# Determination of the surface tension of several polymers: HDPE, LDPE, PP and liquids: water, ethanol, ethylene glycol and decalin

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*Presented by:*

*Cyril Moghabghab*

*Matriculation number: 828293*

*First Reader: Prof. Dr. Lauth*

*Member of committee: Prof. Dr. Prielmeier*

## Preface:

My sincere gratitude goes first to Prof. Dr. Lauth for his support and his very helpful advice. Without him this work could not have been finished.

I would also like to extend gratitude to Prof. Dr. Prielmeier who was always available to help and without whom I would have given up.

Next I would like to thank my family who, although geographically far, were very helpful.

And last of all I would like to thank all my friends for their support and advice.

Thank you all.

I hereby certify that the below mentioned work has been written by me and that no other sources except the ones cited below have been used to complete this dissertation

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List of abbreviations

PP: Polypropylene

HDPE: High Density Polyethylene

LDPE: Low Density Polyethylene

$\sigma_s^p$ = polar component of the surface energy of the solid

$\sigma_s^d$= dispersive component of the surface energy of the solid

$\sigma_l^p$ = polar component of the surface energy of the liquid

$\sigma_l^d$ = dispersive component of the surface energy of the liquid

$\theta$ = contact angle

G= Gibbs free energy

$N_A$ =Avogadro number

mN= milliNewton

m= meter

# 1. Introduction:

**Figure 1: Water Droplet on leaf (1)**

Water as shown in figure 1 adheres weakly to wax and strongly to itself, so it gathers in the form of drops. Surface tension is the reason for the near-spherical shape, because a sphere has the smallest possible surface area to volume ratio of 4.836 for one unit volume (1).

Another form in which surface energy manifests itself is the beading of water on waxed cars. When the rains drops fall on your waxed car, they smoothly slide down keeping your car neat clean and untouched.

Yet another phenomenon where surface energy plays a role is in the formation of drops from liquid: When the liquid is stretched by applying force or it is poured on some surface it tends to form the droplets due to the surface tension the fluid. (2)

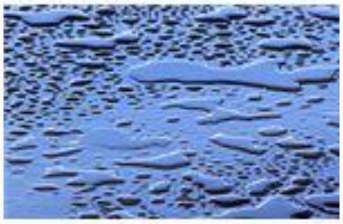


Figure 2: Formation of drops due to rain (2)

The mercury used in the thermometer which is used on a daily basis is yet another aspect of the effect of the surface energy. The mercury used in the thermometer does not stick to the wall of the capillary tube because of the surface tension. Had it stuck to the walls the measurement of temperature would not have been correct. (2)

The separation of oil and water is caused due to the difference in surface tension of the two liquids. There is also separation of the fuel and lubricating oil in the engine due to their surface tension. Had they mixed together, the fuel would have lost its combustion properties while lubricating oil would have lost its viscosity and lubrication properties. (2)

Ordinarily the bubbles in water are unstable, but when surfactants are introduced in water its surface tension is reduced by factor of three or more. As such water the bubbles can remain stable; hence lots of bubbles are seen in such liquids. (2)

Due to the high importance of this property of matter called the surface energy it was the basis for several studies. Similarly this study will be dealing with this concept. The purpose however of this study is the determination of the surface energy of several polymers, namely HDPE, LDPE, PP and liquids, water, ethanol, ethylene glycol and decalin at constant temperature ( room temperature) due to the huge importance of both polymers and the concept of surface energy in modern economics. Since there are many methods to determine surface energy, several methodological restrictions were taken into consideration. The first restriction adopted was that the Sessile Drop Method was used as the primary method to determine the surface energy of the polymers. While the Pendant Drop Method was used to determine that of the liquids (refer to literature for theoretical justification). These restrictions serve the purpose of a controlled methodology that allows for a comparison of the accuracy of the above mentioned methods with respect to values found in the literature.

Another purpose of this experiment is to determine the effect of structural ramifications on surface energy. This goal is achieved through the choice of several polymers, specifically PE/PP with different properties where PE is linear and PP is ramified. The study allows for the evaluation of the effect of ramification on surface energy.

In this context, the four possible interpretation of the Sessile Drop Method (Zisman, Owens/Wendt, Fowkes, and Van Oss) are compared to determine the interpretation that yields the most accurate results given this study's restrictions and experimental parameters. This evaluation is based on a comparative study of the angles obtained from each experiment and applied within each possible interpretation. In this manner, each polymer would be evaluated according to the four interpretations and the results compared to each other.

Figure 3:Insect walking on water (1)

Water striders stay atop the liquid because of surface tension

Figure 4:Wine tears (2)

Wine is mostly a mixture of alcohol and water. When the surface of the wine meets the side of the glass, capillary action makes the liquid climb the side of the glass. Both alcohol and water evaporate from the rising film, but the alcohol evaporates faster, due to its higher vapor pressure. The resulting decrease in the concentration of alcohol causes the surface tension of the liquid to increase, and this causes more liquid to be drawn up from the bulk of the wine, which has a lower surface tension because of its higher alcohol content. The wine moves up the side of the glass and forms droplets that fall back under their own weight. (2)

# 2. Literature review :

## 2.1 General information about the surface energy

DIN 55660 defines the Surface energy as the Energy or Strain that results from the intermolecular forces (3). In the case which this thesis follows it is the border surface strain which results between the polymer/liquid and the gas phase around it.

Surface tension is the force which two different phases exert on each other to prevent them from sinking into one another. This type of forces usually creates glue like properties.

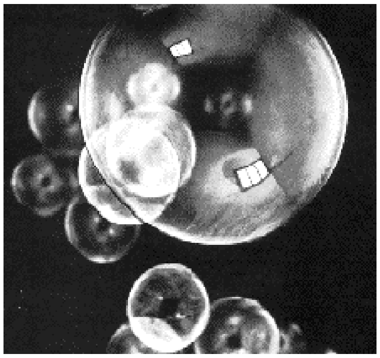


**Figure 5: Example for surface tension in shape of bubbles (4)**

It is also convenient here to emphasize the difference between two terms which are to be used in the following discussion; surface tension and surface energy.

First the surface tension $\gamma$

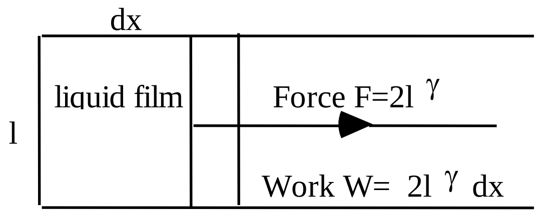


Figure 6: The surface energy as a function of work (5)

When a wire of length l is pulled by a distance dx it increases the area of the liquid by twice the area of the rectangle (because there is a surface on each side).

Work done in increasing the surface area of the film

$$\text{Work} = \gamma\, dA$$

$$= \gamma\, 2l\, dx \quad (\text{units J m}^{-2})$$

Equation 1 : Work and surface energy

Note work can be expressed as force x distance

$$W=Fd$$

Equation 2: Definition of Work

Hence from Equation 1:

Force required to stretch the film is proportional to *l*,

$$F= \gamma\, 2(l) \text{ or}$$

$$\gamma= F / 2l$$

Equation 3: Force and surface tension

The unit of surface tension is force / length, [ ] = N/m

Then the surface energy

This energy has been quantified by simple thermodynamics whereby the mathematical basis for its calculation is as follows:

In thermodynamics, the Gibbs free energy G is a thermodynamic potential that measures the "useful" or process-initiating work obtainable from a thermodynamic system at a constant temperature and pressure (isothermal, isobaric). The Gibbs free energy is the maximum amount of non-expansion work that can be extracted from a closed system; this maximum can be attained only in a completely reversible process where the system is in thermodynamic equilibrium. (6)

The change in the free enthalpy G of a homogenous, condensed phase with a surface area is a function of temperature T, pressure P and the properties of the area A:

$$G = f(T, P, A)$$

Thus, the total differentiation of the enthalpy becomes:

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P,A} dT + \left(\frac{\delta G}{\delta P}\right)_{T,A} dP + \left(\frac{\delta G}{\delta A}\right)_{P,T} dA$$

Equation 4: Change of the free energie

In isothermal (T = constant) and isobaric (P = constant) conditions the equation becomes:

$$dG = \left(\frac{\delta G}{\delta A}\right)_{P,T} dA$$

Equation 5: Isothermal/isobaric conditions

Dividing the equation by dA we obtain a mathematical definition for the surface energy σ

[ ] = mN/m

$$\sigma = \gamma = \left( \frac{\delta G}{\delta A} \right)_{P,T}$$

Equation 6: The surface tension

So the surface energy is the reversible work needed in isothermal and isobaric conditions to increase the surface area of the liquid by 1 unit of area (either $m^2$ or $cm^2$).

It is useful here to note that the surface tension is the specific surface energy.

## 2.2 The parachor as a method of estimating the surface energy

The parachor is a general expression used to solve various structural problems. Its general form is given by the following equation

$$P = \gamma^{(1/4)} M / (D\text{-}d)$$

Equation 7: General equation of the parachor

Where γ is the surface tension M is the molar mass and D is the density of the liquid phase d is the density of the gas phase

According to Macleod in 1923 a relationship between the density and the surface tension is described as follows

$$\gamma = C\ (D\text{-}d)^4$$

Equation 8: Relationship between the surface energy and the density

Where C is a characteristic constant of the liquid and D and d are the densities of the liquid and the gas phase respectively.

Replacing the 2 equations in each other would result in the known definition of the parachor.

$$P=0.78\ V_c$$

Equation 9: Known equation for the parachor

Where the ratio M/(D-d) is the critical molar volume $V_C$

The parachor has several useful properties which help in estimating the surface tension of a polymer

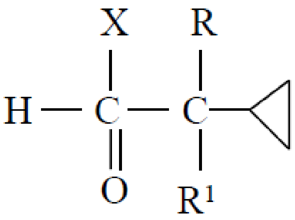


Figure 7: A sample molecule for parachor calculations (4)

P can be reproduced by the addition of 2 constants, one representing the atoms in the molecule, the other representing the ring structure.

P does not depend on how the atom is placed it is only based on its structure. (4)

The constant which is related to the atoms of the molecule do not change from compound to another. (4)

By replacing the equations above in one another a relation between the surface energy and the parachor is established which would help in estimating the surface energy using the parachor

$$\gamma=(P/V)^4$$

Equation 10:Relationship between the surface energy and the parachor

## 2.2.1 Estimation of the surface energy of water

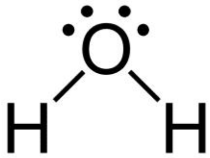


**Figure 8~~8 ~~: Structure of water (8)**

The factor related to H being 15.5 and that for O 19.8 the value for the parachor for water becomes:

$P = 2x\ 15.5 + 19.8 = 50.8\ (cm^3/mol)\times(Jx10^{-7}/cm^2)^{1/4}$

$\rho = 1\ g/cm^3$  $M = 18\ g/mol$

$V = M/\rho = 18\ cm^3/mol$

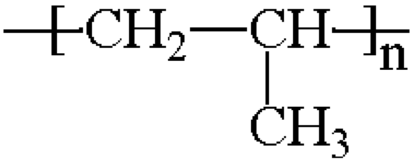
$\gamma = (P/V)^4 = (50.8/18)^4 = 63.44\ mN/m$

This value is reasonably close to the literature value of 72.2 mN/m

This method is very sensitive to Liquid Density.

Density fluctuate 3% change in density = 14% change in surface energy

## 2.2.2 Estimation of the surface energy of PP



$$-\!\!\left[CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}\right]_n\!\!-$$

**Figure 9~~9 ~~: Structure of PP (9)**

$P = 3\text{x}\ 9 + 6\ \text{x}\ 15.5 = 120\ (\text{cm}^3/\text{mol})\times(\text{Jx}10^{-7}/\text{cm}^2)^{1/4}$

$\rho = 0.855$ g/cm3  M= 42 g/mol

$V = M/\rho = 49.22\ \text{cm}^3/\text{mol}$

$\gamma = (P/V)4 = (120/49.22)^4 = 20.48$ mN/m

## 2.3 Some factors that influence the surface energy

### 2.3.1 The effect of temperature

#### 2.3.1.1 Guggenheim

In 1949 Guggenheim discovered that the surface energy decreases with increasing temperature till the temperature reaches the critical temperature of the polymer $T_C$ (a critical point, also known as a critical state, occurs under conditions at which no phase boundaries exist). When the Temperature reaches the critical temperature $T_C$ it vanishes. (4)

$$\gamma = \gamma^o \left(1 - \frac{T}{T_C}\right)^n$$

**Equation 11: Temperature dependence of the surface energy**

Where n is an empiric factor equal to 11/9

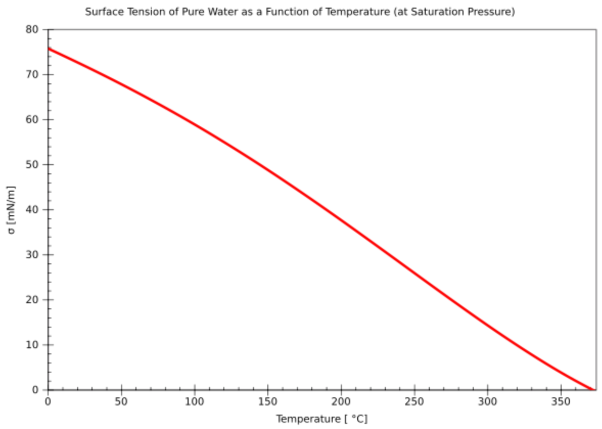


**Figure 10~~10~~: Temperature dependence of the surface energy of water (4)**

### 2.3.1.2 Eötvös rule

The Eötvös rule is the more used method of determining the temperature dependence of the surface energy. It makes several assumptions. The first assumption it makes is that the surface tension decreases linearly with increasing temperature till a value of zero at the critical temperature. The second assumption is that the temperature dependence of the surface tension can be plotted for all liquids in a way that the data collapses to a single master curve. (7)

$$\gamma V^{2/3} = k(T_c - T)$$

Equation 12: Eötvös dependence for the surface tension

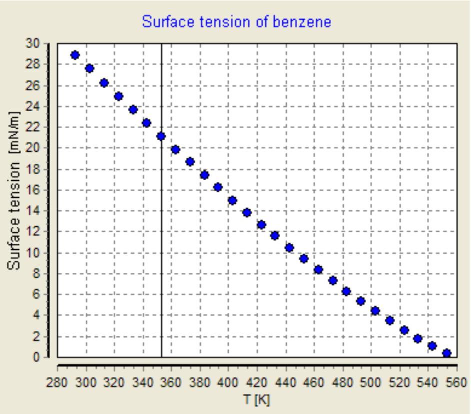


Figure 11: Temperature dependence of the surface energy according to Eotvos (7)

| **Liquid in contact with air** | **Temperature (degrees C)** | **Surface Tension (mN/m, or dyn/cm)** |
|---|---|---|
| Benzene | 20 | 28.9 |
| Carbon tetrachloride | 20 | 26.8 |
| Ethanol | 20 | 22.3 |
| Glycerin | 20 | 63.1 |
| Mercury | 20 | 465.0 |
| Olive oil | 20 | 32.0 |
| Soap solution | 20 | 25.0 |
| Water | 0 | 75.6 |
| Water | 20 | 72.8 |
| Water | 60 | 66.2 |
| Water | 100 | 58.9 |
| Oxygen | -193 | 15.7 |
| Neon | -247 | 5.15 |
| Helium | -269 | 0.12 |

**Table 1: Experimental values for the tempretaure dependence of the surface energy (8)**

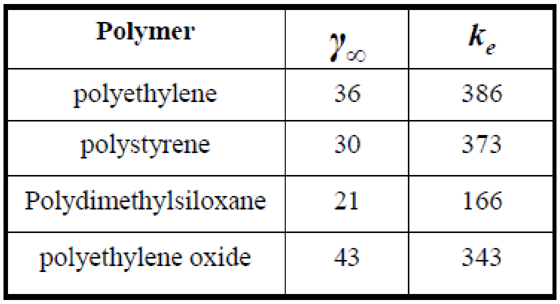
### 2.3.2 The effect of molecular mass

Normally the surface tension is proportional to the inverse of the molecular weight M. While the heat capacity and the specific volume are proportional to the inverse of M the surface tension is proportional to the factor $M^{-2/3}$ (4)

$$\gamma=\gamma_\infty - k_e / M_n^{2/3}$$

**Equation 13: Molar mass dependence of the surface energy**

where ke is a material related constant and $\gamma\infty$ is the finite surface energy at infinite molecular weight. Some values for the material specific constants are given in the following table.



| **Polymer** | $\gamma_\infty$ | $k_e$ |
|---|---|---|
| polyethylene | 36 | 386 |
| polystyrene | 30 | 373 |
| Polydimethylsiloxane | 21 | 166 |
| polyethylene oxide | 43 | 343 |

**Table 2: Some values for the molar mass dependence parameters (4)**

### 2.3.3 The effect of cohesion forces

The work that causes the surface energy can be either adhesive (between 2 different compounds) or cohesive (inside the same compound)

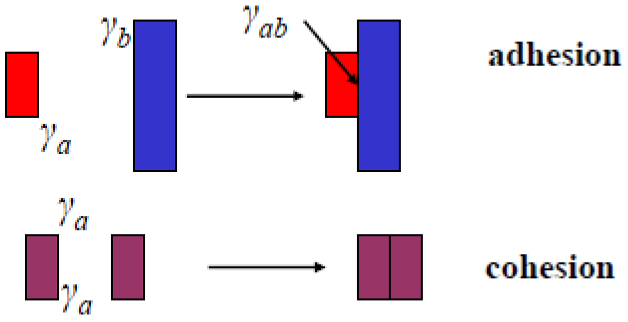


Figure 12~~12~~: Adhesive and cohesive work (4)

Cohesive forces between liquid molecules are responsible for the phenomenon known as surface tension. The molecules at the surface do not have other like molecules on all sides of them. Then they cohere strongly to those directly associated to them on the surface. They form a film. Therefore liquids adjust their shape to expose the smallest possible area.

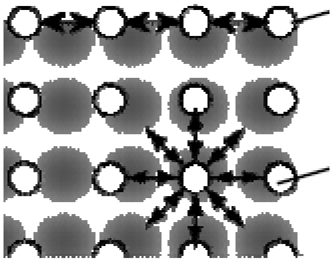


Figure 13~~13~~: Cohesion in substances (4)

According to Grunberg in 1949 the relationship between the cohesive work and the surface energy can be described as follows:

V being the molar volume of the substance dividing it by $N_A$ will result in the molecular volume $(V/N_A)$. The inverse of this ratio to the power of 2/3 becomes the number of molecules in one unit of surface area.

$$(N_A/V)^{2/3}$$

Equation 14: Number of units in one unit surface area

$\gamma$ being the surface energy per unit area multiplying it by the inverse of the above obtained ratio would result in the surface energy per one molecule.

$$\gamma\ V^{2/3}/N_A^{2/3}$$

**Equation 15: Surface energy per one molecule**

The multiplication of the obtained number by $N_A$ would give the molecular surface energy.

$$N_A^{1/3}\ V^{2/3}\ \gamma$$

**Equation 16: Molar surface energy**

which in turn doubled gives the cohesion work.

The end result is shown in the following equation (4)

$$W_{coh} = N_A^{1/3}\ V^{2/3}\ 2\gamma$$

**Equation 17: Cohesive work and surface energy**

## 2.4 Wetting and Young equation

Young established the well-regarded Young's Equation which defines the balances of forces caused by a wet drop on a dry surface.

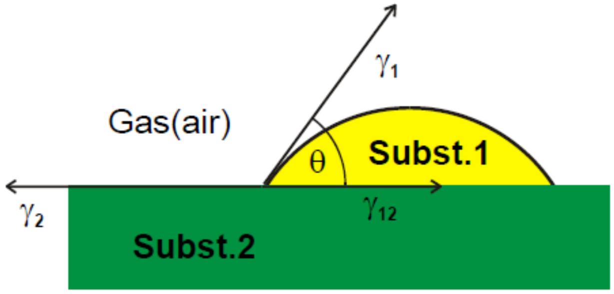


**Figure 14: Young equation (5)**

The Young equation gives the following relation, (10)

$$\gamma_{SL} + \gamma_{LG}\cos\theta_c = \gamma_{SG}$$

**Equation 18: Normal Young equation**

where $\gamma_{SL}$, $\gamma_{LG}$, and $\gamma_{SG}$ are the interfacial tensions between the solid and the liquid, the liquid and the vapor, and the solid and the vapor, respectively. The equilibrium contact angle that the drop makes with the surface is denoted by θ. This equation is only valid in the case of normal wetting.

To derive the Young equation, the interfacial tensions are described as forces per unit length and then a one-dimensional force equilibrium is established along the solid boundary. (10)

In cases of “high wetting” ( see figure 15) , the surface pressure of the liquid vapor on the solid is substantial.

Expressed by the work of adhesion we can write:

$$Wa = \gamma_1 + \gamma_2 - \gamma_{12} = \gamma_1 + \gamma_1 \cos\theta = \gamma_1(1+\cos\theta)$$

Equation 19: Young Dupree equation

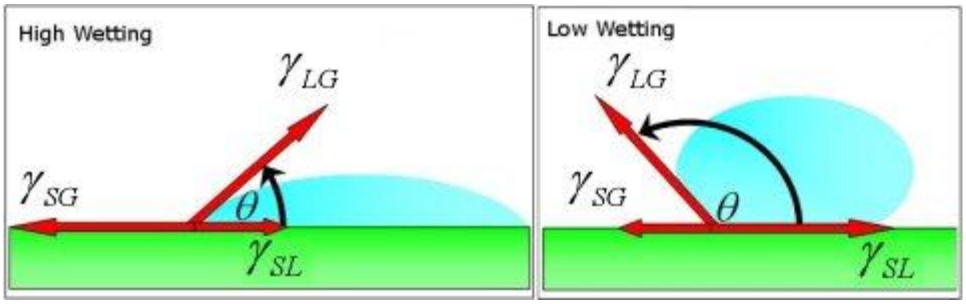


Figure 15: The two cases of wetting

## 2.5 The interaction parameter and the work of adhesion

As the work of cohesion was described in the part before, the work of adhesion is to be discussed through the work of Good and Girafalco.

In 1960 Good and Girafalco postulated that the work of cohesion is the geometric mean of the surface energies of the two substances. (5)

$$W^a = 2\varphi(\gamma_1\gamma_2)^{1/2}$$

Equation 20:Work of adhesion

Where φ is the so called the interaction parameter and ranges between 0.5 and 1.15

This interaction parameter is a function of the two substances as shown in the following equation

$$\Phi = \frac{4r_1r_2}{(r_1+r_2)^2}\frac{\sum A_{12}}{\left(\sum A_{11}+\sum A_{22}\right)^{1/2}}$$

**Equation 21: The interaction parameter**

where r1, r2 = molecular radii and ΣA is the sum of constants for all types of intermolecular forces (dispersive, polar, acid-bas, etc.) (5)

Inserting the Young Dupree equation into equation 20 one receives a relation between γ1 and γ2.

$$\gamma_2 = \gamma_1 \frac{(1+\cos\theta)^2}{4\Phi^2}$$

**Equation 22: Relationship between surface energies**

## 2.6 Equations of state

### 2.6.1 Dupree equation

According to Dupree the work between a solid and a liquid can be described by the following equation

$$Wsl = \gamma_s + \gamma_l - \gamma_{sl}$$

**Equation 23: Dupree equation**

### 2.6.2 Berthelot hypothesis

Using an assumption that the work between a solid and a liquid is the average of the work the solid does on itself and the work the liquid does on itself Berthelot made his step into determining an equation of state for the surface energy. (11)

$$Wsl = (W_{ss}W_{ll})^{0.5}$$

Equation 24: Berthelot assumption

The second assumption in this theory is that the work a solid does on itself is the double of the surface energy of the solid and respectively the same for liquids

$$W_{ss} = 2_{\gamma s} \qquad W_{ll} = 2_{\gamma l}$$

Equation 25: Work of cohesion

Using these 2 assumptions and replacing them in the Dupree relation the well known Berthelot equation of state is obtained (11)

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s\gamma_l)^{0.5}$$

Equation 26: Berthelot Equation of State

This equation is one of the 3 main equations used as basis for the Fowkes interpretation.

## 2.7 The Sessile drop method:

The Sessile drop technique is a method used for the characterization of solid surface energies, and in some cases, aspects of liquid surface energies. The main premise of the method is that by placing a droplet of liquid with a known surface energy on a sample of the solid, the shape of the drop, specifically the contact angle, and the known surface energy of the liquid constitute the parameters which can be used to calculate the surface energy of the solid sample. The liquid used for such experiments is referred to as the probe liquid, and the use of several different probe liquids is required since the different angles will need to be analyzed .The Sessile drop method includes several interpretations as to how to use these angles to determine the surface tension which are to be explained subsequently.

### 2.7.1 Fowkes interpretation

According to the Fowkes interpretation, the surface energy is divided into several components:

- Surface energy due to polar interactions.
- Surface energy due to dispersive interactions

This interpretation combined the Young relation (which relates the surface energy to the contact borderline tension) the Good relation (which relates the borderline tension to the dispersive and polar components to the borderline tension) and the Berthelot equation of state

$$\frac{\sigma_L\ (\cos\theta + 1)}{2} = \sqrt{\sigma_S^P}\sqrt{\sigma_L^P} + \sqrt{\sigma_S^D}\sqrt{\sigma_L^D}$$

**Equation 27 : Fowkes equation**

In this case instead of drawing the diagram two liquids are considered and this equation is solved as a two equation two unknowns system to find the radical of the disperse component and that of the polar component and from them, both components themselves and finally by adding them the total surface energy.

### 2.7.2 Owens/Wendt interpretation

The Owens-Wendt interpretation makes similar assumptions to the Fowkes interpretation. The two methods, although mathematically identical are different in the way they calculate the surface energy.

The resulting equation of Young Good and Berthelot according to this interpretation becomes:

$$\frac{\sigma_L\ (\cos\theta + 1)}{2\sqrt{\sigma_L^D}} = \frac{\sqrt{\sigma_S^P}\sqrt{\sigma_L^P}}{\sqrt{\sigma_L^D}} + \sqrt{\sigma_S^D}$$

**Equation 28 : Owens Wendt**

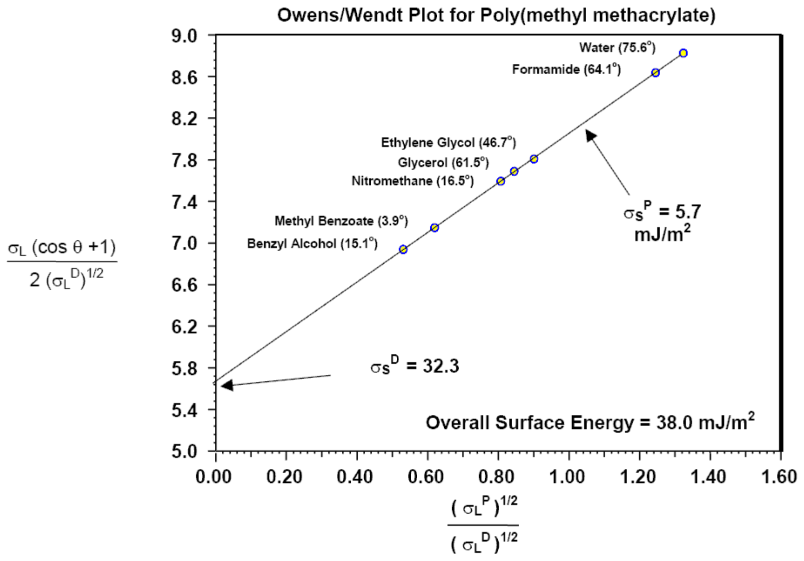


Figure 16: Literature example of Owens/Wendt interpretation (12)

This equation is represented in a diagram where a linear relation is expected y= mx+b where

$$y = \frac{\sigma_L\ (\cos\theta + 1)}{2\sqrt{\sigma_L^D}} \qquad m = \sqrt{\sigma_S^P}\ ; \quad x = \frac{\sqrt{\sigma_L^P}}{\sqrt{\sigma_L^D}} \qquad b = \sqrt{\sigma_S^D}$$

The slope of this graph gives the radical of the polar component of the surface tension while the ordinate intercept is the radical of the dispersive component.

### 2.7. 3 Van Oss interpetation

The Van Oss interpretation divides the surface tension of liquids and solids into three components.

a) The dispersive component similar to the two component interpretations.

b) The polar component due to acidic (positive) interactions hereafter noted as (σ +)

c) The polar component due to basic (negative) interactions hereafter noted as (σ -).

The equation for this interpretation becomes:

$$\sigma_L(\cos\theta + 1) = 2[\sqrt{\sigma_L^D \sigma_S^D} + \sqrt{\sigma_L^- \sigma_S^+} + \sqrt{\sigma_L^+ \sigma_S^-}]$$

Equation 29: Van Oss

The best way to get answers from this interpretation is to follow a similar methodology to the one adopted in the Fowkes interpretation but with three liquids. Therefore, in terms of calculation, the values are determined through a three equations and three unknowns system. Here it is recommended that one of the liquids only have a dispersive component ($\sigma + = \sigma - = 0$), another a dispersive component and a positive component only ($\sigma - =0$) and the third only a negative component ($\sigma + = 0$).

## 2.8 Zisman interpretation

The Zisman interpretation of the Sessile drop method is the simplest, for it is a 1 component theory. It does not break the surface tension into several components. As such, it is usually used for unpolar surfaces or polymers which makes it highly viable to the purposes of the study since polarity is not a main aim.

Figure 15 shows how a typical Zisman interpretation is performed.

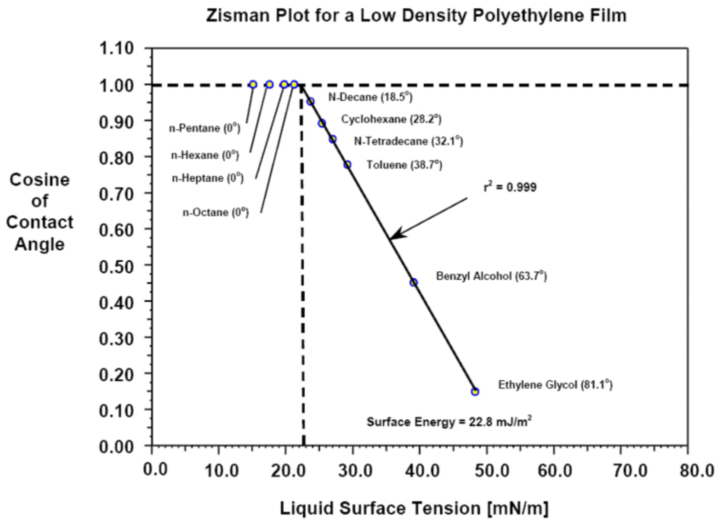


Figure 17: Literature example for Zisman interpretation (12)

The cosine of the contact angle between the liquid and the polymer is drawn as a function of the surface tension of the corresponding liquid. The final surface tension is determined through extrapolation to 1 on the ordinate axis and the reading of the corresponding surface tension. The extrapolated value is called the critical surface tension of the solid Surface, $\gamma_{cr}$ and is a characteristic property of any given solid.  Any liquid with $\gamma_l<\gamma_{cr}$ will wet the surface. It is found that critical surface tension is close to the solid surface tension of polymer. (5)

## 2.9 Pendant drop method:

### 2.9.1 Capilarity and liquid in a vertical tube

Surface energy usually happens between a liquid and a gas but when the liquid comes into contact with a solid it cuves up or own forming a so called meniscus.

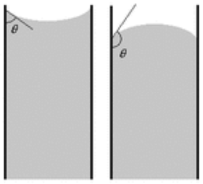


**Figure 18: Liquid in vertical tube (15)**

The contact angle can be used to determine a relationship between the liquid-solid surface tension and the liquid-gas surface tension, as follows:

$$\gamma_{ls} = - \gamma_{lg} \cos \theta$$

**Equation 30: Liquid solid surface energy**

where $\gamma_{ls}$ is the liquid-solid surface tension and $\gamma_{lg}$ is the liquid-gas surface tension

and $\theta$ is the contact angle.

One thing to consider in this equation is that in cases where the meniscus is convex, the cosine component of this equation will be negative which results in positive surface energy

If, on the other hand, the meniscus is concave, then the cos term is positive, in which case the relationship would result in a negative liquid-solid surface tension

What this means, essentially, is that the liquid is adhering to the walls of the container and is working to maximize the area in contact with solid surface, so as to minimize the overall potential energy. (15)

### 2.9,2 Pendant drop method

The Pendant drop Method is commonly used for the determination of the surface tension in the oil industry. The weight of a sample of the liquid and the diameter of the vessel are the main parameters that determine the surface energy of the liquid. This is done by letting a drop of a liquid hang from a needle ( vertical tube) whereby it is only bound by its surface tension. This method is characterized by its simplicity because it only requires a sample of the liquid under study unlike the method discussed earlier which required several liquids to measure the surface energy of one solid.

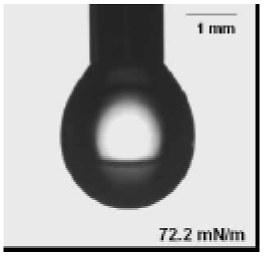


Figure 19: Pendant drop for water (4)

The force due to the surface energy is proportional to the length of the border between the liquid and the needle where the proportionality factor is usually called γ.

$$F_\gamma = \pi d \gamma$$

Equation 31: Pendant drop

where d is the tube diameter in m. [ ]= N

The mass m ( [ ] =kg) of the drop hanging from the end of the tube can be found by equating the force due to gravity (F=mg) with the component of the surface tension in the vertical direction. This generates the following formula:

$$mg = \pi d\gamma \sin\alpha$$

**Equation 32: Force balance for a pendant drop**

where α is the angle of contact with the tube [ ]= degree , and g is the acceleration due to gravity ( g = 9.81 m/s$^2$). When the angle goes to 90° and sinα goes to 1, the maximum weight of a pendant drop is obtained for a liquid with surface tension γ to be determined. [ ] = mN/m

$$mg = \pi d\gamma$$

**Equation 33: Surface tension of a liquid**

## 2.10 Ramification in polymers:

Ramification in macromolecular chemistry and specifically polymers is the state by which polymer single strands are bound in a network forming a 3-dimensional random coil “statisticher knauel”. This bonding can occur either directly in the building process of the polymer or by side reactions on an already existing polymer strand. Radical polymerization reactions of monomers with 2 vinyl functions as well as polycondensation/polyaddition with bi functional monomers lead directly to ramified polymers. The side reactions on an already existing polymer strand can occur either due to certain reaction conditions or due to the addition of multi-functional substances. For instance, the addition of sulfur rich substances during the vulcanization of epoxide resins with amines serves as an example of addition reaction of multi-functional substances

During the process of ramification, the properties of the polymer change. Generally speaking, increases in the hardness and melting point, as well as a decrease in solubility are observed.

The changes in properties including surface energy are directly proportional to the percentage of ramification of the polymer. As such, the higher the ramification, the steeper are the changes in the properties. (13)

# 3. Apparatus:

## 3.1 Hardware ( OCA 20)

An OCA 20 machine normally consists of the following components:

- Sample table where sample is positioned
- A vertical needle component from which the liquid is dropped on the sample
- Software guided needle movement manager
- Temperature regulation and measurement component (14)

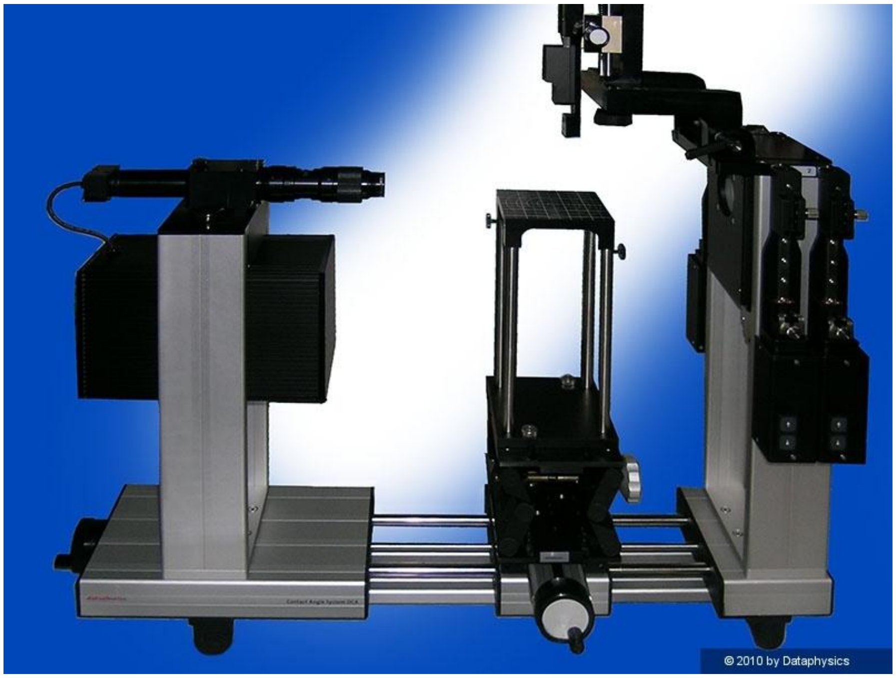


Figure 20: OCA 20 machine (14)

## 3.2 Procedure

Preparation

1. Place sample on the table
2. Fill the needles with desired test liquid
3. Position the sample under the needle
4. Set the brightness
5. Adjust the drop picture
6. Set up the picture recognition system
7. Preheat to specific temperature (room temperature in this case)

The static contact angles are used for the purposes of the Sessile drop method interpretation. They are measured using the tangent method. This is usually performed with OC 5 and 10 machines as well as the OC 20.

In order to describe this procedure the above mentioned points 5 and 6 will be discussed. The setting of the drop picture is of utmost importance to receive acceptable results. The zoom therefore is set to a minimum to ensure maximum sight of the drop. Then the needles are positioned in the middle of the sight field of the camera unit so that they can be raised or lowered if so required. Then a drop is produced and let loose on the sample. The focus on the work place is set under such conditions so as the needle end and the drop appear as sharp as possible.

Next, the basis line and the cursor line are to be focused in a similar manner as portrayed in figure 4 hereunder. (14) .

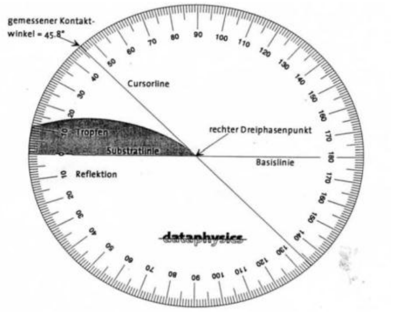


Figure 21: Contact angle measurment (14)

## 4 Experiments and results:

The first part of the experiments is applying the Sessile drop method interpretation for the three different polymers (HDPE, LDPE and PP) where all four above mentioned interpretations in the literature are to be discussed, evaluated and compared.

### 4.1 Sessile drop method:

#### 4.1.1 Sessile drop results for high density polyethylene

The first randomly chosen polymer to be studied is HDPE.

#### 4.1.1.1 Contact angle measurement

The measurement of the contact angle was achieved as mentioned before (see part 3.2) where two different samples of HDPE were considered and handled with the four different liquids (water ethanol ethylene glycol and decalin). This was done on a five times basis and the average of all five was calculated in order to yield the results presented in tables 3-6 below.

Results obtained with water:

| ϴ right/° | ϴ left/° | ϴ average/° |
|---|---|---|
| 83.8 | 88.5 | 86.15 |
| 87.8 | 85.8 | 86.8 |
| 69.3 | 66.4 | 67.85 |
| 60.6 | 64.7 | 62.65 |
| 64 | 62.8 | 63.4 |
| ϴ average/° | | 73.37 |
| Standard deviation/° | | 12.12 |
| Error/% | | 16.53 |

**Table 3: Water and HDPE**

Results obtained with ethanol:

| Ɵ right/$^o$ | Ɵ left/$^o$ | Ɵ average/$^o$ |
|---|---|---|
| 7.4 | 8.3 | 7.85 |
| 24.6 | 24.8 | 24.7 |
| 15 | 15 | 15 |
| 3.9 | 3.9 | 3.9 |
| 8.9 | 8.8 | 8.85 |
| Ɵ average/$^o$ | | 12.06 |
| Standard deviation/$^o$ | | 8.10 |
| Error/% | | 67.23 |

**Table 4: Ethanol and HDPE**

Results obtained with ethylene glycol:

| Ɵ right/$^o$ | Ɵ left/$^o$ | Ɵ average /$^o$ |
|---|---|---|
| 60.1 | 54.1 | 57.1 |
| 53.7 | 53.7 | 53.7 |
| 56 | 56 | 56 |
| 42.4 | 42.4 | 42.4 |
| 48.6 | 48.6 | 48.6 |
| Ɵ average/$^o$ | | 51.56 |
| Standard deviation/$^o$ | | 6.07 |
| Error/% | | 11.78 |

**Table 5: Ethylene glycol and HDPE**

Results obtained with decalin:

**Fehler! Verwenden Sie die Registerkarte 'Start', um Heading 1 dem Text zuzuweisen, der hier angezeigt werden soll.**

| ϴ right/° | ϴ left/° | ϴ average/° |
|---|---|---|
| 29 | 30.5 | 29.75 |
| 40.6 | 41.5 | 41.05 |
| 32 | 36 | 34 |
| 41.7 | 43.7 | 42.7 |
| 45.6 | 46.2 | 45.9 |
| ϴ average/° | | 38.68 |
| Standard deviation/° | | 6.62 |
| Error/% | | 17.12 |

Table 6: Decalin with HDPE

### 4.1.1.2 Evaluation of the surface energy using the four interpretations

The above obtained angles were interpreted according to the four above mentioned interpretations (Zisman Owens/Wendt Fowkes and Van Oss) in order to compare the results.

First according to the Zisman interpretation, the following angles were considered (table 7).

| Liquid | $\sigma_{(Liquid)}$/(mN/m) | θ/° | cos θ |
|---|---|---|---|
| Ethylene glycol | 48.4 | 51.56 | 0.27 |
| Water | 72.75 | 73.37 | -0.44 |

Table 7: Zisman interpretation for HDPE

This table was represented in the following graph (figure 22)

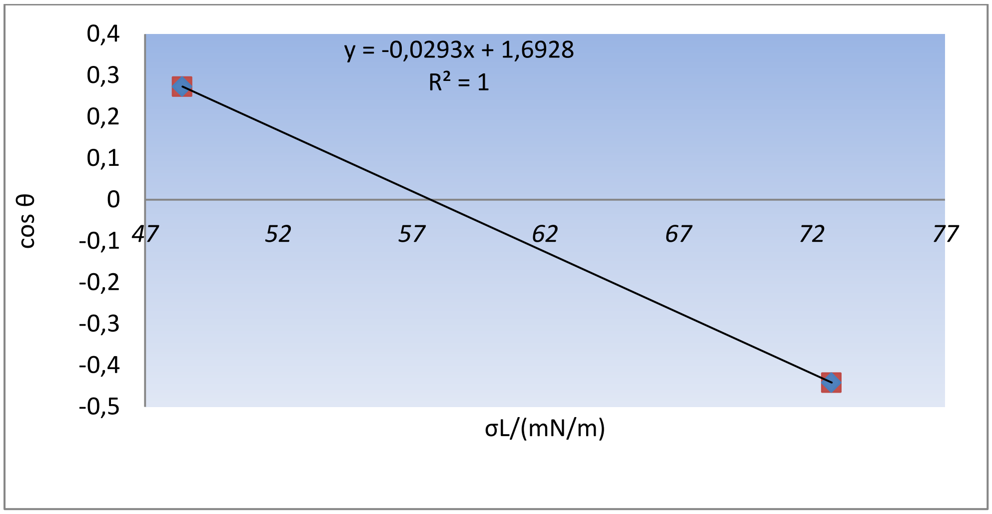


Figure 22: Zisman interpretation for HDPE

From this figure, we conclude that according to Zisman the surface energy is σ = 30.69 mN/m.

This was obtained by solving the linear regression for x with a value for y =1.  (see 2.8)

The second interpretation is Owens Wendt.

Table 8 represents the corresponding data while figure 23 represents the graphical interpretation.

| Liquid | σL/(mN/m) | √ ( σL (P) /σL (D)) | θ/° | σL ( cos θ +1)/2 √ σL (D)/ ( √mN/m) |
|---|---|---|---|---|
| Ethanol | 22.55 | 4.74 | 11.4 | 5.14 |
| Ehtylene glycol | 48.4 | 6.95 | 51.56 | 7.28 |
| Water | 72.75 | 8.52 | 73.37 | 9.10 |

Table 8: Owens interpretation for HDPE

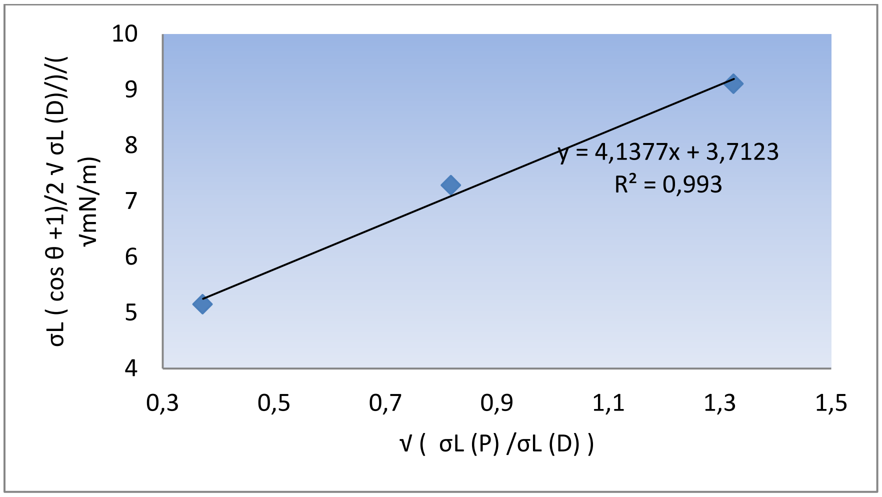


Figure 23: Owens interpretation for HDPE

The RGP function table for this graph is as follows

| | |
|---|---|
| 4.14 | 3.71 |
| 0.35 | 0.32 |
| 0.99 | 0.23 |
| 142.10 | 1.00 |
| 7.79 | 0.05 |

Table 9: RGP function for Owens HDPE

And from this, we note a surface energy of σ = 30.93 +- 5.25 mN/m is obtained. (see 2.7.2)

The third considered interpretation is Fowkes.

Table 10 represents the considered data and corresponding results:

| Liquid | σL(P)/ (mN/m) | θ/° | √σ s (P)/ ( √mN/m) | √σ s (D) / ( √mN/m) | σsD/ (mN/m) | σsP/ (mN/m) | σ s/ (mN/m) |
|---|---|---|---|---|---|---|---|
| Ethylene glycol | 19.4 | 51.56 | 3.58 | 4.53 | 12.85 | 20.50 | 33.35 |
| Water | 46.35 | 73.37 | | | | | |

Table 10: Fowkes interpretation for HDPE

From this we note a surface energy of σ = 33.35 mN/m

For detailed explanation on how this was done please check literature part 2.7.1

The last interpretation to be considered is the Von Oss but due to the fact that it is best suited for polar samples and HDPE is nonpolar no significant results were determined using this method.

### 4.1.2 Sessile drop results for low density polyethylene

#### 4.1.2.1 Contact angle measurement

Here again same as with HDPE two different samples were considered and handled through a five time determination. (See 3.2)

The results with water are represented here in tables 11 through 14.

Table 11: Results obtained with water

| Ө right/° | Ө left/° | Ө average/° |
|---:|---:|---:|
| 75 | 75 | 75 |
| 80.4 | 79.5 | 79.95 |
| 76.2 | 76.3 | 76.25 |
| 80.1 | 79.5 | 79.8 |
| 74.4 | 79.2 | 76.8 |
| Ө average/° | | 77.56 |
| Standard deviation/° | | 2.21 |
| Error/% | | 2.85 |

**Table 11: Water and LDPE**

Table 12: Results obtained with ethanol:

| Ө right/° | Ө left/° | Ө average/° |
|---:|---:|---:|
| 6.7 | 6.7 | 6.7 |
| 23.9 | 23.8 | 23.85 |
| 12 | 12 | 12 |
| 3.6 | 3.6 | 3.6 |
| 8.2 | 8.5 | 8.35 |

| | | |
|---|---|---|
| Ɵ average/° | | 10.9 |
| Standard deviation/° | | 7.84 |
| Error/% | | 71.99 |

**Table 12: Ethanol and LDPE**

Table 13: Results obtained with ethylene glycol

| Ɵ right/° | Ɵ left/° | Ɵ average/° |
|---|---|---|
| 65.3 | 69.2 | 67.25 |
| 73.3 | 75.2 | 74.25 |
| 63.5 | 58.4 | 60.95 |
| 46.9 | 46.9 | 46.9 |
| 65.5 | 66.8 | 66.15 |
| Ɵ average | | 63.1 |
| Standard deviation | | 10.22 |
| Error/% | | 16.19 |

**Table 13: Ethylene glycol and LDPE**

Table 14: Results obtained with decalin

| Ɵ right/° | Ɵ left/° | Ɵ average/° |
|---|---|---|
| 43 | 44.5 | 43.75 |
| 38 | 39.4 | 38.7 |
| 51 | 49.5 | 50.25 |
| 43.6 | 46.5 | 45.05 |
| 47.3 | 48.6 | 47.95 |
| Ɵ average | | 45.14 |
| Standard deviation | | 4.39 |
| Error/% | | 9.74 |

**Table 14: Decalin and LDPE**

#### 4.1.2.2 Evaluation of the surface energy

The aforementioned results were similarly evaluated according to the four interpretations:

First, according to Zisman, the results displayed in table 15 were obtained:

| liquid | σL/(mN/m) | θ/° | cos θ |
|---|---|---|---|
| Ethanol | 22.55 | 11.4 | 0.98 |
| Ethylene glycol | 48.4 | 73.32 | 0.28 |
| Water | 72.75 | 87.65 | 0.04 |

**Table 15: Zisman interpretation for LDPE**

Figure 24 represents the graphical representation of the Zisman interpretation:

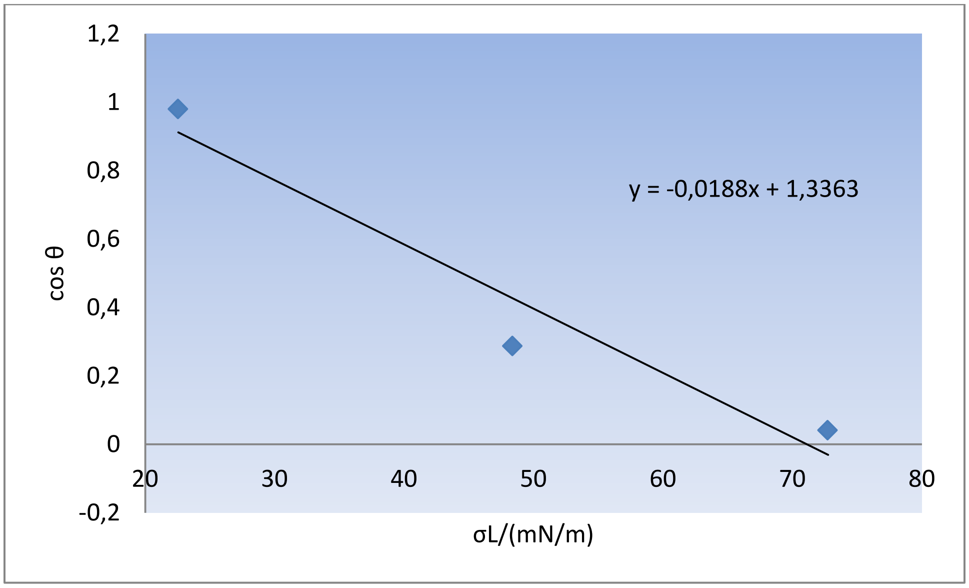


**Figure 24: Zisman interpretation for LDPE**

And the RGP function for this graph is represented below.

| | |
|---|---|
| -0.01878 | 1.335227 |
| 0.004804 | 0.250259 |
| 0.938568 | 0.170723 |
| 15.2781 | 1 |
| 0.4453 | 0.029146 |

**Table 16:RGP function for Zisman LDPE**

From which a surface energy of σ = $17.8^{+}_{-}$ 4.82 mN/m was obtained (see 2.8)

The second interpretation is Owen Wendt.

Table 17 represents the data that was used for this purpose:

| liquid | σL/ ( mN/m) | √ (  σL (P) /σL (D) ) | θ/° | σL ( cos θ +1)/2 √ σL (D)/ ( √mN/m) |
|---|---|---|---|---|
| Ethanol | 22.55 | 0.37 | 11.4 | 5.14 |
| Ethylene glycol | 48.4 | 0.81 | 73.3 | 5.78 |
| Water | 72.75 | 1.32 | 87.56 | 7.38 |

Table 17: Owens interpretation for LDPE

From which the following figure 25 was plotted

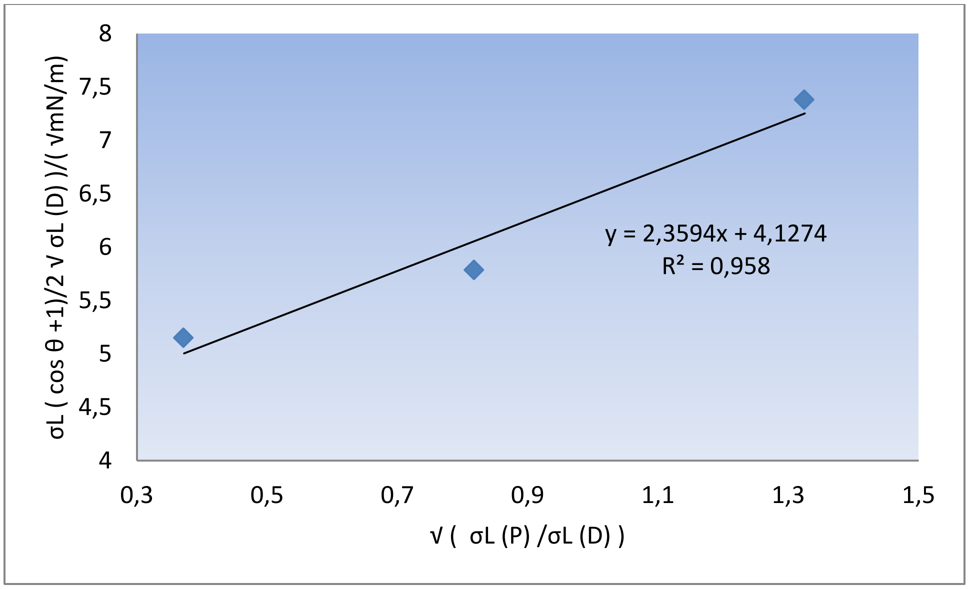


Figure 25: Owens interpretation for LDPE

And the corresponding RGP function table

| | |
|---|---|
| 2.359404 | 4.127354 |
| 0.494177 | 0.456764 |
| 0.957974 | 0.333288 |
| 22.795 | 1 |
| 2.532095 | 0.111081 |

Table 18:RGP function for Owens LDPE

From this we obtain a surface energy of $\sigma$ = 21.33 +- 6.49 mN/m (see 2.7.2).

The third interpretation is Fowkes. Its data and obtained results are represented in table 19:

| liquid | σL/( mN/m) | σL (D)/ ( mN/m) | √σ s(P)/ (√mN/) | √σ s(D)/ (√mN/m) | σ sP)/ (mN/m) | σ s (D) / (mN/m) | σ s/ ( mN/m) |
|---|---|---|---|---|---|---|---|
| Ethanol | 22.5 | 18.8 | 2.365 | 3.77 | 14.24 | 5.593 | 19.83 |
| Water | 72.75 | 26.4 | | | | | |

**Table 19:Fowkes interpretation for LDPE**

From this we note a surface energy of σ = 19.84 mN/m (see 2.7.1)

The last interpretation is Van Oss interpretation. (see 2.7.3)

Table 20 shows the used data as well as the obtained results:

| L | σL/ (mN/m) | θ/° | √σD)/ (√mN/m) | √σP+)/ (√mN/m) | √σP-)/ (√mN/m) | σD)/ (√mN/m) | σP+)/ (mN/m) | σP-)/ (mN/m) | σS)/ (mN/m) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 22.55 | 11.4 | 3.89 | 3.33 | 0.55 | 15.15 | 11.15 | 0.31 | 26.62 |
| 2 | 48.4 | 73.32 | | | | | | | |
| 3 | 72.75 | 87.65 | | | | | | | |

**Table 20: Van Oss interpretation for LDPE**

From this we note a surface energy of σ = 26.62 mN/m

L1 = Ethanol

L2 = Ethylene glycol

L3 = Water

## 4.1.3 Sessile drop results for polypropylene

### 4.1.3.1 Contact angle measurement

As described before for HDPE and LDPE the two samples of the PP were treated with all four different liquids and the results are shown in tables 21through 24. (See 3.2)

Table 21: Results obtained with water:

| ϴ right/° | ϴ left/° | ϴ average/° |
|---|---|---|

| | | |
|---|---|---|
| 85.3 | 85.1 | 85.2 |
| 86 | 85.3 | 85.65 |
| 70.5 | 70.6 | 70.55 |
| 80.2 | 81.1 | 80.65 |
| 88.8 | 88 | 88.4 |
| Θ average/$^{o}$ | | 82.09 |
| Standard deviation/$^{o}$ | | 7.02 |
| Error/% | | 8.55 |

Table 21: Water and PP

Table 22: Results obtained with ethanol

| Θ right/$^{o}$ | Θ left/$^{o}$ | Θ average/$^{o}$ |
|---|---|---|
| 3.8 | 3.8 | 3.8 |
| 16 | 16 | 16 |
| 3.4 | 3.4 | 3.4 |
| 13.3 | 13.3 | 13.3 |
| 9.3 | 9.3 | 9.3 |
| Θ average/$^{o}$ | | 9.16 |
| Standard deviation/$^{o}$ | | 5.60 |
| Error/% | | 61.23 |

Table 22: Ethanol and PP

Table 23: Results obtained with ethylene glycol

| Θ right/$^{o}$ | Θ left/$^{o}$ | Θ average/$^{o}$ |
|---|---|---|
| 73.1 | 72.6 | 72.85 |
| 72.6 | 72.3 | 72.45 |
| 72.1 | 72.7 | 72.4 |
| 69.8 | 70.6 | 70.2 |
| `59.8 | 64.9 | 62.35 |
| Θ average/$^{o}$ | | 70.05 |
| Standard deviation/$^{o}$ | | 4.42 |
| Error/% | | 6.32 |

**Table 23: Ethylene glycol and PP**

Table 24: Results obtained with decalin

| ϴ right/° | ϴ left/° | ϴ average/° |
|---|---|---|
| 63 | 64.7 | 63.85 |
| 58.2 | 62.5 | 60.35 |
| 65.8 | 68.3 | 67.05 |
| 69.8 | 70.6 | 70.2 |
| 59.8 | 64.9 | 62.35 |
| ϴ average/° | | 64.76 |
| Standard deviation/° | | 3.90 |
| Error/% | | 6.02 |

**Table 24: Decalin and PP**

### 4.1.3.2 Evaluation of the surface energy

The above results of section 4.2.3.1 of the angles obtained will be used in this section to determine the surface energy. The results were treated according to the four interpretations of the Sessile drop method (see 2.7)

First, according to the Zisman interpretation, table 26 displays the results and used data:

| Liquid | σL/(mN/m) | θ/° | cos θ |
|---|---|---|---|
| Ethanol | 22.55 | 19.16 | 0.95 |
| Ethylene glycol | 48.4 | 69.95 | 0.67 |
| Water | 72.75 | 79.95 | -0.15 |

**Table 25: Zisman interpretation for PP**

Its graphical representation is found in graph 26 below:

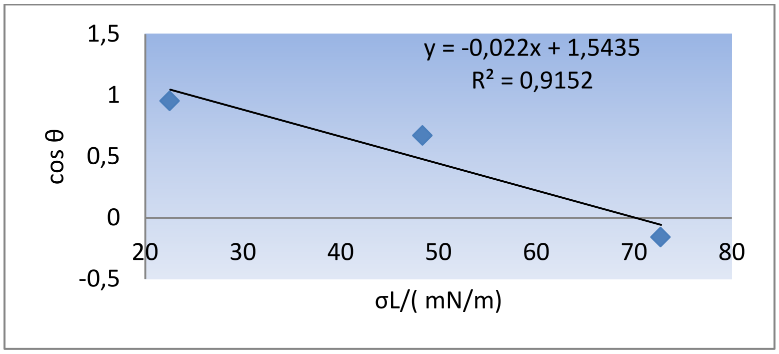


Figure 26: Zisman interpretation for PP

And the corresponding RGP function table

| | |
|---|---|
| -0.0220381 | 1.54345174 |
| 0.00670732 | 0.34945984 |
| 0.91522321 | 0.23812355 |
| 10.7956807 | 1 |
| 0.6121456 | 0.05670283 |

Table 26: RGP function for Zisman PP

This results in a value for the surface tension of σ = 24.7+- 7.87 mN/m. It is determined through extrapolation of the regression curve to the value 1 on the ordinate axis and the reading of the corresponding x value (refer to ch. 2.8 for an explanation of this concept)

Then, according to the Owens Wendt interpretation, table 27 displays the data used to graph the results.

| Liquid | σL/ (mN/m) | √ ( σL (P) /σL (D) ) | θ/° | σL ( cos θ +1)/2 √ σL (D)/( √mN/m) |
|---|---|---|---|---|
| Ethanol | 22.5 | 4.62 | 19.16 | 4.79 |
| Ethylene glycol | 48.4 | 6.95 | 69.95 | 6.03 |
| Water | 72.75 | 8.52 | 79.95 | 8.31 |

Table 27: Owens interpretation for PP

Its graphical representation is shown below in figure 27:

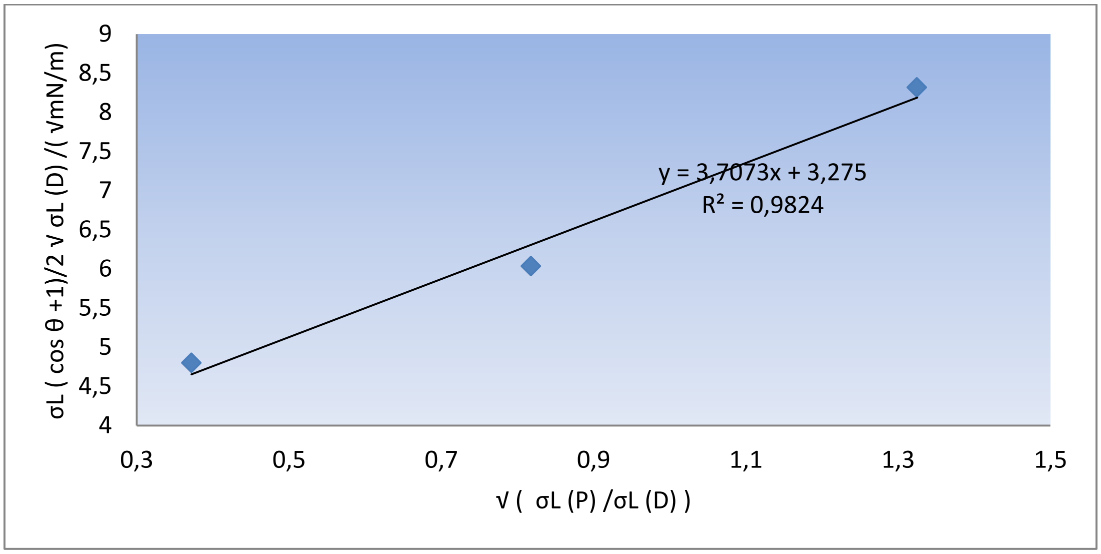


Figure 27: Owens inerpretation for PP

And the corresponding RGP function

| | |
|---|---|
| 3.454350884 | 3.56928885 |
| 0.654417611 | 0.60487274 |
| 0.965353187 | 0.44135967 |
| 27.86268363 | 1 |
| 5.427604984 | 0.19479836 |

Table 28:RGP function for Owens PP

From which we obtain through previously discussed methods (refer to 2.8) a value of $\sigma = 24.46$ +-8.83 mN/m for the surface energy.

The Fowkes interpretation yields table 29 (refer to 2.7.1)

| Liquid | σL/ (mN/m) | σL (D) / ( mN/m) | √ σs(P) / ( √mN/m) | √σ s (P) / ( √mN/m) | σ s (P) )/ ( mN/m) | σ s (D) )/ ( mN/m) | σ s)/ (mN/m) |
|---|---|---|---|---|---|---|---|
| Ethylene glycol | 48.4 | 29 | 4.40 | 2.35 | 20.22 | 5.55 | 25.77 |
| Water | 72.75 | 26.4 | | | | | |

Table 29: Fowkes interpretation for PP

From this we note a surface energy of $\sigma = 25.77$ mN/m

The last interpretation is the Van Oss which yields table 30 (see 2.7.3).

| L | σL/ (mN/m) | θ/° | √σD/ (√mN/m) | √σP+/ (√mN/m) | √σP-/ (√mN/m) | σD/ ( mN/m) | σP+/ ( mN/m) | σP-/ ( mN/m) | σS)/ ( mN/m) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 22.55 | 19.16 | 3.88 | 4.38 | 0.48 | 15.10 | 19.21 | 0.23 | 34.55 |
| 2 | 48.4 | 69.95 | | | | | | | |
| 3 | 72.75 | 79.95 | | | | | | | |

Table 30: Van Oss interpretation for PP

L1 = Ethanol

L2= Ethylene glycol

L3= Water

From this we note a surface energy of σ = 34.55 mN/m

## 4.2 Pendant drop

In this part, the Pendant drop method is used to determine the surface energy of the liquids used in section 4.1 with the Sessile drop method. The liquids are water, ethylene glycol and decalin.

The methodology used is described in the literature (refer to 2.9)

The Pendant drop method experiment is done for each of the four liquids and repeated five times.

The results are tabulated as follows with their averages.

### 4.2.1 Pendant drop method results for water

The results of the surface tensions noted for the Pendant drop test for water:

| | |
|---|---|
| σ Experiment 1/( mN/m) | 73.5 |
| σ Experiment 2/( mN/m) | 69.3 |
| σ Experiment 3/( mN/m) | 74.2 |
| σ Experiment 4/( mN/m) | 67.4 |
| σ Experiment 5/( mN/m) | 74.2 |
| σ Average /( mN/m) | 71.72 |
| Standard deviation /( mN/m) | 3.16 |
| Error/% | 4.40 |

Table 31: Pendant drop for water

### 4.2.2 Pendant drop method results for ethanol

The results of the surface tensions noted for the pendant drop test for ethanol:

| | |
|---|---|
| σ Experiment 1/( mN/m) | 21.6 |
| σ Experiment 2/( mN/m) | 18.3 |
| σ Experiment 3/( mN/m) | 23.4 |
| σ Experiment 4/( mN/m) | 17.6 |
| σ Experiment 5/( mN/m) | 25.8 |
| σ Average /( mN/m) | 21.34 |
| Standard deviation /( mN/m) | 3.44 |
| Error/% | 16.13 |

**Table 32: Pendant drop for ethanol**

### 4.2.3 Pendant drop method results for ethylene glycol

The results of the surface tensions noted for the pendant drop test for ethylene glycol:

| | |
|---|---|
| σ Experiment 1/( mN/m) | 43.4 |
| σ Experiment 2/( mN/m) | 52.7 |
| σ Experiment 3/( mN/m) | 46.2 |
| σ Experiment 4/( mN/m) | 40.3 |
| σ Experiment 5/( mN/m) | 47.8 |
| σ Average /( mN/m) | 46.08 |
| Standard deviation /(mN/m) | 4.67 |
| Error/% | 10.14 |

**Table 33: Pendant drop for ethylene glycol**

### 4.2.4 Pendant drop method results for decalin

The results for the surface tensions noted for the pendant drop test for decalin:

| | |
|---|---|
| σ Experiment 1/( mN/m) | 28.7 |
| σ Experiment 2/( mN/m) | 35.3 |
| σ Experiment 3/( mN/m) | 26.1 |
| σ Experiment 4/( mN/m) | 30.3 |
| σ Experiment 5/( mN/m) | 21.4 |
| σ Average /( mN/m) | 28.36 |
| Standard deviation/( mN/m) | 5.13 |
| Error/% | 18.11 |

**Table 34: Pendant drop for decalin**

# 5 Discussion

## 5.1 Comparison of the four interpretations of the Sessile drop method

The four interpretations used in this study are the Zisman, the Owens/Wendt, the Fowkes and the Van Oss interpretations.

For HDPE, the surface energies found for three of the four interpretations are very similar. They give results of around 31mN/m which passes well with the literature value of 28mN/m. This is true except for the Van Oss interpretation which yielded a large value of 57.36 mN/m for HDPE. This can be explained by the fact that the Van Oss interpretation is based on the polarity of the compound. HDPE, being non polar, gives a large value of surface tension because it lacks any polar component.

For LDPE, Zisman, Fowkes and Owens/Wendt interpretations yield results of similar values that average around 22.4 mN/m . However, LDPE is nonpolar, and as seen earlier with HDPE, it would give a slightly higher result of 26.62 mN/m compared to the others. The results for the four interpretations lie in the same area; around 22mN/m which conforms with the literature value.

The sessile drop method gives different values of surface tension for PP depending on the interpretation used. First, PP gives similar results of surface tension equal to 24.46 mN/m for Owens/Wendt interpretation and 25.77 mN/m for Fowkes interpretation. The Zisman interpretation gives a higher value of surface tension equal to 28.67 mN/m and the Van Oss interpretation gives an even higher value of 34.45 mN/m. The Owens/Wendt and the Fowkes interpretations naturally show similar results since they share the same basis of a two-component surface energy, a dispersive component and a polar one. The Zisman, on the other hand, shows a higher value and the Van Oss an even higher one. This is due to the difference in the structure of the PP itself. However, a comparison with the literature in this case could not be performed as the differences observed between the theoretical and experimental values are too large. This could be due to measurement errors or the structure of the polymer itself.

| Polymer | Zisman /(mN/m) | Owens /(mN/m) | Fowkes /(mN/m) | Van Oss /(mN/m) | Average /(mN/m) | Standard Deviation | Error/% |
|---|---|---|---|---|---|---|---|
| PP | 28.67 | 24.46 | 25.77 | 34.55 | 26.30 | 2.15 | 8.19 |
| HDPE | 30.69 | 30.93 | 30.31 |  | 30.64 | 0.31 | 1.02 |
| LDPE | 22.8 | 22.6 | 19.8 | 26.62 | 21.73 | 1.68 | 7.72 |

**Table 35: Comparison betwween the surface energies of several polymers using several interpretations**

The averages/standard deviations/errors considered exclude the Van Oss method as its values are unreliable

## 5.2 Comparison of surface energy of polymers

The average surface tension for HDPE obtained from the Owens/Wendt, Fowkes, and Zisman interpretations is equal to 30.64+-2.15 mN/m. This is higher than the corresponding value obtained for LDPE equal to 21.73+-1.68 mN/m. The reason for this difference can be found when considering the properties of both polymers. HDPE is formed by coordinative polymerization of ethylene and is therefore linear and non ramified. LDPE, on the other hand, is formed by radical polymerization of ethylene and is therefore branched and subject to ramification. This ramification reduces the surface energy substantially, yielding a value of 21.73+-1.68 mN/m for LDPE, which is lower than the corresponding value for HDPE.

The average surface tension for HDPE obtained from the Van Oss interpretation is equal to 57.36 mN/m while that for LDPE is 26.62 mN/mWhile both are too high to be considered for study, it is relevant to note that HDPE surface tension is much higher than LDPE using the Van Oss interpretation, for the same reasons discussed earlier which depend on the properties of both polymers.

## 5.3 Comparison of surface energy of liquids

Surface energy values of liquids: water, ethanol, ethylene glycol and decalin have been measured using the Pendant drop method. The average surface tension found for water is 71.72 mN/m which is close to the literature value of 72.75 mN/m, previously used in the Sessile drop method. The average for ethanol was found to be 21.34 mN/m. This value is also close to the 22.55 mN/m which is found in the literature. The average surface energy of ethylene glycol is

46.08 mN/m and it is also close to the literature value of 48.4 mN/m. The found average for decalin is 28.36mN/m. It falls within an acceptable range of the literature value of 30.6 mN/m.

As the obtained values show, the surface energy of water is higher than the rest of the liquids. The reason for this difference is the hydrogen bond formation in water which increases the surface energy.

## 5.4 Accuracy of the contact angle measurement

The results found from the contact angle measurement of the polymers: HDPE, LDPE and PP are all rather close. Although two averages were considered; once a left right average, and once the average of the 5 time determination, close results were obtained with a small error. Taking HDPE as an example, the error on the contact angle measurement is less than 10 % when measured with the liquids water, ethylene glycol and decalin.. An exception to this case is ethanol where huge experimental errors up to 68% were observed. The reason for this error is the volatility of the ethanol itself where it starts to evaporate as the picture is taken which leads to huge inaccuracies in the measurement. For the other polymers similar results were observed and the conclusions concur with those for HDPE. As such, the values for the angle measurements obtained for ethanol were subjected to corrective factors in order to achieve reasonable results in the Sessile Drop Method.

## 5.5 Accuracy of the Pendant drop method

Many parameters influence the results obtained from the Pendant Drop method. In the case of water, the results of surface tension are all similar to each other averaging around 71.72+-3.16 mN/m with a small error of 4%. Ethanol, on the other hand, gives slightly different results which average around 21.34+-3.44mN/m. An error of 16% is recorded but considering the volatility of ethanol, this error falls within an acceptable range. For ethylene glycol, an average for the surface tension of 40.08+-4.67 mN/m is obtained with an acceptable error of 10% .For decalin, an average of 28.36+-5.13 mN/m is observed and an error of 18% is noted.

## 6. Summary

The purposes previously mentioned in the introduction for this study are to be addressed consecutively. Therefore the comparison between the four interpretations and between the polymers bzw liquids is to follow here.

- The choice of the used interpretation.
  The four interpretations of the Sessile drop method yield rather similar results with the exception of the Van Oss method. For the polymers which this study follows the three component theory (Van Oss) proved that the partition of the surface energy into a positive a negative and a disperse part has given unreasonable results. The two component theories (Fowkes and Owens/Wendt) give more reasonable results that are slightly different than the literature values. Optimal results however were obtained from the one component theory ( Zisman). So this choice depends on the polymer itself. A highly polar polymer would require the use of a two or maybe three component interpretation.

- Practical aspects for the choice of interpretation
  The practical angle measurement for all four interpretations does not differ. This means that the experimental procedure is the same whichever interpretation is to follow. So the angles obtained and the way of averaging them will not affect the way the experminent will continue. The way this data is processed differs. The Zisman interpretation is the simplest to use since it depends on simple mathematics and graphical interpretation. The Fowkes interpretation uses a two equation and two unknowns system and is therefore somewhat more demanding. The Owens/Wendt interpretation uses a combination of simple mathematical approach and graphical interpretation to give its results. The most challenging of these interpretations is the Van Oss since it needs a three equation three unknowns system. Another aspect to the complexity of a used interpretation is the availability of literature values. The one component theory is here again the simplest since it only requires the set of the surface energies of the used liquids. The two component theories ( polar and disperse) need the components of the surface energies of the liquids for which the literature values differ. The three component theory (disperse

positive and negative) here again is the most difficult since it requires the three components for each used liquid.

- The effect of ramification. The fact that the surface tension of the non ramified HDPE is significantly higher than the ramified LDPE shows that ramification decreases the surface tension of a polymer.
- The choice of liquids in the Sessil drop method. It was obvious that the choice of ethanol proved to be problematic. The errors registered in the contact angle measurement with ethanol suggest that highly volatile liquids such as ethanol are to be preferably avoided since such liquids would evaporate so fast that no acceptable picture can be taken.
- In spite of over two hundred years since its formulation, the Young equation still constitutes a base of many methods for calculating the SFE of polymeric materials in the solid state. The calculations are made while utilising the results of the contact angle measurements for these materials with use of various measuring liquids. The Dupre equation and Berthelot hypothesis are also of a great importance. These three outstanding researchers have elaborated the theoretical fundamentals of all of the methods discussed in the present article (except the Zisman method). (13)
- In the individual methods for the calculation of the SFE of polymeric materials, in which the contact angle measurements are applied, various assumptions have been made. Thus, the SFE values of a given material, determined by various methods and with use of different measuring liquids, are not equal to one another. Hence the results obtained by the same method with use of the same measuring liquids may mutually be compared. (13)

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