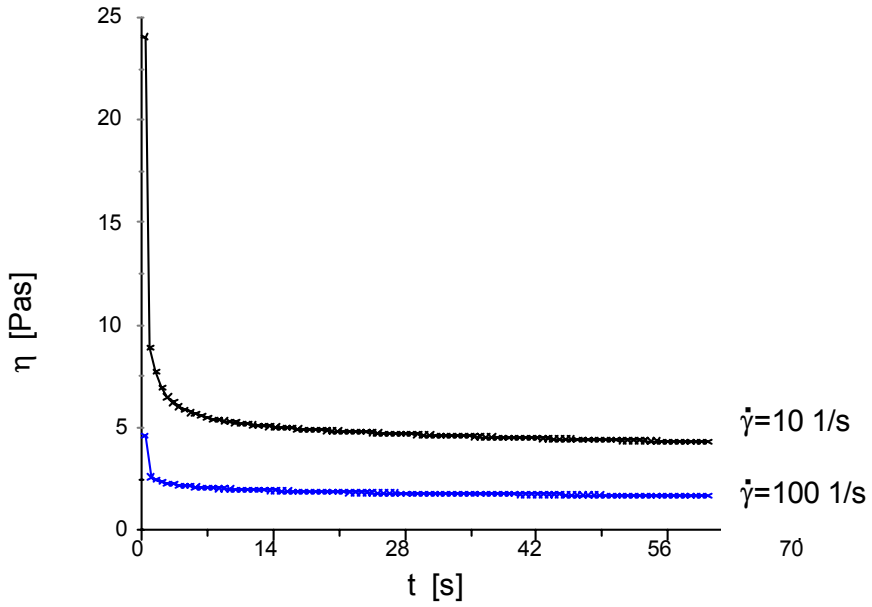


Figure 4.16 Viscosity time curve for uniRez®521 at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s

Viscosity of uniRez®521 added sample were found as 4,289 and 1,675 at 10 1/s and 100 1/s shear rates respectively. So TI was calculated as 2,64. In the case of alkyd resin without thixotropic agent, viscosities were determined as 1,661 and 1,485 at 10 1/s and 100 1/s shear rates respectively. From these values TI was calculated as 1,11.

Table 4.4 Viscosity values of PU_1 with a different stirring ratio at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s

Stirring ratio	Viscosity value at $\dot{\gamma}$ =10 1/s	Viscosity value at $\dot{\gamma}$ =100 1/s	Thixotropic index
0,5%	3,134	2,992	1,047
2,5%	4,55	4,324	1,052
3,5%	5,705	4,152	1,374
5%	7,62	5,032	1,514

Table 4.5 Viscosity values of PU_2 with a different stirring ratio at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s

Stirring ratio	Viscosity value of PU_2 at $\dot{\gamma}$ =10 1/s	Viscosity value of PU_2 at $\dot{\gamma}$ =100 1/s	Thixotropic index
0,5 %	5,088	4,313	1,189
2,5 %	5,345	3,870	1,381
3,5 %	6,131	4,367	1,404
5 %	7,113	4,405	1,615

Table 4.6 Viscosity values of PU_3 with a different stirring ratio at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s

Stirring ratio	Viscosity value of PU_3 at $\dot{\gamma}$ =10 1/s	Viscosity value of PU_3 At $\dot{\gamma}$ =100 1/s	Thixotropic index
0,5 %	6,049	5,077	1,191
2,5 %	7,453	5,374	1,387
3,5 %	6,788	4,375	1,552
5 %	11,53	5,764	2,000

For all polymers thixotropic index values were given on table 4.7.

Table 4.7 Thixotropic index values for all polymers with a different stirring ratio

Stirring ratio	Thixotropic index values of PU_1	Thixotropic index values of PU_2	Thixotropic index values of PU_3
0,5 %	1,047	1,189	1,191
2,5 %	1,052	1,381	1,387
3,5 %	1,374	1,404	1,552
5 %	1,514	1,615	2,000

As a result, increasing polyurethane amount causes higher TI. On the other hand, this causes to increase viscosity. For this reason the optimal polyurethane ratio was not determined for these polymer mixtures. But the important point is that the aromatic structure causes to increase TI. Because as compare the TI of alkyd resins added the same amount of polyurethane, PU_3 based samples showed higher TI and PU_1 based samples showed the lower TI. PU_1 prepared from aliphatic isocyanate. PU_3 had higher amount of aromatic isocyanate in it's structure

5. CONCLUSIONS

The aim of this study is to produce the oil-based polymer and to use them in the preparation of thixotropic alkyd resin. For this purpose first, partial glyceride mixtures prepared from triglyceride oils, hexamethyle diisocyanat and diphenlymethanediisosiyanat (HMDI and MDI) were used in the preparation of polyurethane. The reactions of preparation were achieved in two or three steps. After determining the solubility of the produced polymers, they were mixed with alkyd resins in different ratios and determined flow properties of mixtures. Rheological measurements were carried out with a Model Rheo Stress 1 Haake viscometer.

A new thixotropic mixture was prepared for each test. Recovery time determined as 8 hours.

The next step of the study, Hysteresis loop method was used for determination of thixotropic behavior. By using this method thixotropic flow properties of the polymers can not be determined exactly. Because the areas between the curves were not big enough.

Thixotropic index was determined for each polymer mixture.

As a result, increasing polyurethane amount causes TI to become higher, and also this causes viscosity to increase. For this reason, an optimal polyurethane ratio could not have been determined for these polymer mixtures. The important point is that the aromatic structure causes TI to increase. When, TI of alkyd resins added the same amount of polyurethane are compared, PU_3 based samples showed higher TI, PU_1 based samples showed lower TI. PU_1 was prepared from alphatic isocyanate whereas PU_3 had higher amount of aromatic isocyanate in it's structure.

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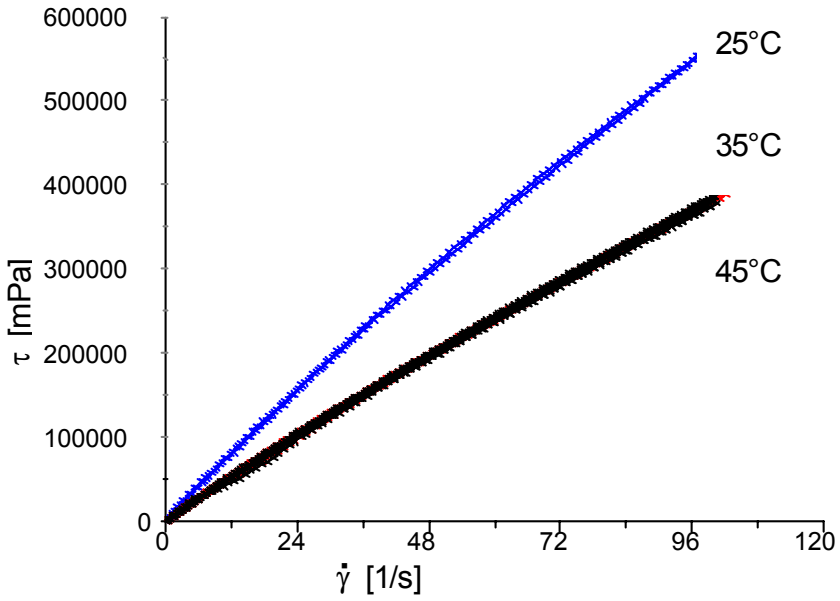
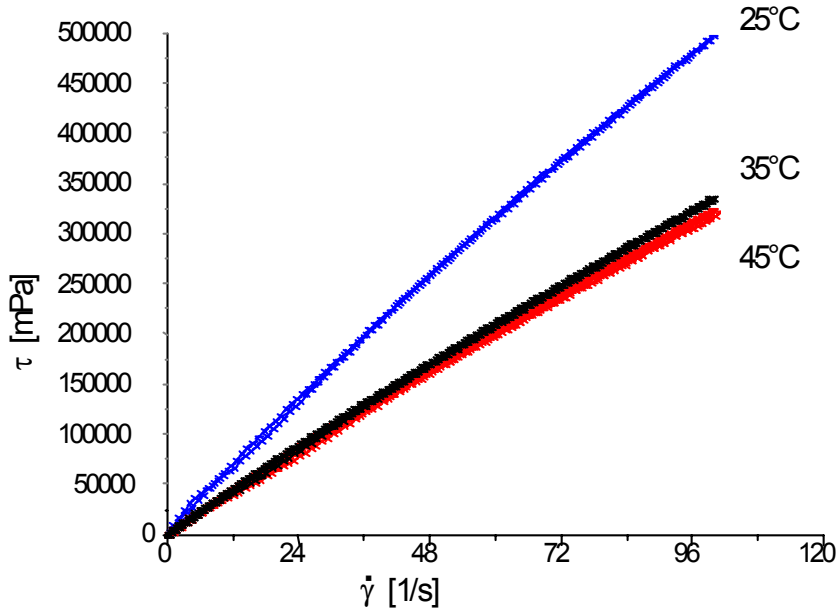
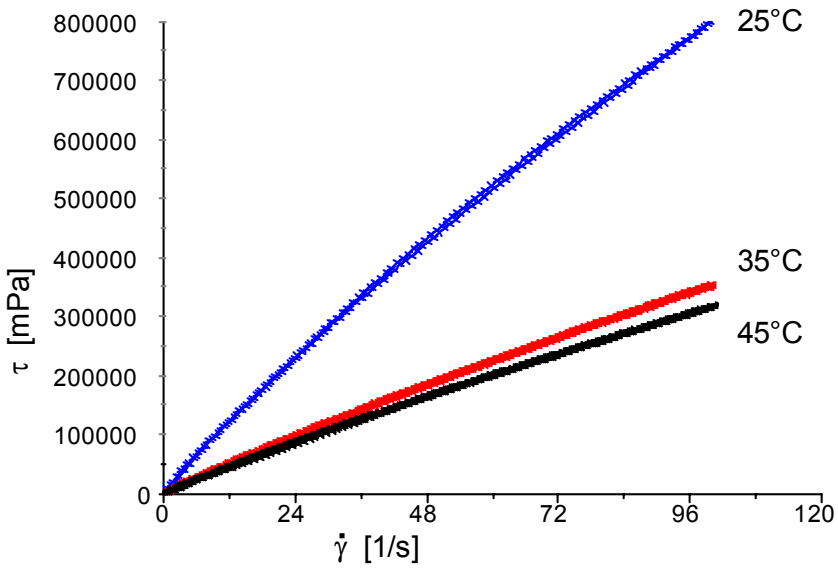
Appendix A. Shear rate – shear stress graphs for all produced polymers



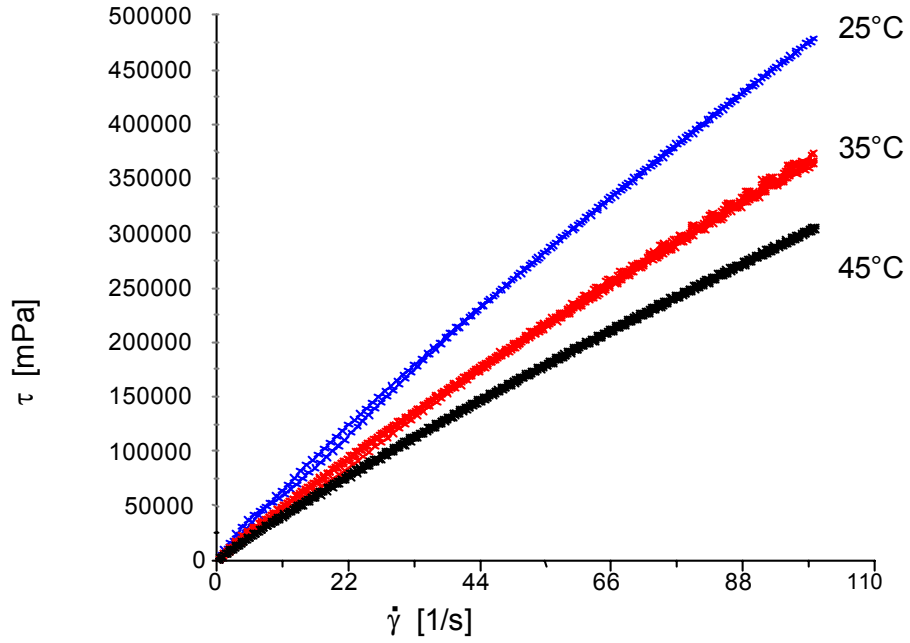
App. A Figure 1 Shear rate-shear stress graph for PU_1 with a stirring ratio of 0,5 % at temperatures 25°C, 35°C and 45°C



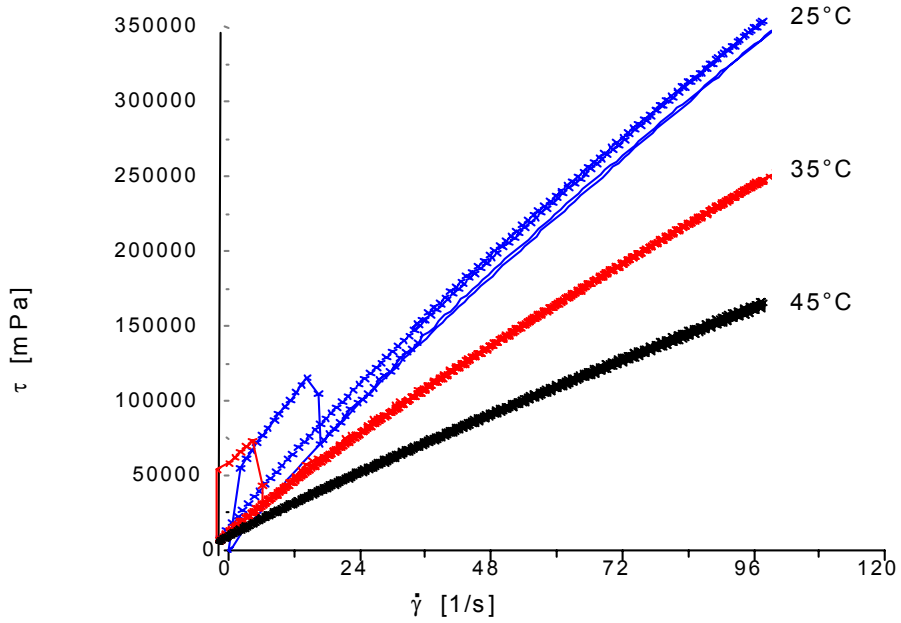
App. A Figure 2 Shear rate-shear stress graph for PU_1 with a stirring ratio of 2,5 % at temperatures 25°C, 35°C and 45°C



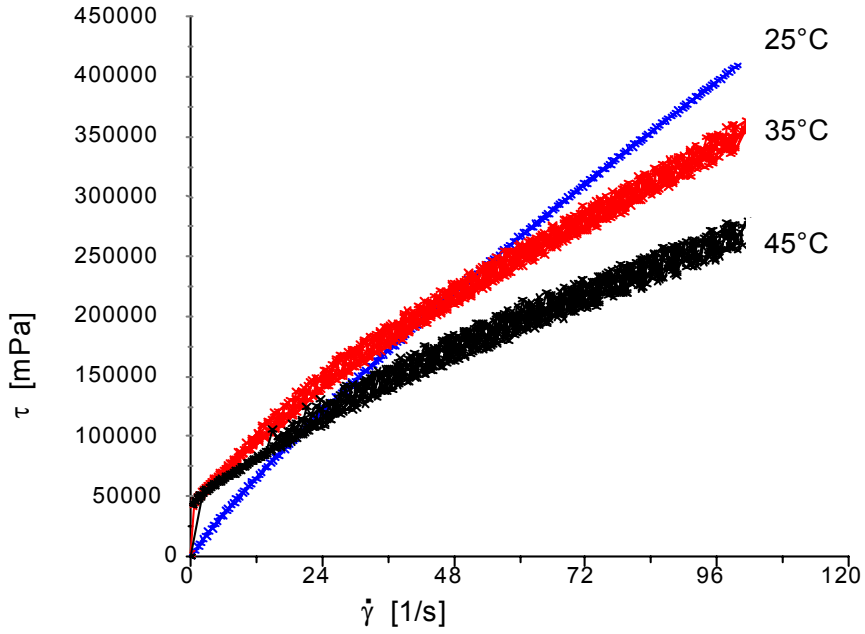
App. A Figure 3 Shear rate-shear stress graph for PU_1 with a stirring ratio of 3,5 % at temperatures 25°C, 35°C and 45°C



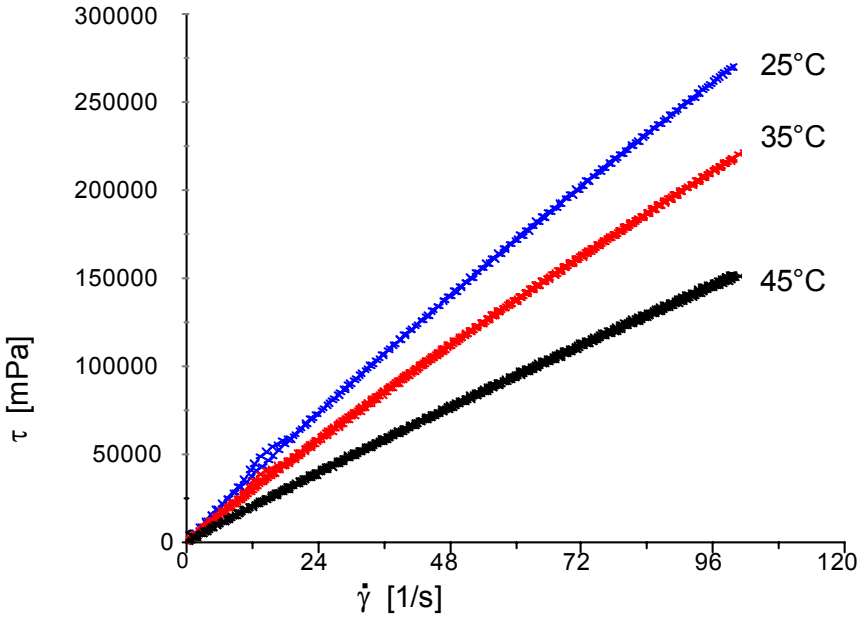
App. A Figure 4 Shear rate-shear stress graph for PU_1 with a stirring ratio of 5 % at temperatures 25°C, 35°C and 45°C



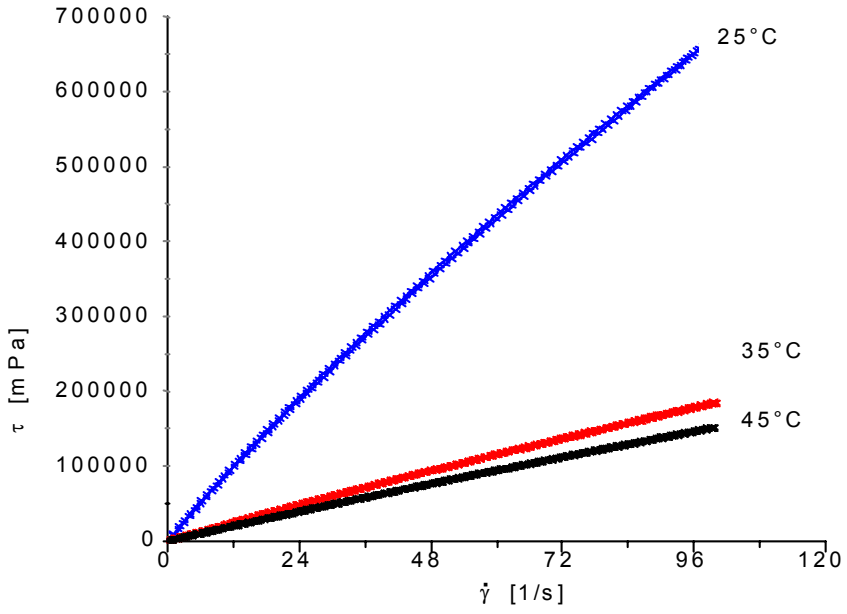
App. A Figure 5 Shear rate-shear stress graph for PU_2 with a stirring ratio of 0,5 % at temperatures 25°C, 35°C and 45°C



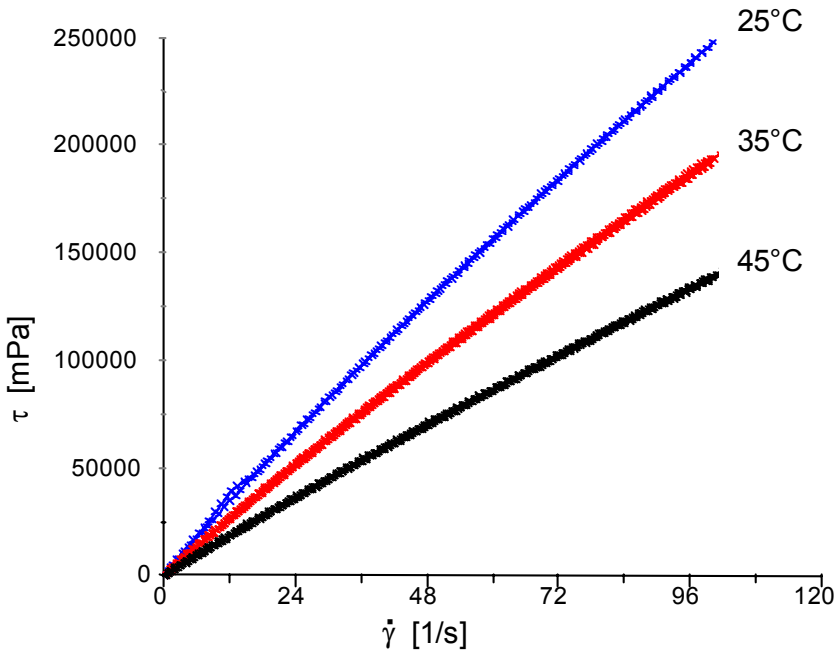
App. A Figure 6 Shear rate-shear stress graph for PU_2 with a stirring ratio of 2,5 % at temperatures 25°C, 35°C and 45°C



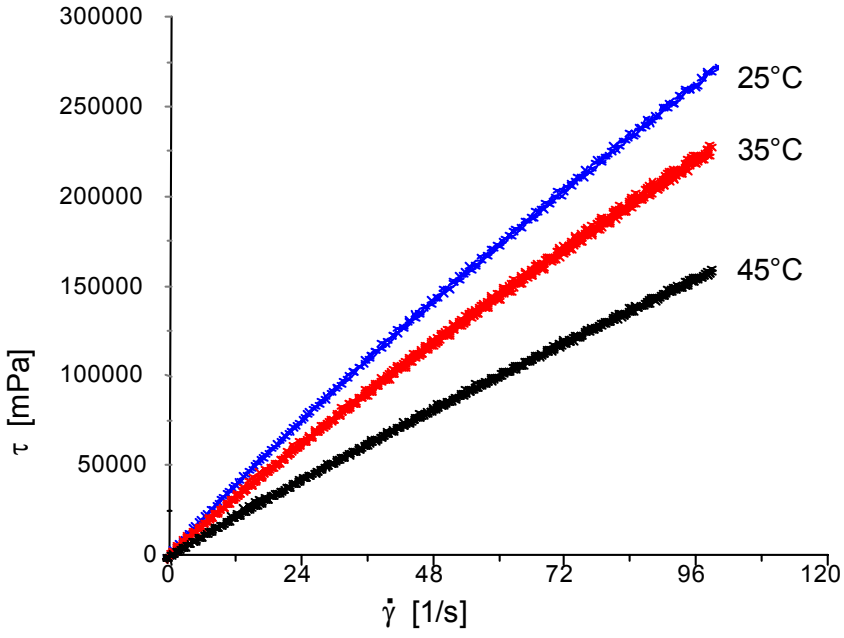
App. A Figure 7 Shear rate-shear stress graph for PU_2 with a stirring ratio of 3,5 % at temperatures 25°C, 35°C and 45°C



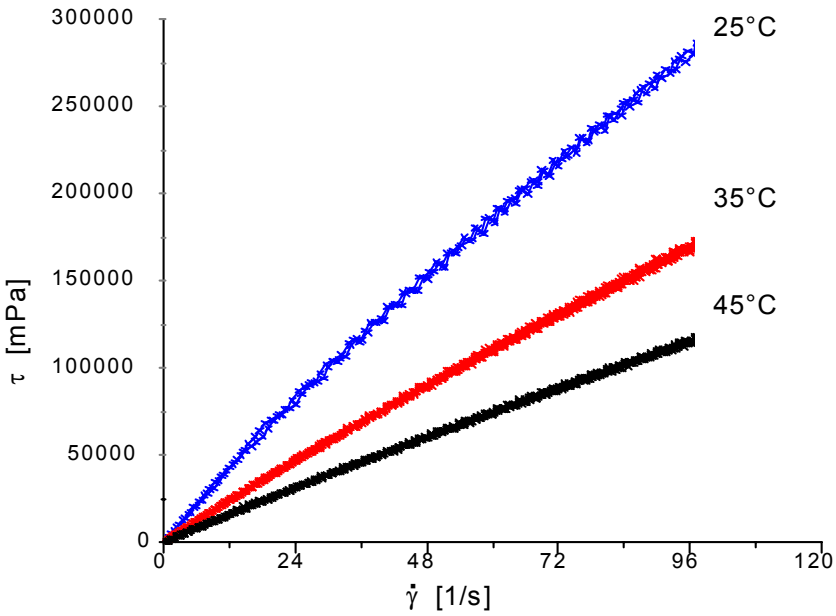
App. A Figure 8 Shear rate-shear stress graph for PU_2 with a stirring ratio of 5 % at temperatures 25°C, 35°C and 45°C



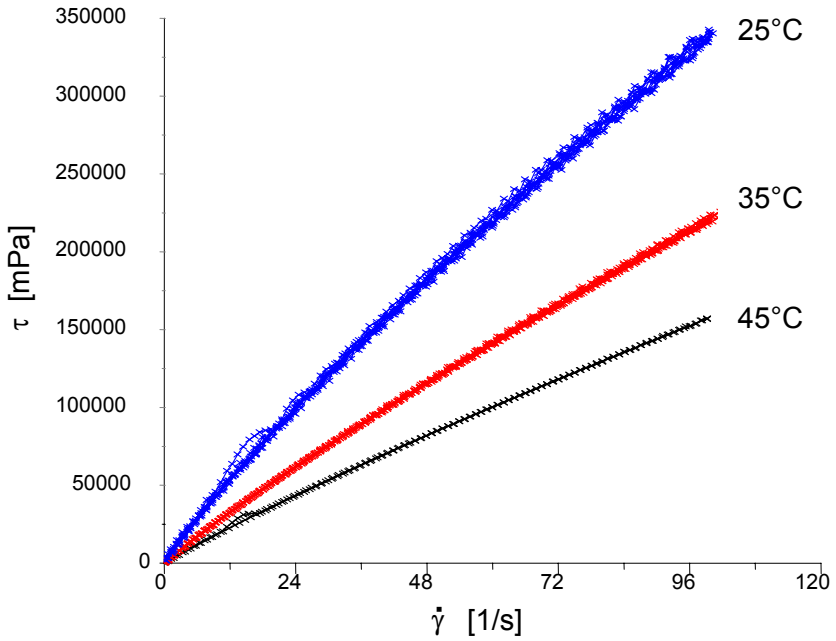
App. A Figure 9 Shear rate-shear stress graph for PU_3 with a stirring ratio of 0,5 % at temperatures 25°C, 35°C and 45°C



App. A Figure 10 Shear rate-shear stress graph for PU_3 with a stirring ratio of 2,5 % at temperatures 25°C, 35°C and 45°C

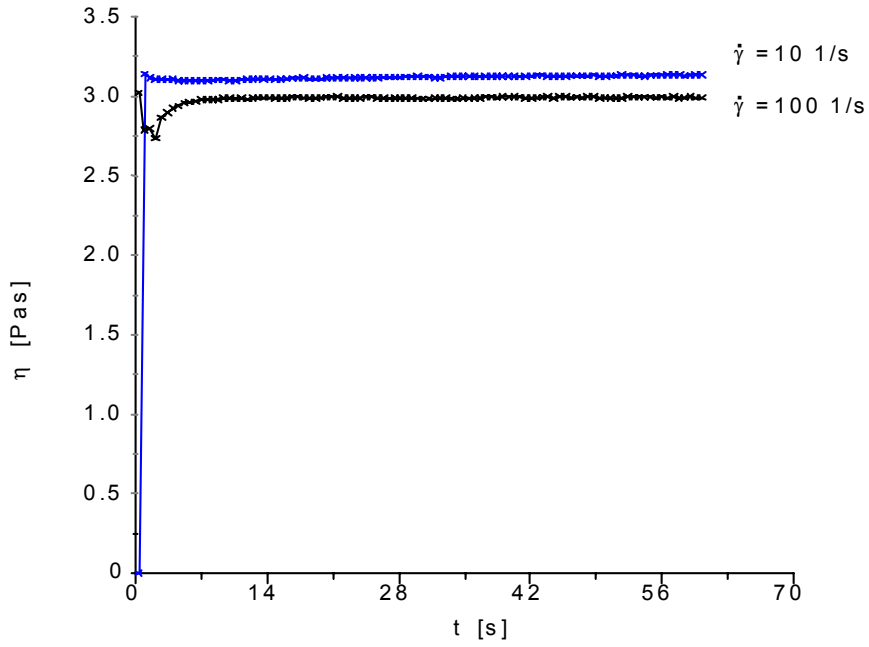


App. A Figure 11 Shear rate-shear stress graph for PU_3 with a stirring ratio of 3,5 % at temperatures 25°C, 35°C and 45°C

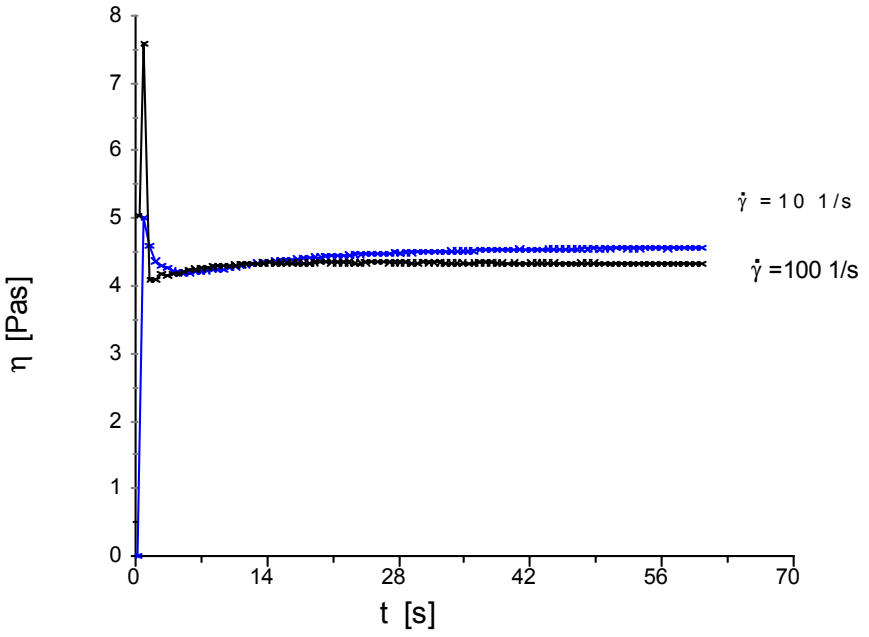


App. A Figure 12 Shear rate-shear stress graph for PU_3 with a stirring ratio of 5 % at temperatures 25°C, 35°C and 45°C

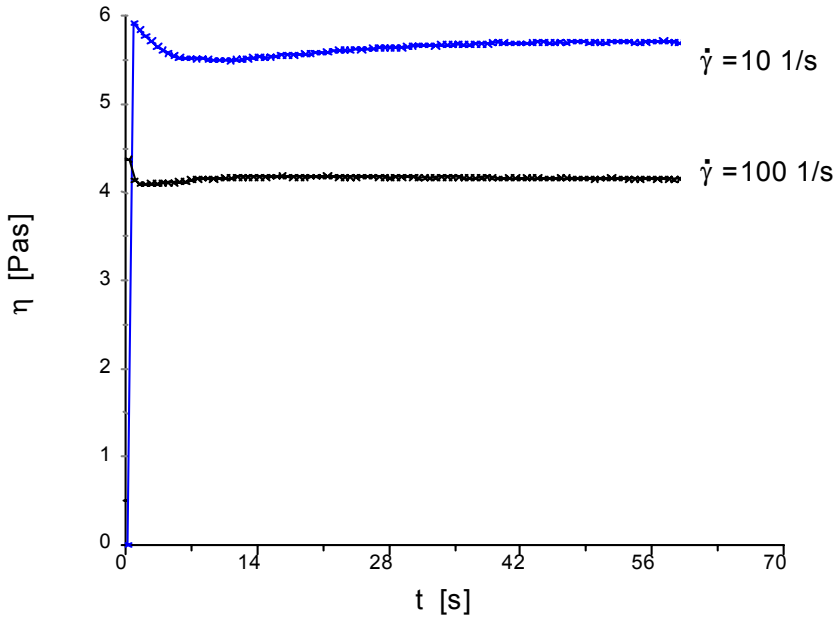
Appendix B Viscosity – time curves for all produced polymers



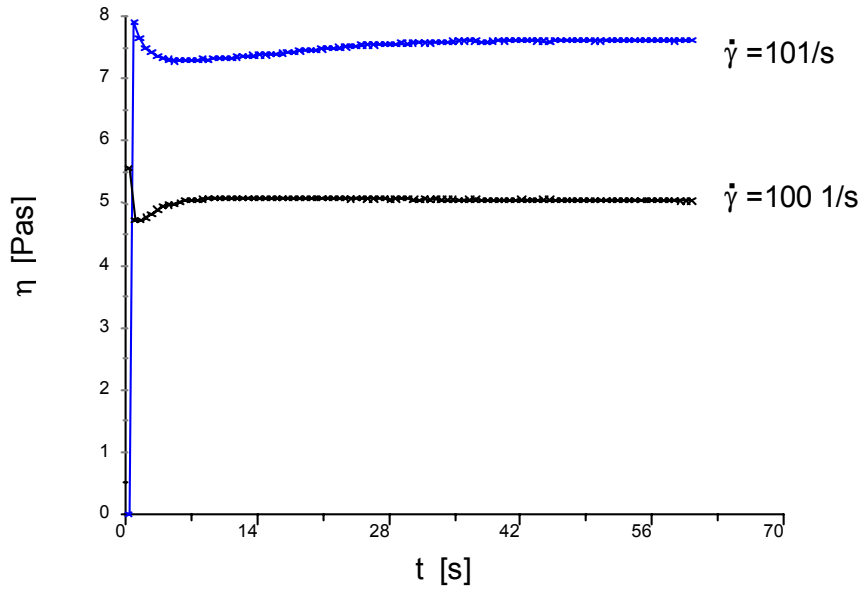
App. B Figure 1 Viscosity – time curve for PU_1 with a stirring ratio of 0,5 % at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s



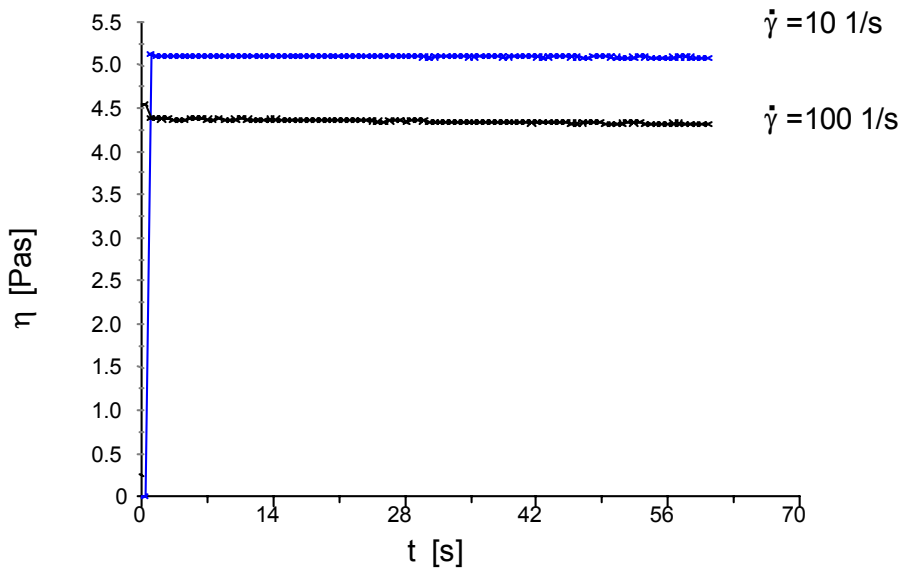
App. B Figure 2 Viscosity – time curves for PU_1 with a stirring ratio of 2,5 % at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s



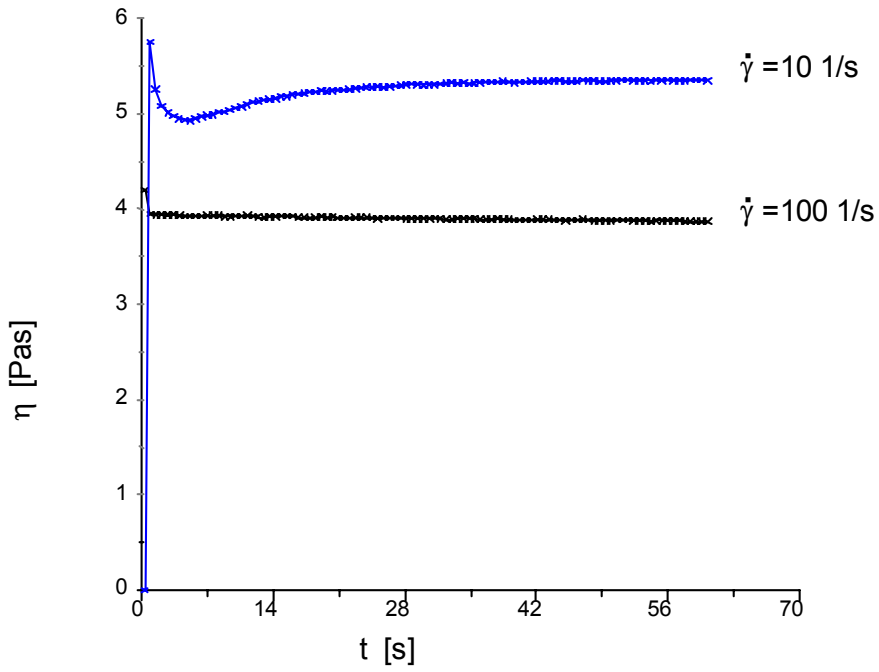
App. B Figure 3 Viscosity - time curve for PU_1 with a stirring ratio of 3,5 % at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s



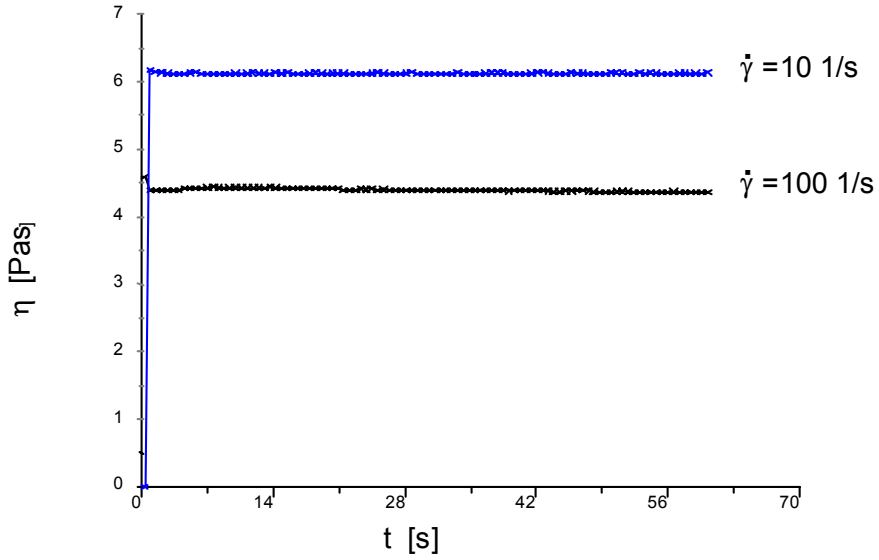
App. B Figure 4 Viscosity - time curve for PU_1 with a stirring ratio of 5 % at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s



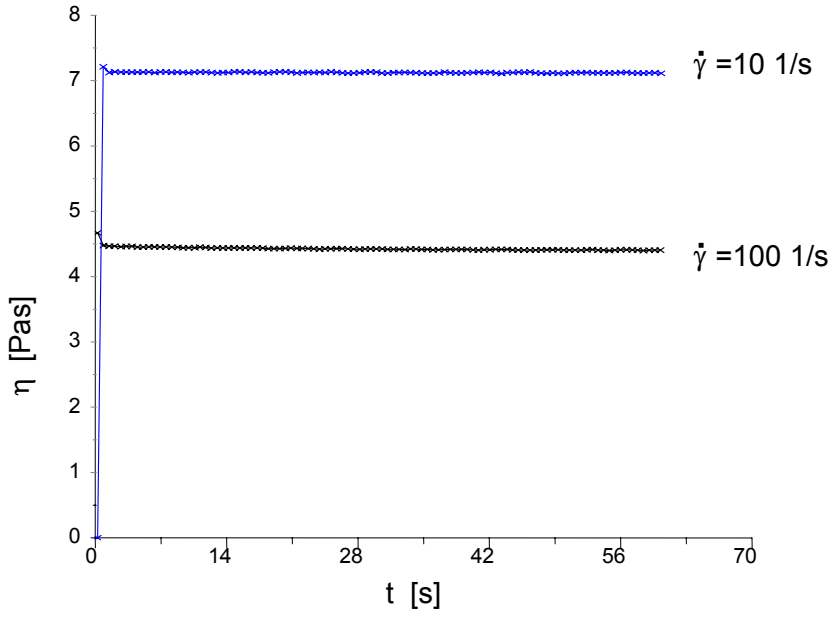
App. B Figure 5 Viscosity – time curve for PU_2 with a stirring ratio of 0,5 % at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s



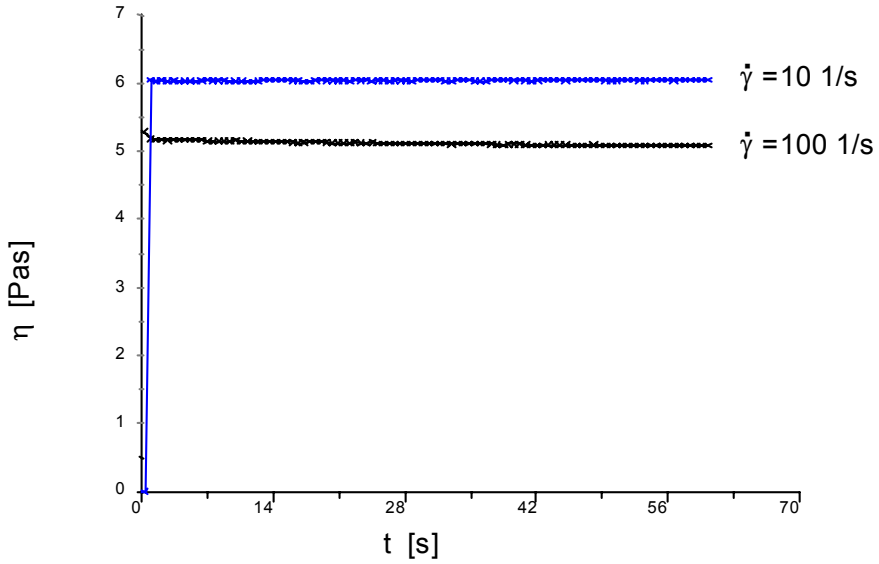
App. B Figure 6 Viscosity - time curve for PU_2 with a stirring ratio of 2,5 % at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s



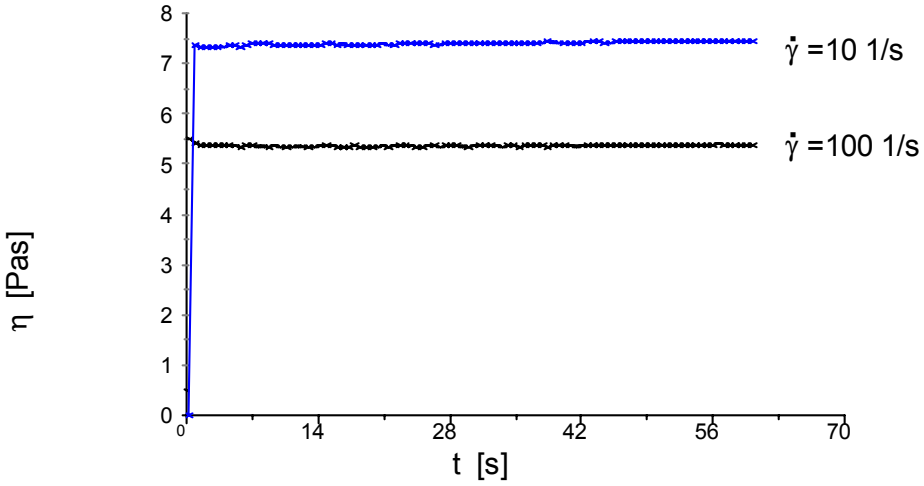
App. B Figure 7 Viscosity – time curve for PU_2 with a stirring ratio of 3,5 % at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s



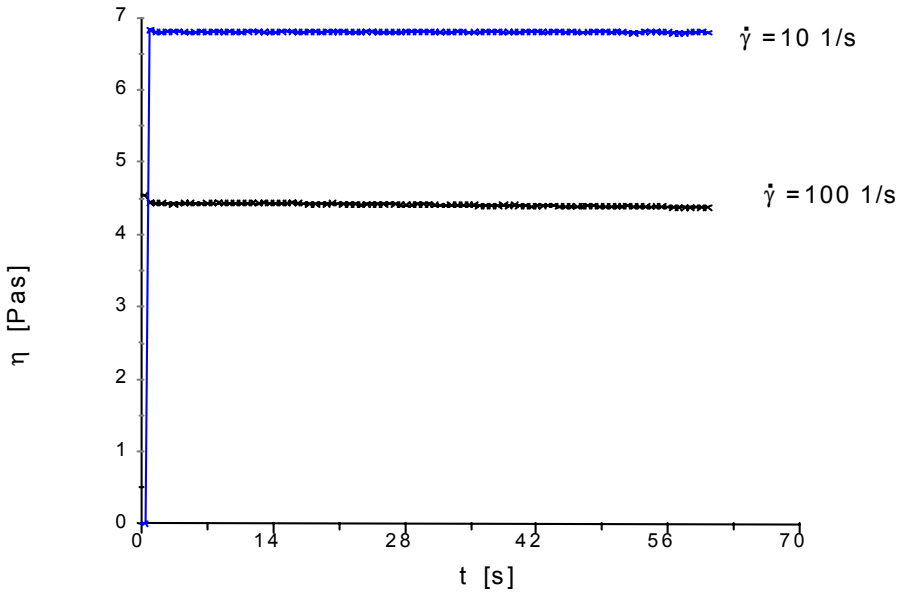
App. B Figure 8 Viscosity- time curve for PU_2 with a stirring ratio of 5 % at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s



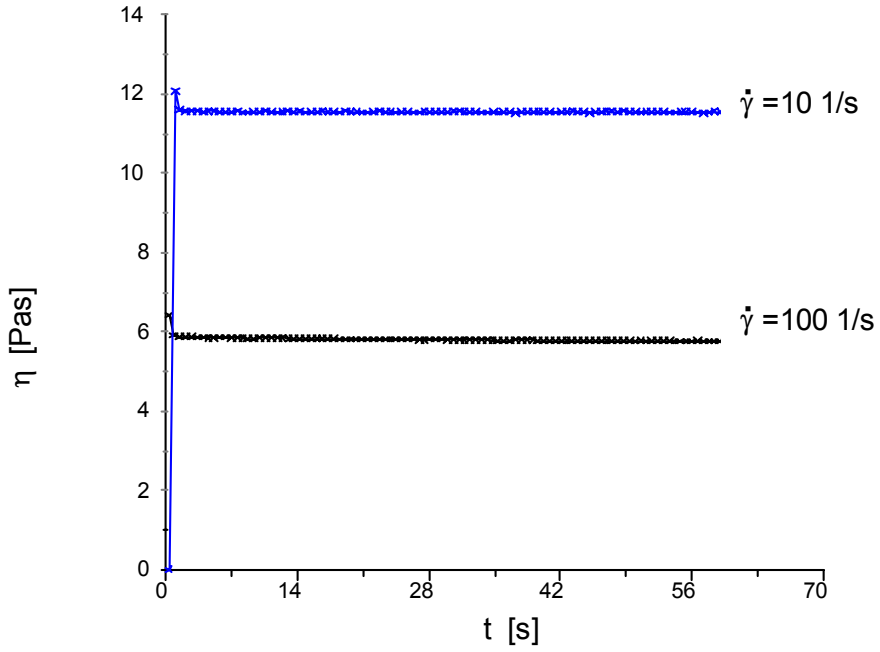
App. B Figure 9 Viscosity - time curve for PU_3 with a stirring ratio of 0,5 % at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s



App. B Figure 10 Viscosity - time curve for PU_3 with a stirring ratio of 2,5 % at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s



App. B Figure 11 Viscosity - time curve for PU_3 with a stirring ratio of 3,5 % at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s



App. B Figure 12 Viscosity -time curve for PU_3 with a stirring ratio of 5 % at shear rate $\dot{\gamma}$ =10 1/s and $\dot{\gamma}$ =100 1/s

BIBLIOGRAPHY

Orçun Yılmaz was born in İzmir in 1978, he concluded his primary school education in Aydın. He was graduated from Aydın Adnan Menderes Anatolian High School. He was admitted to İstanbul Technical University, depertmant of chemical engineering and graduated as a chemical engineer in 2001. And at the same year he was registered as M.Sc student to the Polymer Science and Technology program of the Institute of Science and Technology of İstanbul Technical University.