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The Role of the Solid Substrate on the Spreading Kinetics of a Liquid Droplet

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UAE University

Graduate Studies Deanship

جامعة الإمارات العربية المتحدة

عمادة الدراسات العليا

The Role of the Solid Substrate on the Spreading Kinetics of a Liquid Droplet.

Thesis submitted in partial fulfillment of the requirements for degree of

M.Sc. in Materials Science and Engineering

By

Bashar Jalal Sasa

Materials Science and Engineering Program

United Arab Emirates University

2003 - 2004

Abstract

Classic hydrodynamic wetting theory leads to a linear relationship between spreading speed and the capillary force, being determined only by the surface tension of the liquid and its viscosity.

The theory appears in good agreement with results generated from experiments conducted on the spreading of Polydimethylsiloxanes (PDMS) on soda-lime glass substrate and fails to account for the behavior of other liquids. This thesis examines the role played by the solid substrate on the spreading kinetics of liquid droplets. The set of experiments whose results are presented below used different types of liquids with various properties of surface tension and viscosity tested on three different solid substrates (glass, polymethylmethacrylate (PMMA) and polystyrene (PS)).

The results are summed up in two themes; equilibrial spreading and kinetics. PDMS is found to exhibit complete spreading on all three different solids at similar rate for glass and PS, but at much lower rate on PMMA. Alkanes group, low surface energy liquids, was noted to exhibit equilibrial wetting that is proportional to the critical wetting energy of the solid substrate. Alcohols group, high surface energy liquids, was noted to exhibit equilibrial wetting that is inversely proportional to the wetting energy of the solids. The equilibrial spreading was found explicable on the basis of the axiom “like wets like”. Contributions of the solid substrate to the spreading kinetics are attributed to specific solid-liquid interactions, of dissipative nature, which manifest itself only at the interface. The term “interfacial viscosity” is coined to account for this phenomenon.

THESIS PROPOSAL

The Role Of The Solid Substrate on the Spreading Kinetics of Liquid Droplet.

Bashar Jalal Sasa

ABSTRACT:

Equilibrial wettability is defined in terms of the contact angle between the fluid interface and the solid surface in accordance with Young's equation. However, the rate at which this equilibrium is reached is the subject of active research. The Classic hydrodynamic wetting theory, however (which describes the spreading process of liquid over Solid, which is a linear relationship) ignores the role of surface in this process. It determines only the surface tension of the liquid and its viscosity. Present theory, in general, appears in good agreement with results generated from experiments conducted on the spreading of silicon oil on glass substrate but fails to account for the behavior of other liquids. That the phenomenon essentially entails solid-liquid and solid-vapor interactions suggests that their role should be explored.

The wetting of surfaces by liquid reveals these interactions at a macroscopic level. The measurements will use a small droplet of liquid (to minimize gravitational effect) with constant volume. It will be released over a solid surface from an automatic micro syringe, supported on micromanipulator. The droplet will be located in the field of view of a digital camera, which is connected to a high-speed video. Then by using an image analysis system, we find the rate of change in spreading area vs. time.

OBJECTIVES:

The solid–liquid (SL) and solid-vapor (SV) interfacial energy plays an important role in the spreading kinetics of a liquid on solid substrate. The Interfacial Tension is driving spontaneous spreading in opposition to the surface tension of the liquid. This study will measure the spreading rate for liquid's at different surface energy. and different chemical composition and facilitate the understanding of the role of surface in spreading kinetics.

It will also measure the wetting behavior of a surface. or in other words, the critical Surface energy by using Zissman Plot (the cosine of the wetting angle cos (θ) for a series of liquids is plotted against the surface tension γ of the liquid). Which is used to determine the surface tension of the solid by knowing the surface tension of several Liquids.

METHODOLOGY:

1. Prepare cleaned glass surface as a reference Surface (uncharged).
2. Use other transparent light surfaces (PMMA and Polystyrene).
3. Measure spreading kinetics over those surfaces and compare.
4. Conduct Zisman measurements "formalism widely used to describe the wetting of surfaces by molecular liquids "to assess" the "surface energy" of the modified glass surface.

COST OF THE PROJECT:

Most of the materials and consumables required for this project would be available from the Central Laboratory Unit (CLU) in U.A.E University

EXPECTED IMPACT OF THIS WORK:

The expected outcome of this work will be to devise a better understanding of the behavior of Solid – Liquid (SL) and solid-vapor Interfacial energies to describe the wetting phenomena, and develop a quantitative relationship based on the generated data. It will give a distinct picture for the role of the surface in the spreading process. This understanding of the surface gives the ability to determine whether spreading is complete or incomplete for with any liquids.

Student Name: Bashar Jalal Sasa

Signature:.......................... Date: ....

Supervisor : Name: Dr. Abdullatif M. Al teraifi

Signature:.......................... Date: ....

Approval:

Dean of Graduate Studies: Name & Signature:

-- Date: ....

UAE University

Graduate Studies Deanship

M.Sc. Program in Materials Science and Engineering

Study Plan

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Thesis Title:

The Role of the Solid Substrate on the Spreading Kinetics of a Liquid Droplet.

Course Code	Course Number	Title	Credit Hours	Registration Date
I. Core Course				
MTSE	601	Fundamental of Materials	3	Fall 2001
MTSE	602	Structure and Properties I	3	Fall 2001
MTSE	603	Structure and Properties II	3	Spring 2002
MTSE	604	Thermodynamics	2	Fall 2001
MTSE	605	Mechanical Behaviors	3	Spring 2002
MTSE	606	Materials Sci&Eng Seminar	1	Spring 2002

II. General Elective Courses

BIOL	610	Biomaterials	3	Fall 2002
MTSE	610	Defects In Solids	3	Spring 2003
BUSA	611	Materials Characterization	3	Spring 2003

III. Specialized Courses

MTSE	618	Independent Studies (Polymer)	3	Fall 2002
MTSE	617	Special Topics (Polymer)	3	Spring 2003

IV. Thesis:

MTSE	660	Thesis	3	Fall 2002
MTSE	660	Theses	3	Spring 2003
MTSE	660	Thesis	2	Fall 2003

Examining Committee

1. ***Dr. Abdullatif Alteraifi*** - Assistant Professor.

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2. ***Dr. Kamal M. S. Khalil*** - Assistant Professor

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Research Interests: Preparation of technologically advanced materials (ceramic, electronic, and catalytic) via novel preparation methods such as: vapor phase decomposition (VPD), and sol-gel processing.

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ES/F11

United Arab Emirates University
Graduate Studies
M.S.c. Program in Materials Science and Engineering

THESIS EXAMINATION REPORT

Student ID : 200150216
Student Name : Bashar jalal Sasa

Title of The Thesis : The role of the solid substrate on the spreading kinetics of liquid droplets.

The Thesis Examination as A Partial Fulfillment of M. Sc. Degree in Materilas Science and Engineering Was conducted on .... Based on Examining the Thesis and the Students Presentation and the Subsequent Discussion. The Committee Recommends:

☐ Thesis is Satisfactory as is.

☑ Thesis is Satisfactory After Minor Modifications.

☐ Thesis should be Re-Evaluated After Major Modifications.

☐ Thesis is Rejected.

Examining Committee Members:

Thesis Supervisor: Name: Abdullatif Alteraifi Signature........ Date: 15/12/2003

Thesis Co-Advisor: Name: .... Signature: .... Date:

Member : Name: Daniel Y. Kwok Signature: Daniel Kwok Date: 15/12/2003

Name: Dr. Kamal M-S. Khalil Signature: Kamal Khalil Date: 15/12/2003

Approval of Program Coordinator:

Dr. Yousef Haik .... Date : 15/12/03

APPROVAL:
Dean of Graduate Studies .... Date :........

DEDICATION

To my first valentines ……

Who mean everything to me ……

To two persons ……

Who stood beside me through my toils and thrills

To Dr. Jalal Zohdi Sasa

My Father … Friend … and Guide

And to Mis. Lamis Al-Hammame

My Mother

Without 'you' … none of this could have been possible

Your Loving Son…

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Introduction

1.1 Introduction

By definition, wetting is the ability of liquids to form a boundary surface with solids and it is an indication for spontaneous spreading of liquids over solid surfaces or the ability of solid to interact with or accept a liquid that is spread over it.

Wetting science which also belongs to "colloid / surface phenomena", *Shaw (1992)*, is very much an interdisciplinary subject and the attempts to model the spreading kinetics have been pursued through various scientific disciplines. In spite of the complex physical processes occurring when a liquid contacts a solid. The natural laws of physics, chemistry "or physicochemical" and fluid mechanical are used to describe the behavior of spreading, but often despite the large number of variables, which are involved.

Nowadays, wettability study is the tendency to work when possible in with a well–defined system (like using pure liquid and pure chemical composition of surface), which act as models because the use of materials of doubtful composition put considerable strain on the question of reproducibility and interpretations. Since it is important to understand at both "simple" descriptive and "complex" Theoretical levels. Wetting is a dispersion system which has two phases (at constant air):

1. Dispersed phase where phase forming the particles (liquid).
2. Dispersion medium where medium in which the particles are distributed (Solid and Gas).

These two phases should be reached to balance in own energies. So when a drop of (pure) liquid rests on the flat surface of a (pure) solid (and with or without influence of gravity) the shape is not a simple spherical lens but is determined by a balance between the air or vapor - liquid, air -solid, and liquid-solid interfacial energy densities (interfacial tensions).

But it doesn't inescapable that if the system elements reversed will have the same spreading. There's a difference between liquid interaction with solid and solid interaction with liquid. Consider the interaction between A, with a high surface free energy and B, with a low surface free energy. The figure 1.1 show example of liquid and solid in the first case low spreading is noticed as can be seen there the liquid has a high surface tension and the solid has low surface energy.

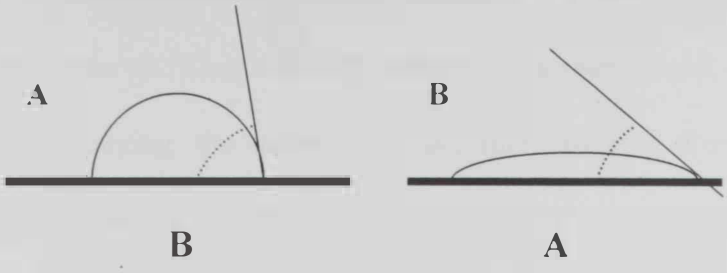


Fig 1.1 show the different behavior in spreading between A&B

For example, the interaction between epoxy, with a surface free energy of 46 mJ/m^2, and polyethylene (PE), with a surface free energy of about 22 mJ/m^2. The first diagram in figure 1.2 show, Liquid epoxy (high energy) tries to wet solid PE (low surface energy). The contact angle is high. However, when the situation is reversed and liquid PE contacts solid epoxy, the contact angle is much lower and the PE wets the epoxy.

Fig 1.2 different behavior in spreading between Epoxy & Polyethylene

Wettability has two levels to describe this phenomenon: macro and micro. At macroscopic levels, is defined when full and complete coverage of solid surface by the liquid. Like other multiphase processes the flux of spreading is measured on the macroscopic scale, i.e., the scale observed by the naked eye or accessible by optical interfacial effects in the spreading kinetics microscope.

In microscopic level (some called Molecular level or Thermodynamic) when a liquid is placed in contact with a solid surface resulting in a contact angle θ of less than 90°. Researchers, *Fan and Cagin (1995),* arrived to atomistic level contact angle measurements when studying the wetting of polymer surfaces from Molecular Dynamics for various crystalline polymer surfaces.

The Classic hydrodynamic wetting theory and several theories deal with the wettability leads to a linear relationship between spreading speed and the capillary force, being determined only by the surface tension of the liquid and it`s viscosity. So that the spreading is low, which are based on classical hydrodynamics, describe the spreading behavior of complete spreading fluids but it's not that effect in the case of other liquids. i.e. Wetting is more easily understood by considering that, wetting isn't present theory in general appears. In good agreement with results generated from experiments conducted on the spreading of silicon oil on most substrate and fails to account for the behavior of other liquids *Alteraifi et al (2002).*

The phenomenon of wetting or non-wetting of a solid by a liquid is characterized by a parameter known as contact angle. Experimental techniques for contact angle measurements have been developed extensively over the past decades. In view of Young's equation (section 1.2), in which the contact angle "θ" is the only measurable parameter, there are several experimental difficulties associated with measurements of the contact angle, which led to several values for contact angle for the same, liquid and solid.

Recently, many new methods and techniques developed for measuring the spreading process of liquids; but most of these techniques depend only on measuring the side image of the droplet and not on entire circumference of the drop (see Appendix : Commercial instrument and software)

Wetting is unquestionably a consequential phenomenon, the direct benefit of studying wettability is to understand how liquids interact with surfaces which lead to improved process control, which associates with several important technologies including composites, adhesives, coatings, printing, agricultural plant treatment and oil recovery.

1.2 Thermodynamic Approach

Surface energies are important in understanding the wettability process. But determining the value of these energies is not trivial. The relation between surface Interfacials is governed by Young's equation:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \qquad (1.1)$$

Where γ_{SV} is the surface free energy of the solid in contact with vapor, γ_{SL} is the surface free energy of the solid covered with liquid, γ_{LV} is the surface free energy of the liquid-vapor interface, and θ is the contact angle.

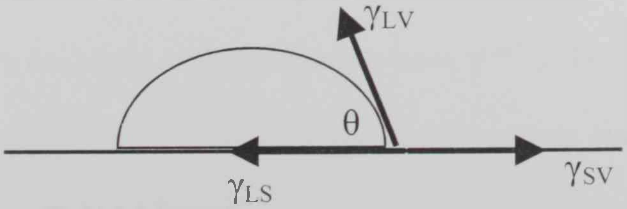


Fig 1.3 showing a liquid drop on a flat surface where γ_{SV} is the Solid – Vapor γ_{SL} solid-liquid, γ_{LV} liquid-vapor and θ is the contact angle

Measuring contact angles is, however, a possible matter by using various techniques. Where simply looking for the angle between the surface and a line that is tangent to a drop of liquid on the surface at the point where it intersects the surface, or calculates the contact angle from spherical cap approximation. Also measurement of γ_{LV} relatively an easy task, but Young's equation still leaves us with two unknowns. For this reason, it is very difficult to measure the surface free energy of a solid due to surface mobility.

In order to determine surface free energy, a recent section describes many thermodynamic approaches relate γ_{SV} and γ_{SL}. These approaches are rather empirical and it doesn't appear to be generally applicable. But we prefer to take the approaches, which involve dividing surface free energies into different components (like dispersive, acid-base, hydrogen bonding... etc.).

1.2.1 Dividing surface free energies:

These approaches (*KAYA et al (2002), Kwok and Neumann (1999), Rekveld (1997) and Walinder (2000)*) have two ways to dividing surface free energies, which are the same in the first, second and third approach but different in the last approach:

1. **First Approach: Surface Tension**

According to Fowkes (1962): The interaction forces a rising from each liquid and solid material consists of two components:

1. Lifshitz-van der Waals (LW) interaction term, γ^{LW}, comprising dispersion (γ^{d}), Non-polar, and induction force or London forces.
2. other term is Lewis acid-base (AB) interaction term, γ^{AB} or Polar interaction (γ^{p}) involving: 1- Electrostatic interaction (electron donor-acceptor interaction)

    2- Hydrogen bond Forces

$$\gamma = \gamma^{d} + \gamma^{p} \qquad (1.2)$$

Or $$\gamma = \gamma^{LW} + \gamma^{AB} \quad (1.3)$$

These interaction (γ^{AB}) are asymmetric consisting of an electron accepting component which can be quantified through surface tension measurements with polar liquids such as water or formamide to γ^{+} and an electron donating component γ^{-} and can be either attractive or repulsive *Grasso et al (2002).*

$$\gamma^{AB} = 2\sqrt{(\gamma^{+}\gamma^{-}} \quad (1.4)$$

2. Second Approach: Interfacial Tension

According to Dupr`e (1869) the change in free energy when creating a unit between material 1 "Liquid "and 2 "Solid "in a medium 3 "Air"

$$\Delta G_{123} = \gamma_{12} - \gamma_{13} - \gamma_{23} \quad (1.5)$$

But when material 1 split in medium 3 this becomes:

$$\Delta G_{123} = 0 - \gamma_{13} - \gamma_{23} = 2\gamma_{23} \quad (1.6)$$

This allows direct calculation of the total interaction energy between these phases or materials.

3. Third Approach: Solid / Liquid system

According to Van Oss (1993) and *Good (1997)* A combining rule is necessary to calculate γ_{SL} from the individual surface tension γ_L and γ_S of the respective materials. They developed a more advanced approach based on the Lifshitz theory *Kwok* and *Neumann (1999)*. They suggested that a solid surface consists of two terms explanted in step 1. The surface free energy is the sum of a non-polar component (γ^{LW}) and an acid-base component (γ^{AB}) as shown in the following equations. For non-polar interactions the geometric mean can be used

$$\gamma_{SL}^{LW} = \gamma_{S}^{LW} + \gamma_{L}^{LW} - 2\sqrt{\gamma_S \gamma_L} \quad (1.7)$$

$$\gamma_{SL}^{LW} = \sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}} \tag{1.8}$$

For polar –interaction where

$$\gamma_{SL}^{AB} = \gamma_S^{AB} + \gamma_L^{AB} - 2\sqrt{\gamma_S^{+}\gamma_L^{-}} - 2\sqrt{\gamma_S^{+}\gamma_L^{-}} \tag{1.9}$$

$$\gamma_{SL}^{AB} = 2(\sqrt{\gamma_S^{+}}\sqrt{\gamma_L^{+}})(\sqrt{\gamma_S^{-}}\sqrt{\gamma_L^{-}}) \tag{1.10}$$

And,

$$\gamma_{SL} = \gamma_{SL}^{LW} + \gamma_{SL}^{AB} \tag{1.11}$$

$$\gamma_{SL} = \gamma_S^{LW} + \gamma_L^{LW} - 2\sqrt{\gamma_S\gamma_L} + \gamma_S^{AB} + \gamma_L^{AB} - 2\sqrt{\gamma_S^{+}\gamma_L^{-}} - 2\sqrt{\gamma_S^{-}\gamma_L^{+}} \tag{1.12}$$

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S\gamma_L} - 2\sqrt{\gamma_S^{+}\gamma_L^{-}} - 2\sqrt{\gamma_S^{-}\gamma_L^{+}} \tag{1.13}$$

4. **Fourth Approach: Using surface Tension component for contact angle measurement**

According to Young-Dupr`e equation 1869:

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL} \tag{1.14}$$

$$\gamma_L\cos\theta + \gamma_L = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^{-}\gamma_L^{+}} + 2\sqrt{\gamma_S^{+}\gamma_L^{-}} \tag{1.15}$$

Or Owens – Wendt – Kaelble approach

$$\gamma = \gamma^d + \gamma^p \tag{1.2}$$

Where γ^P Hydrogen and dipole-dipole

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^d\gamma_L^d} - 2\sqrt{\gamma_S^p\gamma_L^p} \tag{1.16}$$

1.2.2 Empirical Approach:

Recent reviews of the literature on spreading dynamics by *Marmur (1983)*, de *Gennes (1985)* and several others contributors to a more recent book edited by *Berg (1993)* attest to the continued interest in the subject.

Several theories deal with the spreading kinetics of liquids on solid substrate, most of which relate the rate of spreading to the surface tension, and the viscosity of the liquid only. De Genne's model (1985), Tanner's model (1979) and that proposed by *Seaver and Berg (1993)* expressed the rate of spreading in terms of surface tension and viscosity.

In a latter development *Tanner (1979)* derived the spreading equation from Navier-Stokes equations for viscous flow in two dimensions. The author expressed pressure gradient by surface tension curvature, hence, he introduced the surface profile κ which relates to the droplet edge velocity as:

Interfacial Effects in the Spreading Kinetics

$$U = \frac{dR}{dt} = -\frac{\sigma\kappa}{3\mu} \qquad (1.\ 17)$$

Where U is the film advancing velocity with constant profile shape, κ is a profile constant; μ and σ are the liquid viscosity and surface tension, respectively. Here, again, the "surface profile" κ is a non-dimensional parameter that has to be determined empirically. Furthermore, Tanner suggested the following relationships:

$$\tau = \frac{1}{10}\kappa^{10} \qquad \text{For } \kappa < 0.9 \qquad (1.18)$$

And $$1 - k \cong \exp(-6\tau) \qquad \text{For } 0.9 < \kappa < 1.0 \qquad (1.19)$$

Where $k = \frac{R}{R_f}$ and $\tau = \frac{\kappa\sigma t}{\mu R_f}$, R_f is the equilibrium contact radius.

Subsequently, *Seaver and Berg (1994)* assumed that the fluid dynamics of the spreading of spherical cap droplet may be approximated by a cylindrical disk. Then, they examined the disk spreading in quasi-steady laminar Couette flow driven by "effective radial surface tension gradient "at the upper surface. Accordingly, the rate equation has been derived as:

$$\frac{dR}{dt} = \frac{4\sigma V_d^3}{\pi^3 \mu R^9} \qquad (1.20)$$

For complete spreading. For incomplete spreading the authors derived the rate equation as:

$$\frac{dR}{dt} = \frac{4\sigma V_d^3}{\pi^3 \mu R^9} - \frac{\sigma \beta V_d}{2\pi\mu R^3} \qquad (1.21)$$

where R is the radius of the spreading droplet, V_d is the cylindrical disk volume (V_d=πhdR2). β= 1- cos θ∞ and, μ is liquid viscosity, and σ is liquid surface tension.

Interfacial Effects in the Spreading Kinetics apparently due to the difficulty of applying these models. *Lelah and Marmur (1981)* suggested that the kinetics of spreading could be described by a simple power law of the following

$$A\,(t) = C_1 t^n \qquad (1.22)$$

where A is the contact area, measured at time t, and C_1 and n are empirical coefficients. Subsequently the author applied this equation to the spreading data reported by several investigators for a relatively large number of fluids. It was noted that the value of n in most of the cases falls within 0.20 to 0.29.

Further analysis of data where the droplet volume (V) was independently varied revealed that c1 was found proportional to V^m. The power m was found to range from 0.60 to 0.72. This observation prompted Marmur (1983) to suggest that c_1 scales with $V^{2/3}$. Thus, the rate of spreading normalized with respect to $V^{2/3}$ was expressed as:

$$\frac{A}{V^{2/3}} = c_2 t^n \qquad (1.23)$$

Plotting the same data, in terms of equation (1.23) it was noted that the variance of the coefficient c_2 was reduced to about two orders of magnitude. Nevertheless, equation (1.21) was presented as a convenient form for correlating and comparing experimental data.

An early attempt to derive the rate of spreading was advanced by Ogarev and coworkers, *Ogarev (1974)*. The Ogarev model approximated the shape of the spreading droplet as a cone, whose geometric parameters were used to derive the spreading equation through a force balance implementation. For a given moment, the authors balanced the forces due to change in the free surface energy of the (droplet-on-solid substrate) system and the viscous resistance. They concluded the following equation for spreading kinetics:

$$R(t)=\left(\frac{24\,Vf}{\pi\,\mu}\right)^{1/4} t^{1/4} \qquad (1.24)$$

where R is the radius of the contact area, V is the droplet volume, and μ is the viscosity. The function f relates to the surface energy of the spreading liquid as defined by Young's equation (1.1).

Recognizing earlier inference by *Hoffman (1975)* and others that the spreading process is generally driven by surface forces and is retarded by viscous forces, *de Gennes (1985)* introduced what may be considered as a theoretical rational for the empirical power law of *Marmur (1983)*. The argument suggested by de Gennes is based on the earlier finding of *Hoffman (1975)* that the "apparent" contact angle can be correlated as a function of the capillary number ω plus a shift factor when interfacial and viscous forces are the dominant forces controlling the system. The capillary number ω defined as

$$\omega=\frac{U\mu}{3\sigma} \qquad (1.25)$$

where U is the velocity of the contact line, μ is the viscosity of the spreading fluid and γ is its surface tension. In this regard it is worth noting that a related expression was suggested earlier by *Schonhorn et al (1966)* to correlate the kinetics of spreading of surfaces by polymer melts *de Gennes (1985)* argument further assumes that Hoffman's data, in the low velocity limit, may be presented as

$$\omega = \text{constant} * \theta^{m} \qquad (1.26)$$

It is further suggested that for relatively small droplets, where gravitational effects are negligible, the macroscopic shape of the spreading droplet may be approximated by spherical cap geometry, *de Gennes (1985)*. This approximation has been used to relate the contact angle to the radius and the volume of the spreading droplet, i.e. the droplet height $h = ½ R\theta$, and it is volume $V = ½ \pi h R^{2}$. Accordingly *de Gennes (1985)* derived "the spreading law" as:

$$R^{3m+1} = \frac{\sigma}{\mu} t V^{m} \qquad (1.\ 27)$$

Furthermore, the author ascertained that m=3 is "indeed expected theoretically for all cases of dry spreading" which doesn't satisfy all liquids *Alterifi et al (2002)* and *de Geanes (1985)*.

1.2.3 Complete wetting or Spreading wetting

The spontaneous process of wetting can also be derived from the differential between the work of adhesion and cohesion by substitution of the Dupré equation, as follow:

$$W_A - W_C = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} - 2\gamma_{LV} = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL}) \qquad (1.28)$$

Where W_A is the work of adhesion and W_C is the work of cohesion, within the liquid layer is shown below:

$$W_C = 2\gamma_L \qquad (1.29)$$

Implies that spontaneous spreading will occur if the work required to separate the liquid-solid interface is greater than liquid separation itself. The Dupré equation can therefore be further derived by introducing the initial spreading coefficient S defined by Harkins, as follows.

$$S = -\frac{\Delta G_{Spreading}}{A} = W_A - W_C = \gamma_{SV} - (\gamma_{LV} + \gamma_{SL}) \qquad (1.30)$$

Where $\Delta G_{Spreading}$ is the free energy increase due to spreading, the liquid spreads spontaneously over the solid surface when S is positive or zero. When S is negative, the liquid remains as a drop having a definite angle of contact, θ, with the solid surface.

Spreading is the movement of liquid across a solid surface. Contact angle is a measure of wettability. Spreading increases as the contact angle decreases until wetting is complete. *Meathrel et al (2003) and Duncan (1998)* hence, spreading will occur spontaneously when S is greater than zero, which also indicates that the surface tension of the solid must be greater than that of the liquid, as shown in the above equation. From this initial spreading coefficient equation, it follows that wettability can be increased either by increasing the surface energy of the solid or decreasing the surface tension of the liquid.

1.2.4 Incomplete wetting or adhesional wetting

From the spreading coefficient (equation 1.30), When S is negative, the liquid remains as a drop having a definite contact angle (θ) *Stokes and Evans (1997).*

The thermodynamic definition of incomplete wetting is rooted in the concept of surface energy or surface tension. Surface tension results from an imbalance of molecular forces in a liquid. At the surface of the liquid, the liquid molecules are attracted to each other and exert a net force pulling them together.

High values of the surface tension means the molecules tend to interact strongly. Lower values mean the molecules do not interact as strongly. Water has a very high value of surface tension because it has a high degree of hydrogen bonding.

Organic molecules with polar groups such as iodide and hydroxyl have a slightly lower surface energy than water. Pure hydrocarbons are even lower, while fluorinated compounds are very low because the fluorine atom won't share electrons very well so only dispersion interactions occur.

1.2.5 Equilibriums of multiphase Fluid

In Liquid –Liquid system, when three or more phases are in thermodynamic equilibrium and in contact with a solid surface, the contact angles between the phases are not all independent. In three-phase systems, although three contact angles can be defined, only two of them are independent (which following the phase rule F=C-P+2). In four-phase systems, six contact angles can be defined, but only three are independent *Blunt (2001)*.

In a "two-interface" system in which a liquid phase is both above and below a vapor phase and the vapor phase forms a solid–vapor interphase in one region, the pressure profile in the liquid phases is the same as it would have been if the vapor phase were not there; thus in a gravitational field, the pressure is smaller in the liquid phase above the vapor phase than it is in the liquid phase below the vapor phase. This results in the contact angle at the upper three-phase line necessarily being smaller than that at the lower three-phase line. This difference in contact angles is conventionally referred to as contact angle hysteresis; the contact angle difference predicted to exist in the presence of gravity does not violate the Young equation, but the Young equation does impose a restriction on the equilibrium adsorption isotherms at the solid–vapor and solid–liquid interfaces *Ward and Sasges (1998) and Sasges and Ward (1998)*.

1.2.6 Thermal effect in solid-liquid interface

The measured temperature distribution normal to interfaces showed a distinctive jump near the solid-liquid interface *Maruyama and Kimura (1999)*, which could be regarded as the thermal resistance over the interface. Owing to molecular dynamics, which cannot be, neglected even when a system size is very small. The temperature jump was considered to arise from the difference of vibrational frequency range of solid and liquid molecules or from the layered structure of liquid molecules just on a solid surface.

The small thermal resistance (*Maruyama et al. (1998) and Matsumoto et al (1995)*) is due to molecular level ordering is noticeable even for the perfect solid-solid contact. Likewise, the very small liquid-solid contact thermal resistance may be significant at some small system size because the thermal resistance by heat conduction monotonically decreases with the reduction of the system size. A considerable temperature jump over a liquid and solid interface was actually suggested in our molecular dynamics simulation. Evaporation and condensation through the droplet were simulated by preparing two solid surfaces with temperature differences on the top and bottom of the calculation domain.

A considerable temperature jump over a liquid and solid interface was actually suggested in molecular dynamics simulation *Maruyama et al (1998)*. The temperature jump was considered to arise from the difference of vibrational frequency range of solid and liquid molecules or from the layered structure of liquid molecules just on a solid surface.

1.2.7 Capillary Force

The capillary phenomena had been studied in the early period of the 19th century *Yang et al (2002).* The capillary phenomena can be defined quantitatively in terms of surface tension. Surface tension makes the surface of a liquid act as an elastic cover, which minimizes the surface area of liquid so as to minimize the energy of the fluidic system minimal. Although liquid/solid contact angle method has been established for decades to measure the surface energy of a flat surface, there is no existing method to measure the surface properties inside a capillary tube especially in the micro domain.

It is commonly theorized that capillary forces balanced by viscous resistance are the sole forces acting in the spreading process. Thus continuum based kinetic equations relate the rate of spreading to the surface tension and the viscosity; both are properties of the liquid.

Nevertheless, a liquid droplet in equilibrium on a solid substrate is a system governed by the three energies defined by Young-Dupree equation. As the contact line moves towards equilibrium, viscous dissipation processes control its rate.

The droplet is a curved surface reservoir whose pressure is determined by the surface tension γ and the radius of curvature as show in fig. 1.4

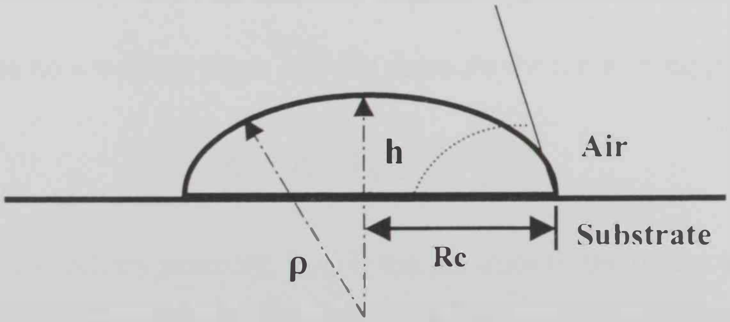


Fig 1.4 show the Young-Laplace equation element

In accordance with Young-Laplace equation, i.e.

$$\Delta p = \frac{2\gamma}{\rho} \qquad (1.31)$$

Where Δp is the pressure across the surface. γ is the surface tension of the liquid; ρ is radius of curvature. The radius of curvature as seen in the fig 1.4 is related to the contact radius *Rc* as

$$\rho = \frac{R_c}{\sin\theta} \qquad (1.32)$$

so we can write as direct relation between pressure at the surface and contact radius *Rc which* can be measured experimentally:

$$\Delta p = \frac{2\gamma\sin\theta}{R_c} \qquad (1.33)$$

According to *Alteraifi and Moet (2003)*, It is imperative to note that as the contact area increases, the radius of curvature increases giving rise to a corresponding lessening of the of Laplace pressure, which amounts to a continual decrease in the driving force. Consequently the spreading must cease to grow when the driving component can no longer overcome its resistance. The latter is obviously dictated by the specific nature of the liquid/solid pair.

Laplace's equation describes the pressure inside a drop because its surface is curved, and the Young-Laplace equation describes how a drop's curvature will change from gravity. In dynamic systems, however, the "dynamic" contact angle is not well defined *Ramé (2000).* We can describe capillary pressure as the difference in the pressure for the non-wetting phase and the pressure for the wetting phase.

$$\mathrm{P_C} = \mathrm{P_{NW}}\ \mathrm{P_W} = \frac{2\gamma\cos\theta}{\mathrm{r}} \qquad (1.34)$$

Where P_C is the capillary pressure, P_{NW} is the pressure of the non-wetting phase, P_W is the pressure of the wetting phase, γ is the interfacial tension, θ is the contact angle, and r is the radius of the curvature. The difference in pressure is related to the interfacial tension and as interfacial tension increases, the capillary pressure increases.

1.3 Zisman Plots and Critical Surface Energy

This plot was developed by Zisman at the Naval Research Laboratory, *Zisman (1964)*. The plot is made by plotting the cosine of the contact angle versus the surface free energy of various wetting liquids on a given solid. The resulting plot can be interrupted as a is a straight line. Thus, there exists some unique value for each polymeric solid where the cosine of the contact angle is unity.

This value is termed the critical surface free energy. The term "critical" is used because any liquid on the Zisman plot whose surface tension is greater than the "critical surface tension" makes a finite contact angle with the substrate, i.e. A liquid with surface free energy below the critical value will wet and spread over the solid surface, whereas a liquid with surface energy above the critical value might wet but won't spread.

In figure 1.5, the Zisman Plot dividing to three regions. "Non-wetting" region, where the angle between liquid and solid is grater than 90^{o}. And "Wetting" region, where the angle between liquid and solid is from 1^{o} than 90^{o}. And "Spreading" region where the angle between liquid and solid is less than 1^{o}. The line separated between "Wetting" region and "Spreading" region called "critical surface energy" of solid.

A liquid with surface energy above the critical value may leave micro voids at the fiber-matrix interface because complete, intimate molecular wetting may not occur. This example plot is for a variety of liquids wetting solid Teflon (see Fig 1.6).

Critical surface tension values are useful empirical values that characterize relative degrees of surface energy of polymer substrates *Shaw (1992)* and *Frohn (2002)*. Using the concept of critical surface energy, it is possible to characterize a wide variety of polymers and correlate the critical surface energy with polymer structure. Fluorinated materials have low values of critical surface energy.

Hydrogenated materials, such as polyethylene and polypropylene, have slightly higher values. For other sub-stituents (Cl, O, N) the critical surface free energy is a little higher still. From the critical surface energy data just given, fluorinated and hydrogenated materials will be among the least wettable.

Contact angles were measured *Zisman (1964) and Shaw (1992)* at 20°C, under an atmosphere saturated with the probe liquid. Alkanes and other hydrocarbons were percolated through neutral grade 1 alumina immediately prior to measurement of contact angles. The alcohols were high-purity solvents and were not purified further.

The following liquids were used (the surface tension is in parentheses (mN/m)): 2, 3-dimethylpentane (20.1), n-heptane (20.2), 2, 2, 4-trimethyl (20.6), n-octane (21.7), n-nonane (22.9). n-undecane (24.8), cyclohexane (25.4), n-dodecane (25.4), n-tetradecane (26.6), n-hexadecane (27.6), cyclooctane (29.9), bicyclohexyl (32.8), 2-propanol (21.6), ethanol (22.5), 1-propanol (23.8), l-butanol (25.5), 1-pentanol (25.9), 1-octanol (27.6), cyclohexanol (33.5).

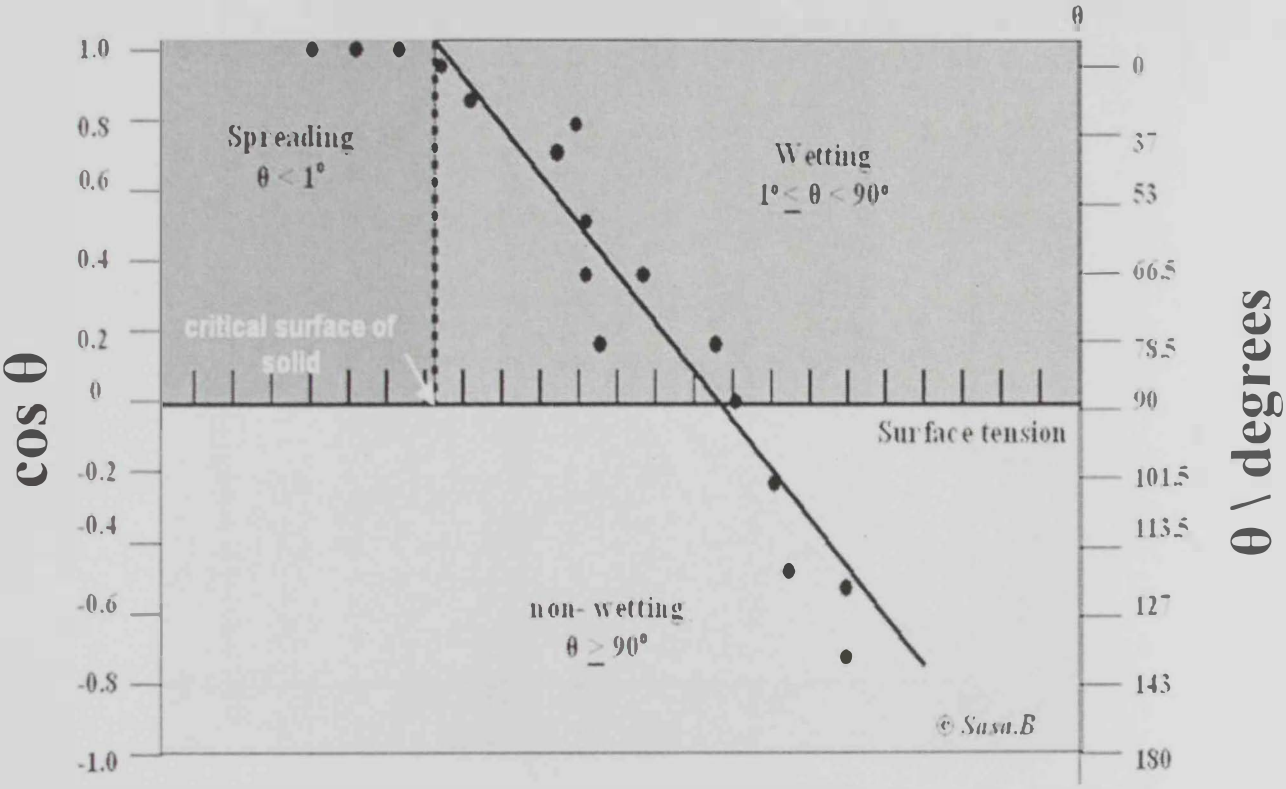


Fig 1.5 Illustrative sketching shows Zisman plots regions

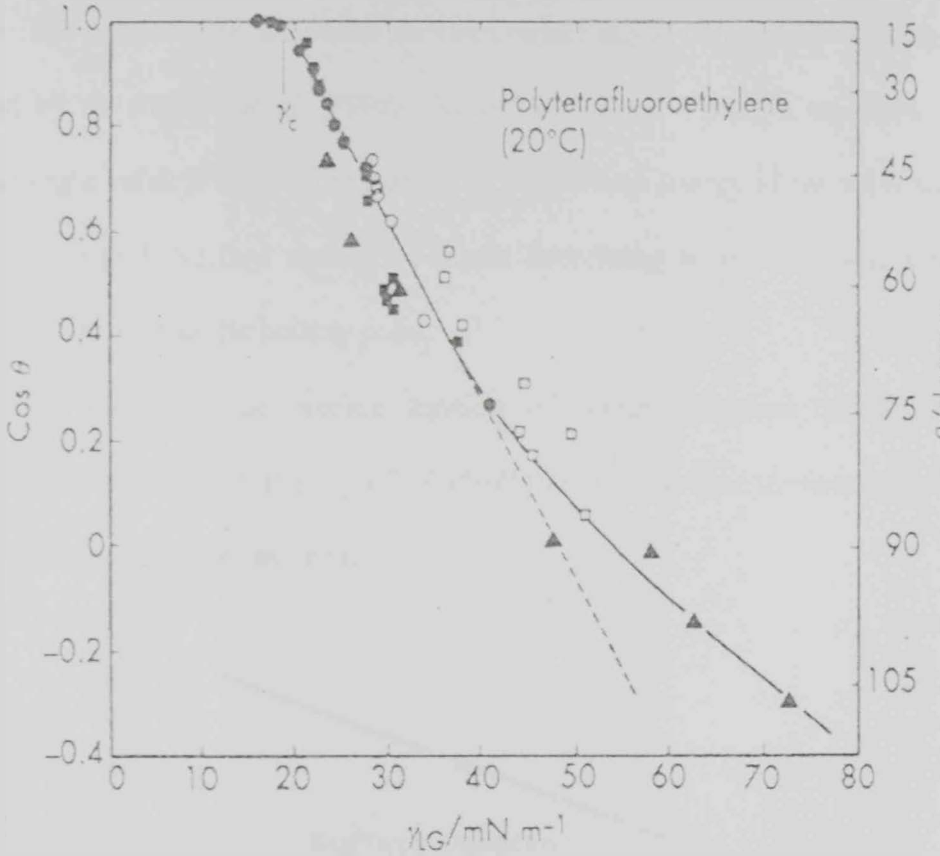


Fig 1.6 Zisnam plots of contact angle of various homologous series on Teflon (Polytetrafluoroethlene) at 20°C (Ref *Shaw (1992)*) •, n-alkanes; ○, other hydrocarbons; ■, esters and ethers; □, halocarbons and halohydrocarbons; ▲, different liquids.

1.4 Parameters that effects spreading.

The spontaneous spreading of liquid is a very sensitive process and is effected by many parameters like: Temperature. Evaporation rate. Roughness of the surface. Chemical Effect. Heterogeneity. Gravity. Volume of liquid and Humidity.

1.4.1 Effect of Temperature

The temperature influence on the contact angle of partially wetting drops is studied by *de Ruijter et al (1998)*. According to the Young's equation (1.1). the contact angle value is depending mainly on the surface energy of the solid and surface tension of liquid. Surface tension of liquid decreasing with increasing temperature. which goes to zero at the boiling point.

For example. the surface tension of water decreases significantly with temperature as shown in the fig 1.7. *Lide(1997)*. The surface tension arises from the polar nature of the water molecule.

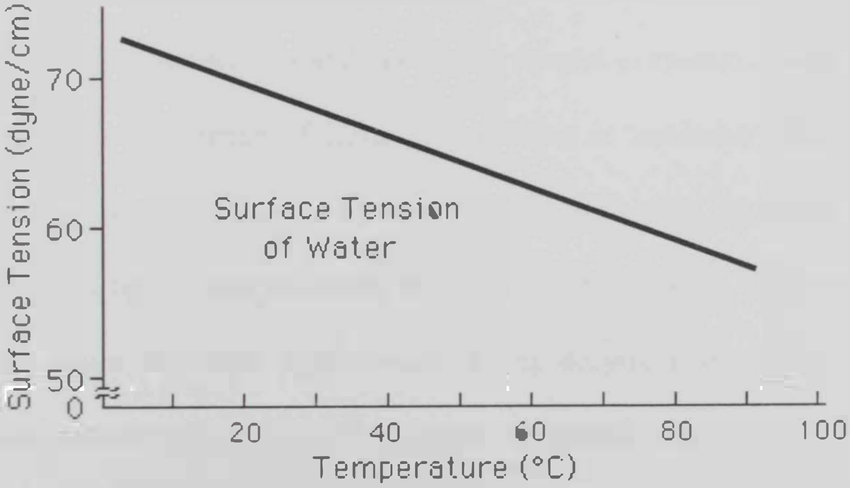


Fig 1.7 Show the change of surface tension of water with increases temperature

For a solid, surface energy stays relatively constant with temperature. This effect increases weakly with temperature increases. Thus. the value of surface tension at the melting point is the value for the solid as well.

The same temperature effects occur for polymeric liquids like (Silicon oil or Polydimethlsiloxane PDMS) with a few exceptions. Since polymers don't boil, the surface tension doesn't go to zero. The surface energy does decrease with temperature, but not as dramatically as it does for small molecule liquids. The solid surface energy is also approximately equal to that of the melt. This makes sense, since freezing "locks" the surface conformation at whatever orientation it had just before freezing.

1.4.2 Evaporation rate of liquid:

One would expect that the evaporation process of liquid droplets was described many years ago. Most studies on liquid drop spreading have focused on the nonvolatile liquid sessile drops for their simplicity both in the experimental measurements and the theoretical analysis. The contact angle affected by thermal radiation incident upon a droplet *Chandra et al (1996) and van den Doel el at (1999).*

Inferred radiation is absorbed at the surface of an evaporation droplet *Chandra et al (1996)*, heating it and reducing surface tension. This causes droplet to spread out, increasing liquid –solid contact area and decreasing droplet evaporation time.

However, the occurrence of liquid evaporation is inevitable, the effects of evaporation on the spreading and the contact angle become very important for more complete understanding of these processes *Zhang and Chao (2001), Chao and Zhang (2001).* Contact angle decreased continuously during droplet evaporation, while the diameter of the wetted region under the droplet remained constant *Chandra et al (1996).*

On the contrary, just recently some underlying principles of the dynamic process of evaporation have been published *van den Doel el at (1999)*. It seems that during the evaporation of a liquid droplet, the liquid at the edge of the droplet is "pinned" to the underlying surface. This pinning prevents the droplet from shrinking.

This implies that the footprint of the droplet remains constant. The evaporated liquid at the edge is replenished by liquid from the bulk of the droplet.

This means that there is a flow of liquid moving towards the edge of the droplet. If the liquid droplet contains particles, like in a droplet of coffee, these particles will be transported outwards by the flow. Finally, when all the liquid has evaporated, the (coffee) particles will form a ring of stain *van den Doel el at (1999).*

We take this effect and we study the evaporation rate. So we will go back to discussion of this effect in Chapter 3 Results at pint 3.1 Evaporation from two phases: Mass balance. Confirm by allowing droplet to spread.

1.4.3 **Effect of Roughness:**

The effect of surface roughness on wettability was studied more than half a century ago. Recently, more interest has been stimulated by experimental results showing that wettability can be tuned by surface geometry. *He and Lee (2003); Patankar and Chen (2002); Kwok and Neumann (1999) and Schlangen (1996).*

Surface roughness has the effect of making the spreading further the wetting of solid. The liquid penetrates and fills up most of the hollows and pores in the solid. So the surface is part solid and part liquid *Duncan (1998)* and *Bico et al (2002).*

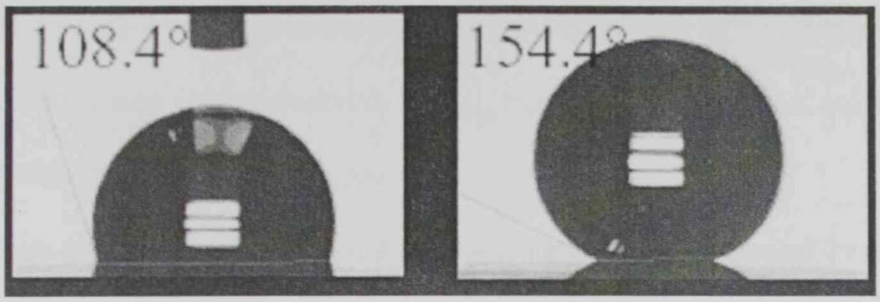
In 1936, Wenzel recognized that a rough surface would alter the relative effective contribution of the solid-liquid interface to the surface free energy. Thus, the apparent equilibrium contact angle for a liquid on a rough surface, is related to that for the same liquid on a smooth surface of the same material, by the relation

$$\text{Cos}\ \theta r = r\ \text{Cos}\ \theta s \qquad (1.35)$$

where θr "roughness" is the apparent or measured contact angle and θs "smooth "the true contact angle. Wenzel looked specifically at roughness and found that the ratio (r) of the true area of a solid (the molecular area including all roughness) to the geometric area *He and Lee (2003)*, as we would measure with a ruler had a simple relationship to the ratio of Cos θr to Cos θs

$$r = \cos\theta_r / \cos\theta_s \qquad (1.36)$$

The interesting consequence of this relationship *Roura and Fort (2002) is* that if θs < 90° then θr < θ but when θs >90° θr > θ. (see example in fig 1.8)



Flat surface *Rough Surface*

Fig 1.8 Wettability shift due to surface roughness (*He and Lee (2003)*).

It is known that the wettability of a surface is a function of its roughness Non-wetting liquids exhibit superhydrophobicity on a rough surface. It has been demonstrated that surfaces with micro-machined structures can have similar effects. This phenomenon has many applications *Patankar and Chen (2002)*.

1.4.4 Chemical Effect:

The natures of a colloidal system are dependent on *Duncan (1998)*:

- Particle size
- Particle shape and flexibility
- Surface properties (including electrical)
- Particle – Particle interactions
- Particle – solvent interactions

Lower surface energy polymers have weakly interacting atoms in the backbone, whereas high values arise from strong interactions in polar materials *Schlangen (1996)* and *Frohn (2002)*.

Chemical Composition & Molecular structure depending on side groups & secondary bonding forces & cohesive-energy density & chain branching & entanglements & cross-linking.

Surface free energy varies widely with the types of functional groups at the surface. For hydrophobic surfaces, free energy decreases in the order $-CH_2 > -CH_3 > -CF_2 > -CF_2H > -CF_3$. Hence the inertness of Teflon. In the case of a self-assembled monolayer, if the surface is well-ordered, it will expose $-CH_3$ and have a different surface energy than if it exposes $-CH_2$ groups.

Also Free electrons, ions, metastables, radicals and UV generated in plasma regions can impact a surface with energies sufficient to break the molecular bonds on the surface of most substrates. This creates very reactive free radicals on the polymer surface. These free radicals can form, cross-link, or in the presence of oxygen react rapidly to form various chemical functional groups on the substrate surface.

Polar functional groups which can form and enhance bondability include carbonyl (C=O), carboxyl (HOOC), hydroperoxide (HOO-), and hydroxyl (HO-) groups. Even small amounts of reactive functional groups incorporated into polymers can be highly beneficial to improving surface characteristics and wettability.

1.4.5 **Heterogeneity:**

Wettability increases directly with increasing affinity between the surface tension of liquid and the surface energy of a solid, *Good (1997)*.

Solid surfaces (as compared with liquid surfaces) are heterogeneous, even after careful polishing. Measurements are hence prone to error because of unavoidable sample differences *Duncan (1998) and Schlangen (1996)*.

The interaction is important in the study of liquid spreading on anisotropic or non homogeneous surfaces. *Zhang and Chao (2001); Chao and Zhang (2001); Chao and Zhang (2002).*

Surface	Liquid	Spreading rate
Non-Polar	Non-Polar	Low
Non-Polar	Polar	High
Polar	Polar	Low
Polar	Non-Polar	High

Table 1.1 effect of Heterogeneity between Liquid and surface on spreading rate.

1.4.6 Gravity & Volume of the droplet :

On a sufficiently smooth and homogeneous surface θ is independent of fluid volume. and since the tendency for a given mass of fluid to spread increases as θ decreases. the contact angle is a useful inverse measurement of wettability : Cos(θ) is thus an obvious direct measure of spreading ability.

It is sometimes said that the volume of the test drop influences the contact angle; and corrected to the Gravity effect.

1.4.7 Effect of humidity:

If the humidity is high, moisture coats the surface of the material providing a low resistance path for electron flow. The charge imbalance will not remain for a useful amount of time. Humidity is the measure of moisture in the air. If the humidity is high. the moisture coats the surface of the material, providing a low-resistance path for electron flow. This path allows the charges to "recombine" and thus neutralize the charge imbalance. Likewise, if it is very dry, a charge can build up to extraordinary levels, up to tens of thousands of volts *Website [2].*

1.5 The Applications of Contact Angle Measurement

Neutrally, the contact angle of liquid on solids plays great role in our life. This is mainly true with water; where the solid in contact controls its contact angle value. For example, contact angle of water on our skin is about 90 degrees. If it was zero, water could have penetrated the pores of the skin and possibly been absorbed by blood. Another example is the structure of a bird's feather is constructed such that the contact angle of water on a typical feather is as high as 150 degrees. Applications:

1. Adhesives
2. Biology system
3. Biomedical research
4. Coatings assessment & Quality
5. Cosmetics
6. Dental materials
7. Detergents
8. Dewetting of metallic surfaces
9. Environment
10. Evaporation & Heat exchanger
11. Extinguish Fire
12. Lacquers and paints
13. Lubricants
14. Mining industry
15. Oil recovery
16. Optics
17. Painting inks industry
18. Paper Industry

19. Pharmaceutical industry
20. Polymers
21. Primer Preparation
22. Preservation of buildings
23. Semiconductor
24. Sprays
25. Surface Cleanliness & treatment
26. Synthetic-foils
27. Textiles
28. Other "Automotive, Flat Panel Display, Hard-Disk, Image processing, Microelectronics, Wafer Inspection, Plastic packaging Soldering and brazing Material Research".

1.5.1 Adhesives

The adhesion between different components of composite structures, between different materials like glass and metal, leather and fabrics, wood and paper, can be determined by contact angle measurement. Today, a wide variety of material combinations, which have been connected in the past by soldering, welding, and means of mechanical connection are more easily and durably connected by adhesives. The work of adhesion of two surfaces connected with adhesives, the wetting of adhesives on the substrate can be determined by contact angle measurement, *Ashleya et al (2003)*.

Plastics adhesion problems are widespread throughout the industry. Major components of these problems are due to the fact that many plastics have chemically inert and nonporous surfaces with low surface tensions. That is, most plastics are hydrophobic and are not naturally wettable. These properties, although advantageous to the design engineer, often result in secondary assembly and decorating concerns – bonding, printing, coating and painting. Surface pretreatments on today's high performance engineering resins solve many adhesion problems while increasing bond strength performance.

As a general rule, acceptable bonding adhesion is achieved when the surface energy of a substrate (measured in dynes/cm) is approximately 10 dynes/cm greater than the surface tension of the liquid. In this situation, the liquid is said to "wet out" or adhere to the surface. Surface tension, which is a measurement of surface energy, is the property, due to molecular forces, by which all liquids through contraction of the surface tend to bring the contained volume into a shape having the least surface area. The higher the surface energy of the solid substrate relative to the surface tension of a liquid, the better its "wettability".

1.5.2 **Biology system**

Wetting of plant surfaces by pesticides and fungicides is very important in determining the effectiveness of the pesticide and fungicide formulations. Interaction of plant leaf and acid rain is important to know for protecting valuable corps. Critical surface tension of cell surfaces and bacteria to implants or drug surfaces needed to be identified for curing disease or for an artificial organ implantation. Example: Lotus leaf.

Physical background of the Lotus-Effect. The surface physics behind the Lotus-Effect can be derived from the behavior of liquids applied to solid surfaces. Up to present, there are only a few investigations dealing with the interaction between rough biological surfaces, particles and water. However, since the wettability of solid surfaces is well investigated in surface science, it is possible to draw conclusions about the conditions on leaf surfaces *Barthlott and Neinhuis (1997 B)*.

If a droplet is applied to a solid surface, it will wet the surface to a certain degree. The amount of wetting depends on the ratio between the energy necessary for the enlargement of the surface and the gain of energy due to adsorption, which compensates for the former. At equilibrium, the energy of the system is minimized *Barthlott and Neinhuis (1997 A).*

Surfaces with only few or completely lacking polar group's exhibit a very low interfacial tension *de Gennes (1985)*. This applies also to many components of epicuticular waxes (e.g. hydrocarbons). In the case of water repellent rough surfaces, air is enclosed between the epicuticular wax crystalloids, forming a composite surface. This enlarges the water/air interface while the solid/water interface is minimized. On such a rough "low energy" surface, the water gains very little energy through adsorption to compensate for any enlargement of its surface. In this situation, spreading does not occur, the water forms a spherical droplet, and the contact angle of the droplet depends almost entirely on the surface tension of the water. *Barthlott and Neinhuis (1997B).*

1.5.3 **Biomedical research**

Example of biological Studies depending mainly on measurement surface energy: Biological compatibility, Behavior and detection of proteins biomedical application, *Kasemo (2002) and Ashleya et al (2003).*

One example of this application is that this work can have important in designing a blood –contacting implant, many properties of the materials should be considered as influencing coagulation and hemolysis as the surface energy –low surface energy is less likely to cause blood cell adhesion, *Kasemo (2002),* reduces coagulation whereas high surface energy causes a build-up of cells on surface, which reduces hemolysis.

Air-tightness of glass vessels containing medicinal fluid. The tightness of rubber sealing caps on glass surfaces can be predicated by surface free energy measurements. Artificial bones and artificial organs have to have a certain surface free energy to be accepted by the human body. Tubes transporting body fluids have to avoid the buildup of agglomerates. The same is the prerequisite for bio-membranes.

The wicking movement of a biological fluid through the channels of a diagnostic device occurs via capillary flow. Achievement of capillary flow is a function of cohesion forces among liquid molecules and forces of adhesion between the liquid and the walls of the channel. *Meathrel et al (2003)*.

Particles deposited on a waxy surface consist, in most cases, of material, which is more readily wetted than hydrophobic wax components. In addition, they are in general larger than the surface microstructures and rest only on the very tips of the latter. As a result, the interfacial area between both is minimized. In the case of a water droplet rolling over a particle, the surface area of the droplet exposed to air is reduced and energy through adsorption is gained. The particle is removed from the surface of the droplet only if a stronger force overcomes the adhesion between particle and water droplet *Adamson (1997*). On a given surface, this is the case if the adhesion between particle and surface is greater than the adhesion between particle and water droplet. Due to the very small interfacial area between particle and rough surface, adhesion is minimized. Therefore the particle is "captured" by the water droplet and removed from the leaf surface *Barthlott, Neinhuis (1997 B).*

In surfaces with high contact angles, spreading is very limited, and the velocity of droplets running off a surface is relatively low *Barthlott and Neinhuis (1997) B and Aleksandra et al (1999).*

1.5.4 Coatings

Studies to maximize cleaning methods, solutions, adhesive properties, spreading rates and application methods *Adamson (1997)*.

1.5.5 Cosmetics

The contact angle is an important parameter for the cleaning process of shampoos and for the effectiveness of cleaning solutions. Surface tension as well is a parameter for the effectiveness of surfactant solutions. Furthermore, it is necessary for the development of time and temperature-stable emulsions for various cosmetic products. Titanium Dioxide is used as a sun blocker in suntan creams. The development of a stable, ultra-fine dispersion of Titanium Dioxide in the sun tan emulsion can be simplified by measuring the surface free energy of the particles to be suspended and the surface tension of the liquid carrier.

1.5.6 Dental materials

The contact angle of saliva on tooth surfaces depends on the materials used in the cleaning process. Artificial material must have a certain surface tension and polarity in order to avoid deposition of bacteria and in case of transplants to ensure good adhesion between tooth and embodiment *Adamson (1997)*.

1.5.7 Detergency

Another area where contact angle plays an important role is in detergency, the process of cleaning clothes, etc., by a surface-active agent. If the soiled cloth is to get rid of dirt, grease, oil, etc. it is necessary that water must spread and penetrate the dirt particles. If spreading is to occur, the interfacial tension between solid-liquid and liquid vapor must be as small as possible. What the detergent does exactly is to lower these interfacial tensions by the process of adsorption. Contact angle measurements of lotions, oils, soaps and other toilet preparations on human skin and hair strands provide valuable information for their correct formulation and are now routine *Adamson (1997)*.

Also hot water is a better cleaning agent because the lower surface tension makes it a better "wetting agent" to get into pores and fissures rather than bridging them with surface tension. Soaps and detergents further lower the surface tension. Detergency has been defined as removal of foreign material from solid surface-by-surface chemical means. The washing of clothes is a common example of detergent action *Frohn (2002)*.

1.5.8 **Dewetting of metallic surfaces.**

Machines such as Lathes are usually coated with a thin layer of grease or oil especially during transportation to prevent corrosion by water. This is achieved by the fact that grease or oil layer forms a highly non-wetting system with water *Ashleya et al (2003)*.

1.5.9 **Environment**

Sands polluted by oil can be cleaned by treatment with surfactant solutions. The progress of the cleaning process can easily be controlled by contact angle measurements on the treated and pretreated samples. (Studies to maximize coverage of pesticides, herbicides & insecticides).

1.5.10 **Evaporation & Heat exchangers**

Control droplet surface area to increase or decrease evaporation, optimal wetting of heat exchanger surfaces.

In heat exchangers and condensers used in chemical industries, maximum efficiency is achieved if a non-wetting agent like calcium stearate or oleic acid coats the metal surface. Liquids condensed on such coated walls form droplets because of high contact angles and fall down easily. This technique is called "drop-wise" condensation. Contact angle measurement is important in controlling droplet surface area to increase or decrease evaporation and to optimize wetting of heat exchanger surfaces, *Adamson (1997)*.

The spreading of an evaporating liquid on a solid surface occurs in many practical processes and is of importance in a number of practical situations such as painting, textile dyeing, coating, gluing, and thermal engineering. Typical processes involving heat transfer where the contact angle plays an important role are film cooling; boiling, and the heat transfer through heat pipes *Zhang and Chao (2001), Chao and Zhang (2001) and Chao and Zhang (2002).*

1.5.11 **Extinguishing Fire**

Reducing contact angle increases contact angle area between the droplet and solid surface, and also reduces droplet thickness. Enhancing heat conduction through the droplet. Both effects increase droplet evaporation rate. Decreasing the initial contact angle from 90° to 20 ° reuses droplet evaporation time by approximately 50% *Chandra et al. (1996)*.

A study of the effect of contact angle on droplet evaporation is important not only in formulating accurate model, but also in suggesting strategies to improve cooling efficiencies by enhancing surface wetting. For Example, it is known that the addition of "wetting agents", which reduces surface tension of water, increases the fire extinguishing capabilities of water. Tests show that addition of a wetting agent reduces by up to 60% the volume of water required to extinguish fire of wood, cotton bales and rubber tires.

Though wetting agents have been used for about 40 years. Little information is available on the mechanism by which surfactants enhance heat transfer from a hot surface to impinging droplet in water sprays *Chandra et al (1996).*

1.5.12 Lacquers and paints

Measurement of hydrophobicity of lacquer surfaces, especially for the automobile body coating. Developments of stable emulsions for paint's storage shelf life also involve the interfacial tension between the particle and carrier in the paint formulation.

Measurement of interaction/adhesion between paint and substrate surfaces (paper, metal, wood, plastics) is critical in the coating processes, especially for the change from solvent-based paints and lacquers to water-based systems, which usually causes a lot of problems for the coating processes *Ashleya et al (2003).*

1.5.13 Lubricants & Release Agents

Minimize adhesion, mold release/anti-stick materials. Controls spreading characteristics. For many practical applications the spreading of lubricating oil is as important as the oils viscosity for some applications such as, mechanical clocks, or fine mechanical meters non-spreading properties of oil are desired *Frohn (2002).*

1.5.14 Mining industry

Understanding of contact angle is also important in the mining industry. An example is froth flotation, the process of concentrating minerals of heavy metals (e.g., zinc blende, galena, chalcopyrite, etc.).

This is achieved by agitating finely divided minerals in froth of water and air, so that some float and others sink. The useful minerals become attached to the air bubbles, rise with them into the froth layer and are collected. If the contact angle between the particle-water-air interfaces is smaller, the particle does not float easily. Therefore this contact angle is increased to as much as 60 degrees by adding 'collectors' like alkyl xanthanates (e.g., CH3.O.CS.Sna) *Adamson (1997).*

1.5.15 Oil Recovery

An important technological application that emerged out of contact angle studies is in the enhanced oil recovery from sand beds. Laboratory experiments on displacing petroleum by water in glass capillaries have demonstrated that a considerable fraction of the oil remains attached to the wall when the central space of the capillary is already filled with water.

In a sand column, the amount of oil remaining in the sand when water appeared at the downstream end of the column was greater, the greater the contact angle. Flooding the oil wells with surfactants along with water or steam reduces the pressure drop across each oil-water meniscus, reduces the oil-water interfacial tension and changes the contact angle so that water displaces oil at the liquid-solid interface.

The process is called 'tertiary oil recovery' and it is now possible by this method to recover more than 90% of oil from an oil well *Adamson (1997)* and *Drummond and Israelachvili (2002).*

These constraints have important consequences in determining the wettability of multiphase systems. It is shown that in oil-wet systems, gas is wetting to water, with complete wetting in the limit of gas/oil miscibility. Some low-temperature oil reservoirs may contain two liquid hydrocarbon phases, and during gas injection four phases may be present.

In these circumstances the wettability of the system is defined by a vapor/oil contact angle, oil /water contact angle, and the contact angle between the two nonaqueous liquid phases *Blunt (2001).*

Capillary pressure is the term that environmental engineers and scientists often use to describe this balance of forces. They learned the term from the petroleum engineers and scientists who applied it to enhanced oil recovery (EOR) processes

1.5.16 Optics

The wettability of contact lenses as well as the interaction and the effectiveness of cleaning solution formulation for contact lenses can be examined by contact angle measurement.

1.5.17 Printing inks

In the manufacture of printing inks, the contact angle formed by a drop of ink on paper determines the printing quality of ink. It has been practically observed that θ must be ideally between 90^o and 110^o degrees. If it's less than 90^o degrees, the ink will spread on paper. If it's more than 110^o degrees, breaks will occur while printing.

1.5.18 Paper Industry

Like the printing industry the paper industry is involved in wetting problems. According to its use the paper has to be strongly or weakly hydrophobic or hydrophilic. A beaker made of paper must have a different surface energy than a sheet of newspaper. A juice container must have different surface energies on the outside (printability) than on the inside (liquid-resistant and microbiologically inert).

1.5.19 Pharmacy

Controlled drug release, wettability and dissolving behavior of pharmaceutical powders, tablets and capsules of various body liquids *Adamson (1997).*

1.5.20 Polymers

The interfacial tension and surface free energy of polymers and polymer blend can easily be controlled by surface tension measurement. The interfacial tension between various polymers in a polymer blend or between carbon fibers and surrounding polymer in fiber reinforced material is an important parameter for the stability of the materials. (Studies of surface active agents, controlled oxidation, adhesion)

Most of the polymers like polyethylene, polypropylene, Teflon, etc. show high contact angle behavior with many liquids. A number of applications of polymers have taken advantage of this situation. An example is the Teflon coated frying pan. Contact angle measurement has shown that the contact angle is about 35 degrees for cooking oil on Teflon; thus oil must not stick to the surface making it easier for cleaning *Adamson (1997).*

1.5.21 Printing industry

Wettability processes are of major importance for the offset printing processes. All materials involved, like paper, metal surfaces, and rubber surfaces, must have a certain surface tension value to have an optimum printing quality. This value depends on the surface tension of printing ink and the dampening solution respectively. (Evaluate marking fluids, papers, foils, coatings, transfer platens and rolls).

1.5.22 Preservation of buildings

Historical buildings have to be protected and preserved against pollution like acid rain. Their surfaces have to be impregnated by silicide acid or synthetic materials.

1.5.23 Semiconductor

The cleanness and the surface chemical composition on pure semiconductor surfaces and treated surfaces like nitrides; oxides are correlated to the surface energy of these surfaces. Therefore, the measurement of contact angles is a simple and fast method for quality control in this field. (Eliminate delamination problems, determine wafer cleanliness, and evaluate surface energy values of coatings and adhesives).

1.5.24 Sprays

The efficiency of insecticide sprays also depends on their wetting behavior on the surface of insects. Usually in most insecticides, an organic liquid having a low surface tension is used a spray so that it spreads completely. Contact angle is therefore an essential parameter to be considered in any pesticide or insecticide spray formulation *Adamson (1997).*

1.5.25 Surface Cleanliness & Treatments

Plasma treatments to increase wettability on polymers. Oxidation of silicon wafers. Surfaces prepared for soldering and solder flux efficacy.

Detect monolayer contamination and evaluate cleaning methods. - Evaluate finishes. cleaning methods, treatments and coatings. Evaluate finishes, cleaning methods. treatments and coatings. Studies of additives, wetting agents and soil removal. Given the above reasons, a small difference (<5 degrees) between advancing and receding angles suggests that the surface is free of contamination, well organized, and smooth.

1.5.26 Synthetic foils

Corresponding to the production process and the surface treatment (chemical, plasma. and flame treatments) the composition of foils and their surface characteristics can be varied remarkably. Very often the foils have to be printable.

1.5.27 Textiles

The wettability of single fiber as well as the wettability of fabrics can be determined using tensiometer and contact angle meter. Synthetic fibers are usually coated with hydrophobic materials. The degree of hydrophobicity as well as the homogeneity of the coating can be checked through contact angle measurement. (Fabric treatments, fiber treatments, water and soil repellency).

The importance of contact angle measurement in the textile and fiber industry need not be overstressed. Cotton yarn is usually wetted by water, but synthetic fabrics have definite contact angle for water. Nylon, for example, gives a contact angle of about 40 degrees. Fabrics must be coated, therefore, with suitable wetting agents. Otherwise, it will be difficult to remove dirt and soil while washing the fabric with water. But it is advantageous to use a non-wetting surface for a raincoat or umbrella cloth. Coating by a silicon polymer gives a highly non-wetting system. Waterproofing or water-repellency is an important industrial process, which depends on contact angle values *Adamson (1997)*.

1.6 Thesis Objectives

This thesis examines the role played by the solid substrate on the spreading kinetics of liquid droplets. The set of experiments whose results are presented below used different types of liquids with various properties of surface tension and viscosity tested on three different solid substrates (glass, polymethylmethacrylate (PMMA) and polystyrene (PS)).

This thesis introduces a recent technique to measure wettability that is based on the measurements of the contact area of a liquid droplet on a solid surface instead of contact angles. Results presented compare the data of contact angle based on spherical cap approximation to experimental measurements of contact angle.

Chapter 2

Material
&
Methods

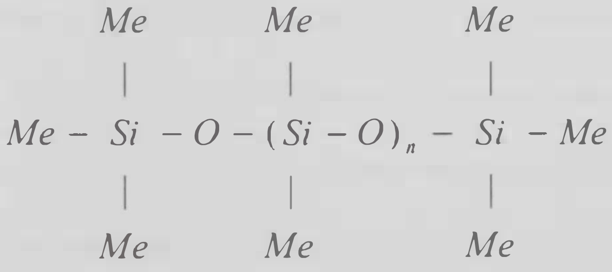
2.1 Liquid

2.1.1 Silicon oil (PDMS)

Synonyms: Silicon oil; alpha-Methyl-omega-methoxypolydimethylsiloxane; carboxypropyldimethyl; Dimethylpolysiloxane hydrolyzate; Polydimethyl silicone oil; Polydimethylsiloxane, Polyoxy (dimethylsilylene), Silicon and Siloxane.

Major applications *Mark (1999)*: Release agents, rubber molds, sealants and gaskets, surfactants, water repellents, adhesives, foam control agents, biomedical devices, personal care and cosmetics, dielectric encapsulation, glass sizing agents, greases, hydraulic fluids, heat transfer fluids, lubricants, fuser oil and process aids.

The name silicone was given in 1901 by Kipping *Elschenbroich and Salzer (1992)* to describe new compounds of the generic formula R_2SiO. These were rapidly identified as being polymeric and actually corresponding to polydialkylsiloxanes, The name silicone was adopted by the industry and most of the time refers to polymers with the formulation where R = Me (methyl group) as shown Fig 2.1 .



$$\begin{array}{ccccccc} & Me & & Me & & Me & \\ & | & & | & & | & \\ Me - & Si & - O - (& Si & - O)_n - & Si & - Me \\ & | & & | & & | & \\ & Me & & Me & & Me & \end{array}$$

Fig 2.1 **Chemical formula of Silicone oil (where n=0, 1...)**

The accompanying number of the Silicone is the viscosity value in cp, which is reciprocally, correlated reciprocal to the Si density, which is connected to the molecule weight only (with no change in volume). Molecule weight is dependent on the n value in Fig 2.1 *Valignat et al (1999)*.

The polydimethysiloxanes have a low surface tension (20.4 mN/m) and are capable of wetting most surfaces. With the methyl groups pointing to the outside, this gives very hydrophobic films and gives it good spreading area on most surfaces. Even the hydrokinetics do not effect the spreading on the Glass and PS which both have the same rate of spreading in spite of two surface are carrying the opposite properties (hydrophilic and hydrophobic respectively) although Silicon oils describe as hydrophobic liquid.

The extraordinary properties of silicon materials may be traced back to the idiosyncrasies of the Si-O-Si (Siloxane) bond. The high flexibility of (-Me_2SiO-) n chains suggests low barriers of conformational changes *Elschenbroich and Salzer (1992)*.

The simultaneous presence of "organic" groups attached to an "inorganic" backbone gives silicon a combination of unique properties *Stark et al (1982)* and allows their use in fields as different as aerospace (low and high temperature flexibility). electronics (high electrical resistance), medical (excellent biocompatibility) and construction (resistance to weathering).

Depending on the structure of the silicon oil is obtained. Thanks to its outstanding properties, silicon is almost ubiquitous in modern technology. It's Their advantages include high thermal stability, small temperature coefficients of viscosity and water repelling action combined with it's physiologically innocuous nature , And high Flexibility owing to low bending vibration energy *Elschenbroich and Salzer (1992)*.

Hydrophobic and physiological inertness. Shear stability, weak intermolecular forces, and excellent dielectric strength. Low volatility at high molecular weight like Si100 and Si 1000, *Marke (1999)*.

In the absence of surface tension gradients, and on smooth, chemically homogeneous substrates, wetting liquids build molecularly thin films, conveniently studied at the edge of spreading microdroplets. Spatially resolved ellipsometry is a relevant technique for this study.

Since silicone oil wets glass "perfectly," its contact angle is very close to zero. The side graph can't show the angle between the solid and the droplet interface, so we manly use the shadowgraph image and measurement the contact Area, as a function of the distance to the contact line, r. The solid line is the solution of the static capillary theory. Clearly, the slope may be safely extrapolated to the contact line, r = 0, at which point the angle equals the static contact angle of the system *Ramé (2000).*

The so-called "complete" spreading of PDMS droplets could be resolved into three regimes. The first was a flow regime, driven by Laplace energy and was believed to be resisted by the liquid/solid contact energy. The second was a diffusive regime, driven by Fickian-type forces. The third was a fragmented island regime, which ensued by excessive film thinning. It is therefore suggested that PDMS, like other liquids, experience partial wetting with a finite contact angle of about 8 degrees. The diffusive regime, leading to the fragmented island regime, is thought to be associated with extraordinary molecular mobility of PDMS *Alteraifi and Moet (2003).*

In silicone, the activation energy to the viscous movement is very low, and the viscosity of silicone is less dependent on temperature than are the viscosities of hydrocarbon polymers. Moreover, chain entanglements are involved at higher temperature and limit the viscosity reduction.

2.1.2 Alkanes group

Alkanes are one of the hydrocarbon families that have only sp3 carbons. Each carbon atom in the molecule is surrounded by single covalent bonds. As a result, the molecules are tetrahedrally shaped and are non-polar molecules since all of the C-H bond dipoles cancel each other. The general molecular formula for the members of the alkane family is: C_nH_{2n+2} where n = number of carbon atoms in the alkane molecule *Masterton and Hurley (1993)* and *Brown (1995).*

In our study, three liquids are used with relative high Molecular Weight like Undecane, Dodecane and Hexadecane. These intermolecular attractions are called "van der Waals forces", "London forces" or "dispersion forces". The Dispersion forces (0.02-2 kcla /mol) are the weakest of all intermolecular forces. It is the existence of these forces that accounts for the fact that low-molecular-weight, non-polar substances can be liquefied *Brown (1995)*.this give explanation to the low value of surface tension of alkane.

The melting point, boiling point, and density of a hydrocarbon are related to the strength of these forces. And also is direct proportion to the molecular weight.

The general properties can be summarizined at two points. Alkane Liquids Molecular Weight is high when compared to other groups and they are insoluble in water "Hydrophobic" as shown in Table 2.1

Table 2.1 **Physical properties for Alkanes group.** ***Ref Website [1]***

liquid	Synonyms	Formula	Density	Molecular Weight	Melting point	Boiling point	Refractive Index:	
Undecane	Alkane C(11) n-Undecane; Undecane;	$C_{11}H_{24}$	0.74	156.3106	-25.59°C	195.9°C	1.4173	Insoluble in water, flammable, colorless liquid
Dodecane	Alkane C(12); n-Dodecane; Dodecane.	$C_{12}H_{26}$	0.749	170.3374	-9.6 °C	216.3 °C	1.4216	Colorless liquid, Solubility in water <0.1 g/100 mL at 25 °C
Hexadecane	Hexadecane; n-Cetane; n-hexadecane.	$C_{16}H_{34}$	0.773	226.4446	18.17°C	287 °C		Colorless liquid

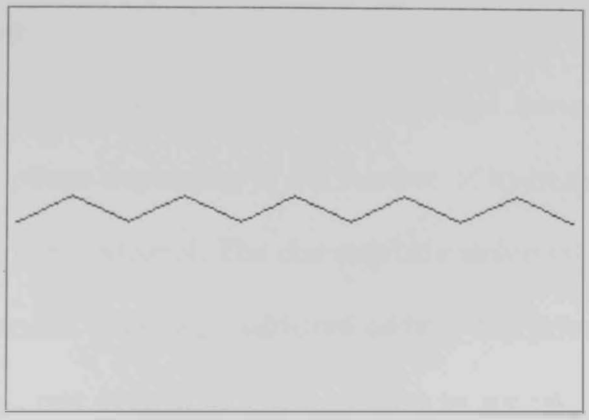


Fig 2.2 Chemical formula of Undecane

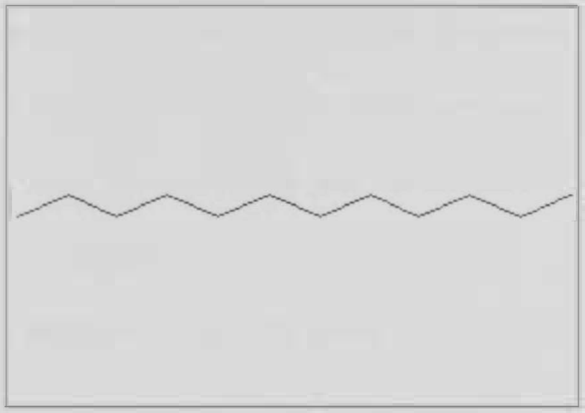


Fig 2.3 Chemical formula of Dodecane

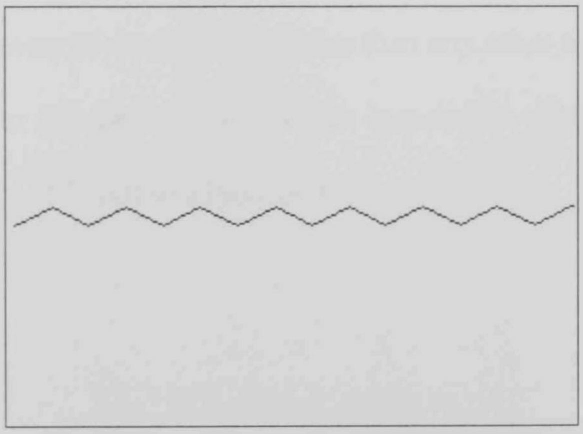


Fig 2.4 Chemical formula of Hexadecane

2.1.3 Alcohol group

The Alcohol group is one of the Organic groups having a hydroxyl (–OH) group, contain three groups depending in the number of hydroxyl group to: primary alcohol, di-Alcohol and tri- Alcohol. The characteristic structural feather of an alcohol is an (-OH) group bonded to an sp3-hydridzed carbon. For primary Alcohol it has a have high evaporation rate even at low temperature so we take out this category of liquid *Masterton and Hurley (1993)* and *Brown (1995)*.

In the IUPAC system *Brown (1995)*, the longest chain of carbon atoms containing the –OH groups is selected as the parent compound and number from the end closer to –OH. And changed the suffix –e of the corresponding alkane to –ol. But common name for alcohols are derived by naming the alkyl group attached to –OH and then adding the word "alcohol".

Because of the presence of the –OH group, alcohols are polar compounds. The attraction between the positive end of the one dipole and the negative end of another is called dipole-dipole interaction *Brown (1995)*. This attractive between dipoles is particularly strong and is given the special name of hydrogen bonding. And for that reason the surface tension of alcohols are higher than any other liquids.

We also add to this group, water which containing –OH group and similar in the spreading behavior of Polythlenglycol and Glycerin.

Table 2.2 Physical properties for Alcohol group ***Ref Website [1]***

Name	Synonyms	Formula	Density	Molecular Weight	Melting point	Boiling point	Refractive Index	
Glycerin	1,2,3-propanetriol; 1,2,3-Trihydroxypropane; glycyl alcohol; Glycerol;.	$C_3H_8O_3$	1.261	92.0944	17.8°C	290°C	1.473	Clear colorless viscous liquid, HYGROSCOPIC, miscible in water
Polythlenglycol or EthyleneGlycol	1,2-Dihydroxyethane; 1,2-Ethanediol; Ethane-1,2-diol; ethylene alcohol; Ethylene Glycol ; Glycol Alcohol; Polyethylene glycol.	$C_2H_6O_2$	1.1155	62.0682	65°C	195°C	1.431	Clear, colorless, viscous liquid. Suitable for use as a fusogen in the production of lymphocyte-myeloma hybrids. HYGROSCOPIC.Solubility in water miscible. Vapor pressure: 0.06
Water	Aqua; Dihydrogen oxide; Deionized Ultra-filtered Water; Water; Hydrogen oxide; Ice; Snow; Steam	H_2O	0.995	18.0152	0 °C	100°C		Vapor pressure: 3.2 kPa at 25 °C Clear colorless liquid Resources: Ultra Pure Water system produced by MiLLi Proc (Milli-Q plus 185)

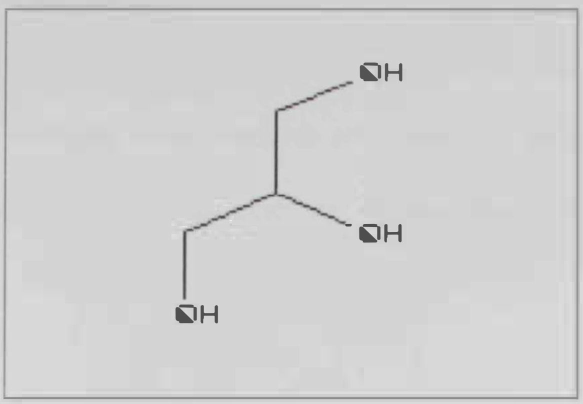


Fig 2.5 Chemical formula of Glycerin

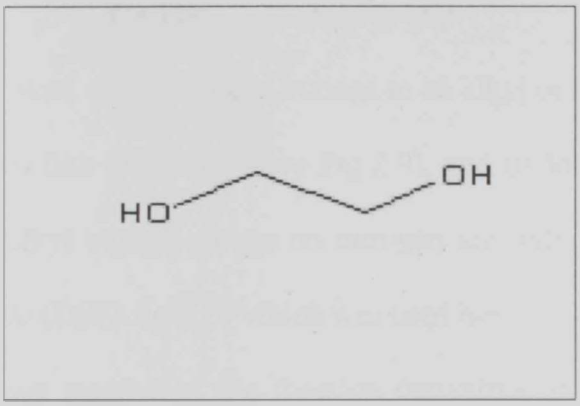


Fig 2.6 Chemical formula of Polythlenglycol

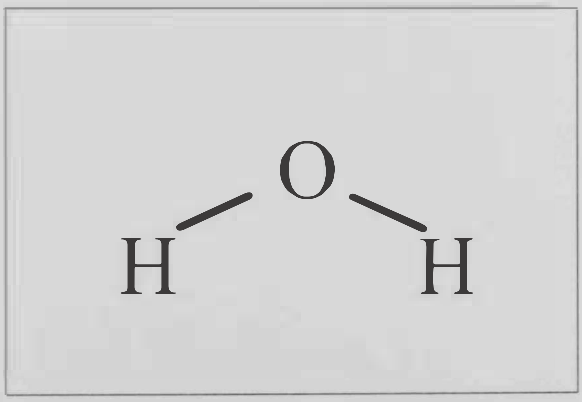
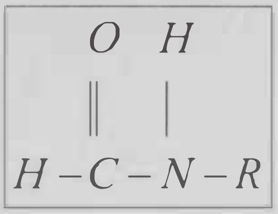


Fig 2.7 Chemical formula of Water

2.1.4 Primary amide group

The characteristic structural feature of an amide is an acyl group (O=C-NHR) bonded to a trivalent nitrogen atom. Amides are named by dropping the suffix –oic acid from IUPAC name of the parent acid, or –ic acid from its common name, and adding –amide *Brown (1995)*.



$$\begin{matrix} & & O & & H & & \\ & & \| & & | & & \\ H & - & C & - & N & - & R \end{matrix}$$

Fig 2.8 Acyl group

If the nitrogen atom of an amide is bonded to an alkyl or aryl group, the group is named *Brown (1995)* like Formamid (see Fig 2.9), and its location on nitrogen is indicated by *N*-. The alkyl or aryl groups on nitrogen are indicated by *N, N-di* like *N,N-dimethylformamide* (DEF) fig 2.10 which was used here.

Amides, the least reactive of the function derivative of carboxylic acids, do not react with alcohols but it dissolve in water *Brown (1995)*.

Table 2.3 Physical properties for Primary amide group *Ref Website [1]*.

Name	Synonyms	Formula	Density	Molecular Weight	Melting point	Boiling point	Refractive Index	
Formamid	Carbamaldehyde; Formamide; Formimidic Acid; Methanamide.	CH_3NO	1.134	45.0408	2.5°C	210°C	1.4305	Vapor pressure: 0.08 Colorless, slightly viscous liquid. HYGROSCOPIC. Miscible in water.
N.N dimethyformanid	Dimethyl formamide; N,N-dimethylformamide	C_3H_7NO	0.944	73.0944	-61°C	153°C		Vapor pressure: 2.6 Colorless liquid with a faint, ammonia-like odor detectable at 100 ppm. AIR/MOISTURE SENSITIVE. miscible in water

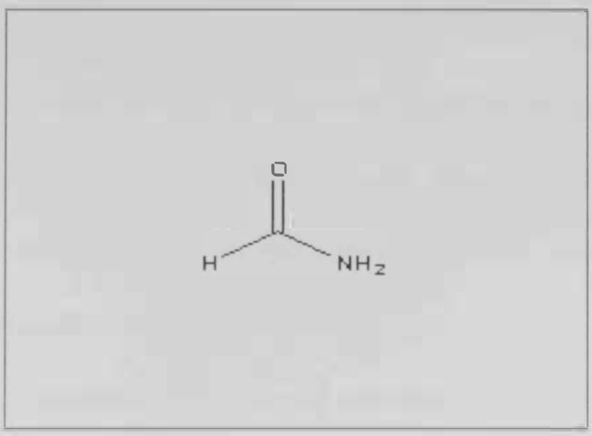


Fig 2.9 Chemical formula of Formamid

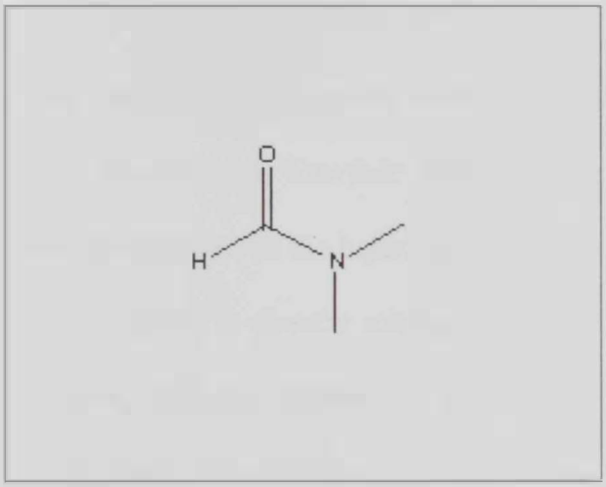


Fig 2.10 Chemical formula of N.N dimethyformanid

2.1.5 Measurement of surface tension "σ"

Surface tension is often defined as the force acting at right angles to any line of unit length on the liquid surface or the work required to increase the area of a surface isothermally and reversibly by unit amount. There are many techniques used to measure surface tension based on the measure of the force required to work between gas / liquid interface.

The technique used in this study is (du Nouy ring). The ring tensiometer method .In this method we measure the maximum force (the force per unit length of two circumferences) will measured as the ring pulls a tube of liquid (two-sided) out of the liquid.

The du Nouy ring method for measuring surface tension mininze wettibilty effects at the conditions of the surface or interface. Since the adhesion of a liquid to a metal ring is greater than the cohesion of the liquid itself, the force required to detach a ring from the surface of a liquid is directly related to the size of the ring and the surface tension of the liquid, with the addition of a correction factor to adjust for liquid still remaining on the ring.

Some of the other techniques used to measure surface tension are oscillating jet (dynamic), hanging drop, spinning drop, sessile drop, capillary rise and maximum bubble pressure. The key to du Nouy's new apparatus was the use of a torsion wire, which could be twisted to apply torque to a lever arm, from which a ring of interest was suspended in contact with the liquid. In the original design du Noüy proposed simply calibrating the instrument by measuring the force maximum pull of pure liquids for which surface tension was known, making the technique useful but still relative.

This method utilizes the interaction of a platinum ring with the surface being tested. The ring is submerged below the interface and subsequently raised upwards. As the ring moves upwards it raises a meniscus of the liquid. Eventually this meniscus tears from the ring and returns to it's original position. Prior to this event, the volume, and thus the force exerted, of the meniscus passes through a maximum value and begin to diminish prior to the actually tearing event.

Although all liquids used are known surface tension values *Reid et al* (1987), these values of surface tension were examined experimentally. Because this values can be effect by the conduction measurement *Pellicer et al (2002)*. (see Table 2.4). The Torsion balance used in this study produced by White elec. inst COLTD shown in Fig 2.11. Capacities 0 - 0.12 n/m (where 1 newton / meter = 1000 dynes/cm), 0 - 1 gram (graduated in 2mg increments). The instrument uses a 4cm circumference Platinum (Du-Nuoy) Ring shown in Fig 2.11.

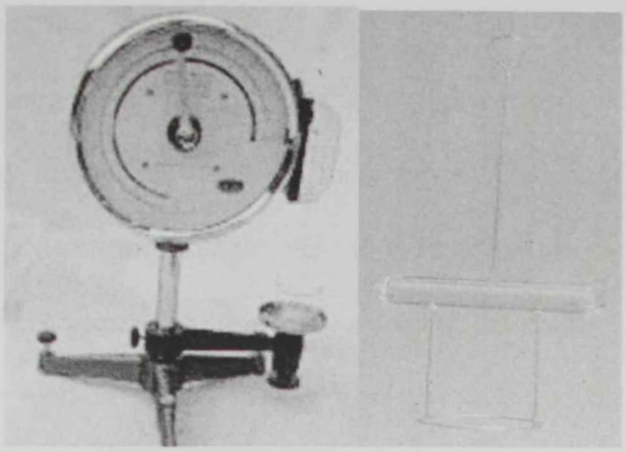


Fig 2.11 Torsion balance and the Du-Nouy Platinum Rings

Liquid	Surface tension (At 23^{o}C)
Silicone oil-100	21.0
Silicone oil-1000	21.0
Undecane	29.0
Dodecane	30.0
Hexadecane	32.7
Formamid	47.5
N.N dimethyformanid	38.7
Polythlenglycol	47.5
Glycerene	67.6*
Water	72.2

Table 2.4 **Surface Tension values for used liquids** *(* Reid et al (1987))*

2.1.6 Measurement the Viscosity "μ"

Viscosity resistance to the internal friction between molecules. Viscosity can be measured by an instrument called a viscometer. Viscosity is affected by the temperature. At higher temperatures the viscosity decreases, as the molecules take on more kinetic energy allowing them to move past each other faster.

The popular method for measuring viscosity is based on the flow though a capillary tube. This can be determined by using simple Ostwald viscometer. A fluid of ρ density is allowed to fall from high h_1 in to h_2 (see figure 2.12) in a determined time. The time required for a liquid to flow between the two marks is a function both of dynamic viscosity and density. The relationship between dynamic viscosity and density is called the kinematics viscosity and is defined as

$$\text{Kinematics viscosity} = \frac{\text{Dynamic Viscosity}}{\text{Density}} \qquad (2.1)$$

An Ostwald viscometer is normally supplied with a viscometer constant, which can be used to calculate viscosity. The Viscosity values are summarized in Table 2.5.

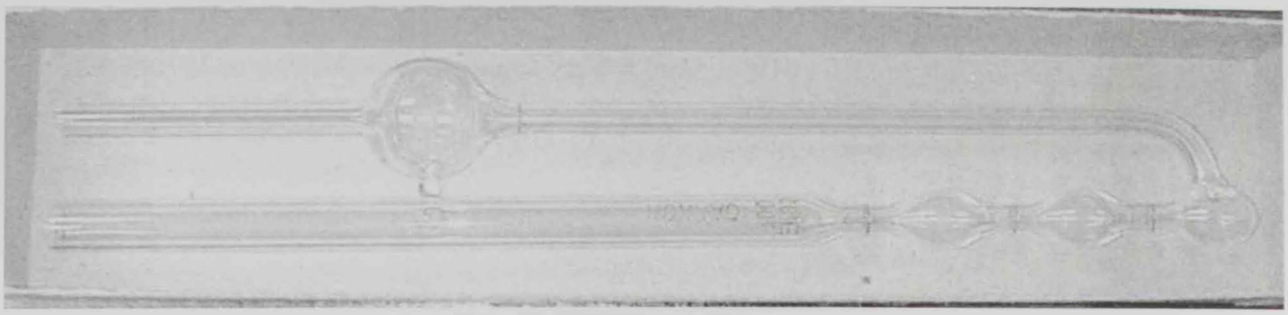


Fig 2.12 Simple Ostwald viscometer

Liquid	Dynamic viscosity
Silicone oil -100	99.5
Silicone oil -1000	999.8
Undecane	1.1
Dodecane	1.4
Hexadecane	3.2
Formamid	3.3
N.N dimethyformanid	2.2
Polythlenglycol	62.7
Glycerene	953.9*
Water	0.9

Table 2.5 Viscosity values for used liquids (* *Reid et al* (1987))

2.1 Solids (Glass, PMMA and PS)

2.1.1 Glass

Chemical composition &Physical Properties

Dry silicon, Soda-lime (SiO_2) (or borosilicate) (or fused silica) glass slides obtained from Menzel-Glaser Company Geschnitten, Germany.

Sodalime glass, commonly known as window glass, is generally the most commonly used substrate. Microscope slides are commonly made from this glass, either using afloat glass process or a draw glass process. In the case of a float glass process, the glass is cooled over a bath of molten tin, enriching its "float" side with tin oxide. Both the float and draw glass forming processes result flat glass sheets that are smooth on a molecular scale, requiring no further polishing.

Glass Densityis 2.6 g/cm^3 Glass is one of the materials that is more able to give up electrons when in contact with another material. It's more positive in the triboelectric series) *Ref Website [1]*.

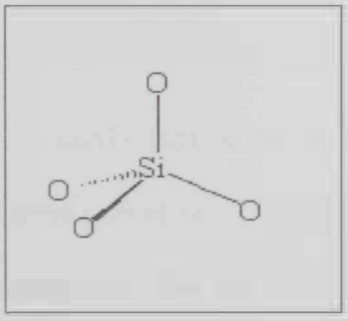


Fig 2.13 Chemical Compassion of Glass

Soda-lime glass contains about 13% sodium oxide. This component is highly soluble in water, reacting to form sodium hydroxide this wills gave glass the hydrophilic propriety. This reaction occurs in ambient air. The humidity in the air will generate a coating of sodium hydroxide, coating the surface of the glass. This layer may interfere with adhesion to the glass surface and it is best removed by rinsing in water. Another effect of forming sodium hydroxide is its reaction with carbon dioxide in air, leading to the formation of a white sodium carbonate powder on the glass surface, also referred to as "blooming."

Cleaning process

Cleaning glass is a very strict process, because glass can be polluted very easily, and catches the grime or chemical from the air *Berg (1993), as* shown in Fig 2.13. The efficiency of the method of the cleaning is tested by using SEM technique. Effective glass cleaning is achieved using the following procedure:

1. Immersion in Chromic Acid solution ($K_2Cr_2O_7 + H_2SO_4$) with high concentration .
2. Allow to dry for and leave it 4-6 Hour`s
3. Rinse with Distilled Water followed by Acetone.
4. Allow to dry by placing glass slide in a vacuum-oven for ½ hr at 90^oC to evaporate the acetone.
5. The slides are allowed to cool under vacuum.
6. The sliders are carefully transferred to the dissector, where they are stored for short time period until the time of use. Slides are used only for a single measurement. The cleanness of glass are tested using SEM as shown in Fig 2.15.

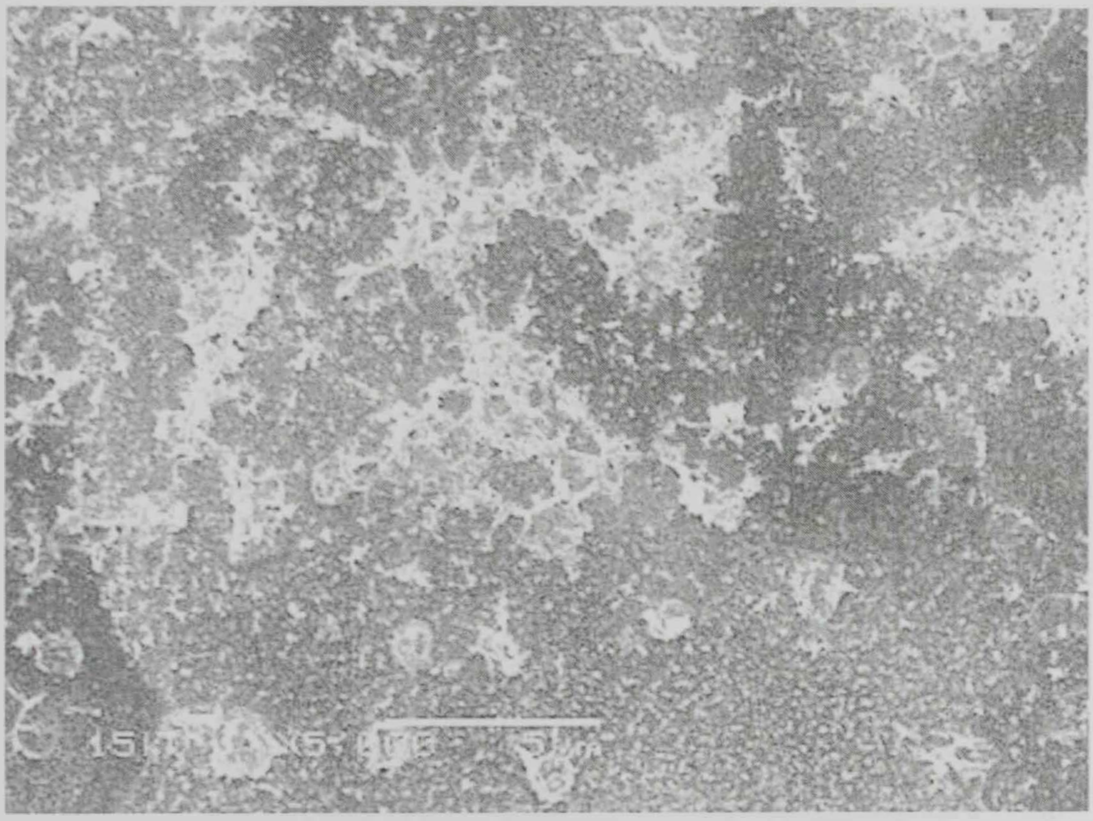


Fig 2.14 **Unclean Glass surface (before cleaning) show the grime and the impurities.**

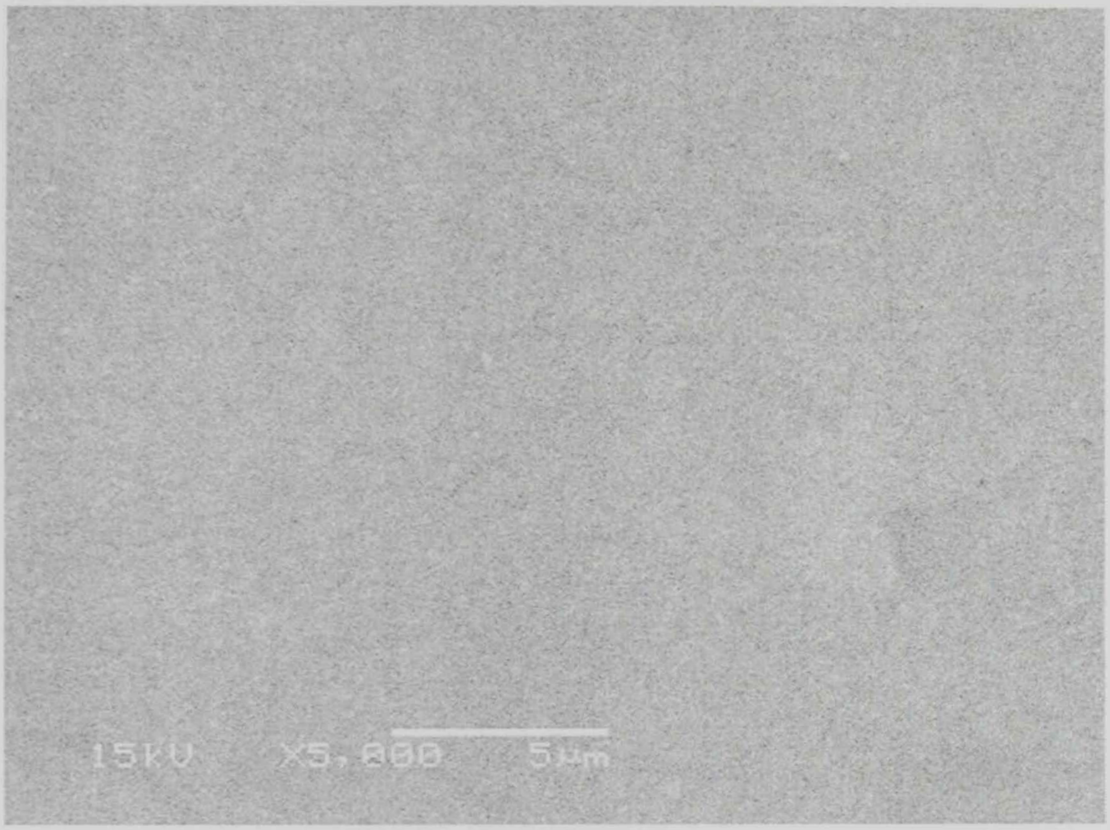


Fig 2.15 SEM image for clean glass show no partials in the surface and it's clean.

2.3.2 Ploy Methyl methacrylate (PMMA)

PMMA is available commercially under trade names like: Lucite, Perspex or Plexiglass. It has uses as objects that must be clear, transparent and tough. The physical and chemical properties of PMMA is show in Table 2.6

Materials	State	Properties
PMMA	Solid	Formula: $C_5H_8O_2$ Density: 1.188 (but it's less than half that of glass (approximately 2.6 g/cm3) Molecular Weight: 100.117 Water white, highly transparent, crystal like solid similar to glass at room temperature, and light weight.

Table 2.6 Physical properties for PMMA. ***Ref Website [1]***

PMMA are polymer materials. Basically it is a long chain polymer made from Methyl methacrylate (MMA) $C_5H_8O_2$ which is liquid at room temp (Molecular weight: 100.117 and Density: 0.943, and free-radical addition polymerization, Polarity: Hygroscopic of hydrophilic *Ref Website [1]*.

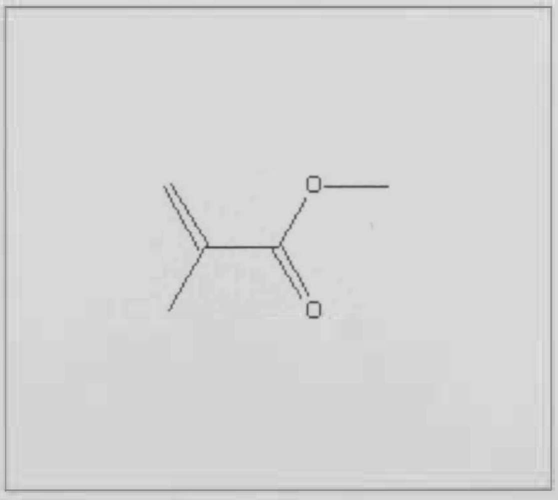


Fig 2.16 Chemical compassion of Methyl-meth-acrylate

Cleaning process

Commercial PMMA slides are used. Slides are usually covered by adhesive sheet of paper to protect it from crash or scratch as shown in Fig 2.17.

The cleanliness of PMMA is examined by using SEM. The effective cleaning method is achieved by following methods, see Fig 2.18.

To clean PMMA piece immerse in Ethanol for 2 hours and rub the surface with a soft sponge to get rid of any gum layer (or the sides were rubbed gently with soft sponge in order to get rid of adhesives layer). Subsequently, slides were rinsed with water and immerse in Di H_2O for at least five minutes. Finally slides were allowed to dry in fresh air just before the start of Experiment.

To ensure that no scarification has taken place during the cleaning process, SEM technique is used which proves that the surface is smooth and there is no rending or crevassing even in micro scale.

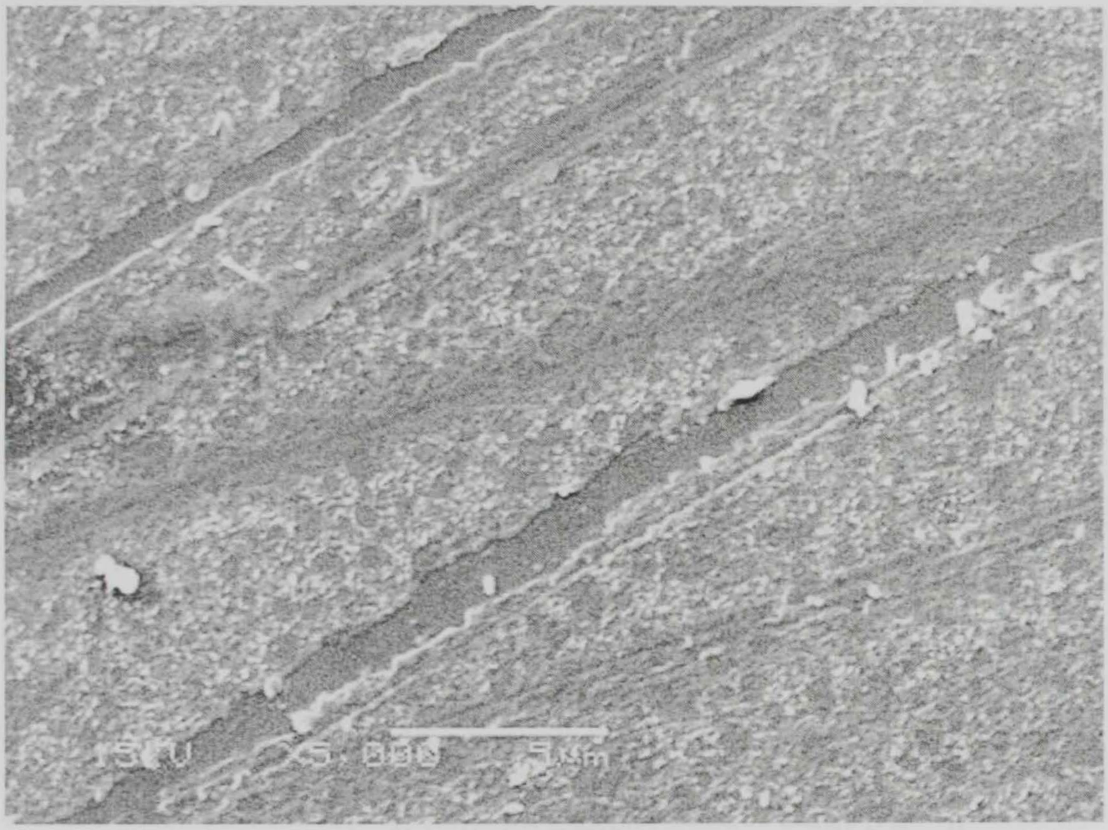


Fig 2.17 **Unclean PMMA surface with adhesives layer**

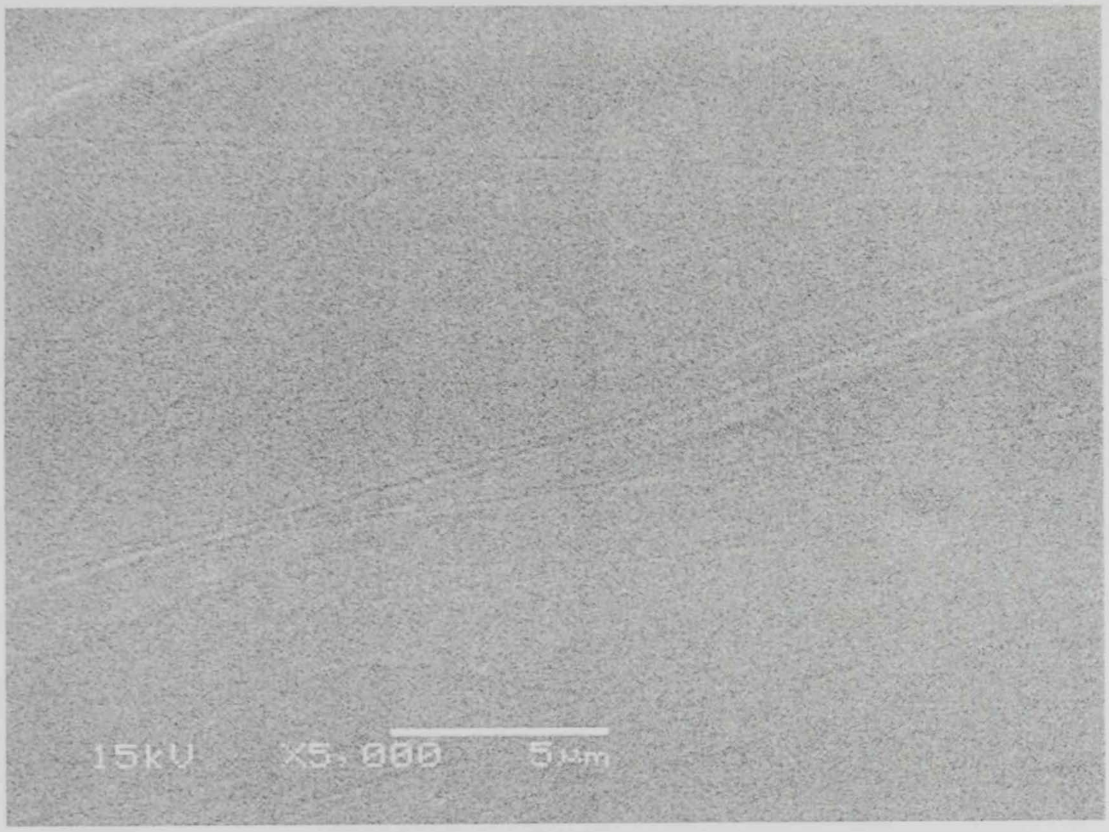


Fig 2.18 **Clean PMMA surface**

2.3.3 Polystyrene (PS)

Chemical composition &Physical Properties

Synonyms: Styrene polymers; Styrene Resin, vinylbenzene polymer afcolene; atactic polystyrene; average M.W. 250.000and PS. Physical and chemical properties is show in table 2.7

Materials	State	Properties
PMMA	Solid	Formula: C_8H_8 Density: 1.05 Molecular Weight: 104.1512 Melting Point: 240 °C Refractive Index :1.59 White powder.

Table 2.7 Physical property for PS. ***Ref Website [1]***

Polystyrene is an amorphous, thermoplastic polymer and white powder. Free radical growth polymer, styrene is easily polymerized by benzoyl peroxide, and the product polystyrene has a molecular weith in the range of 1 to 3 million (that is, n=10-30.000) (benzoyl peroxide).

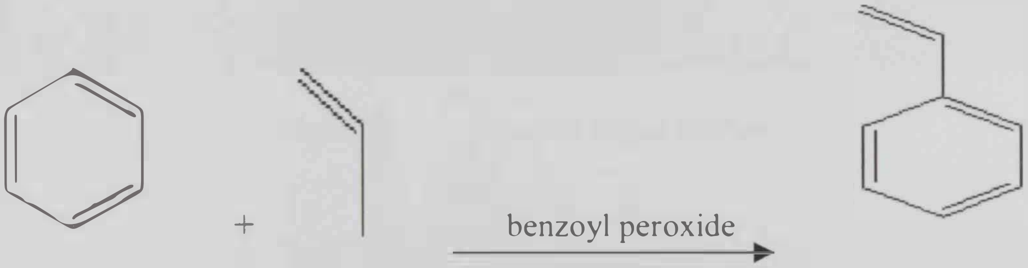


Fig 2.19 Constituting polystyrene

Cleaning process

A clean lab sheet of Polystyrene (Biddy Sterilin. Lab Company, UK.) is used, this PS sheet has cleaned surface as the surface roughness and cleaness are tested by using the SEM of the surface as show in Fig 2.20.

Fig 2.20 **PS with clean surface**

2.3 Experimental setup

2.3.1 Spreading measurement Set up

The experimental setup is shown in Fig 2.21. To conduct the experiment, the liquid was charged into a 5-µl syringe obtained from SGE International Company, Australia. The syringe was attached to a metal stand and suspended vertically by micromanipulator on top of the substrate surface slide.

The micromanipulator is used to adjust the position of the needle tip of the syringe carefully above the clean glass slide. The tip of the syringe was positioned a few micrometers from the surface of the glass to eliminate impact effect when the droplet was released. The droplet volume was selected to be 1.5 µl so that gravity effect is negligible *Cazabat (1987).*

Also the head of the syringe should be a straight, circular type to minimize any remaining amount of droplet volume on the syringe knife by capillary force of liquid.

The syringe is cleaning thoroughly with acetone and allowed to dry it in an oven. In addition, syringe is flushed with the solvent of interest once or twice before measurements. At least ten measurements were taken with each liquid over the same solid.

The solid substrate was placed on an optical stand within the focus of a CCD digital video camera (½ inch CDD Digital produced by JVC TK-c1380 color video camera), requires a camera with a higher sensitivity or a camera that facilitates field integration *Van Vliet et al(1998) and Mullikin et al (1994)* . A 10x eyepiece magnification is placed underneath a test surface slide. The camera was connected to a video recorder, which was in turn connected to an image analysis system.

The light source is ring light fiber optics (model LG-R66. OLYMPUS – JAPAN). using fiber optics light reduces the heat produced normal light. Heat may affects the surface tension of the liquid and also produce blurred image.

All experiments were carried out under the following condittions:

- Isolated Chamber: to protect the whole system from runway air which may be carry fine sand or dust, a closed hood from was build Plexi-glass to allow light to transfer throughout a load to light press through it.
- Temperature : around 24° C ± 2° C , lab temperature was controlled using split unit air condition with thermal sensor (produced by SONYO Japan)
- Humidity was maintained at 47% RH.

Typical image frames acquired by the image analysis system are displayed in Fig. 2.22 below. The images were grabbed by the image analyzer from which the contact area was digitized and measured as a function of time.

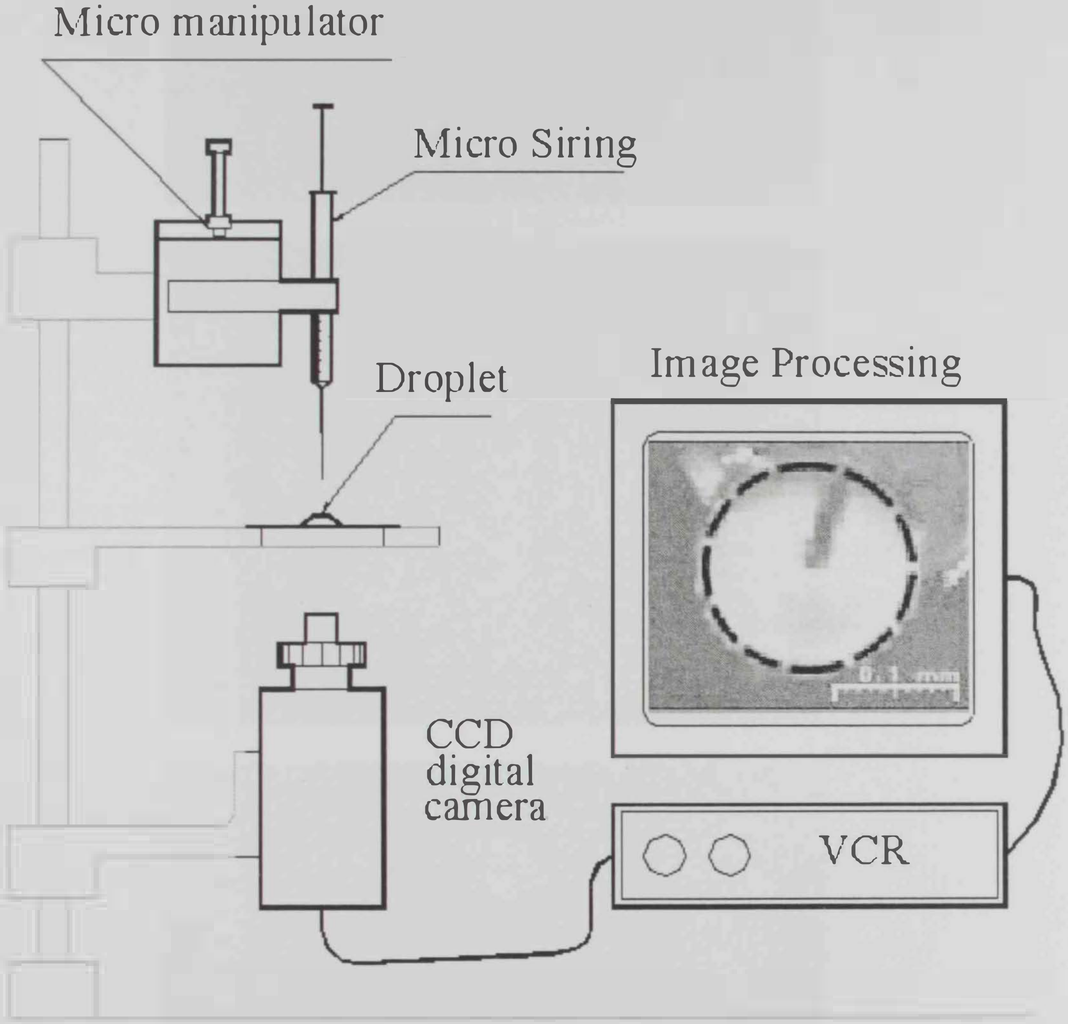


Fig 2.21 shows the experimental setup. The distant between slide and camera are fixed to keep the magnification of eyepiece, and the source of light should be above the syringe

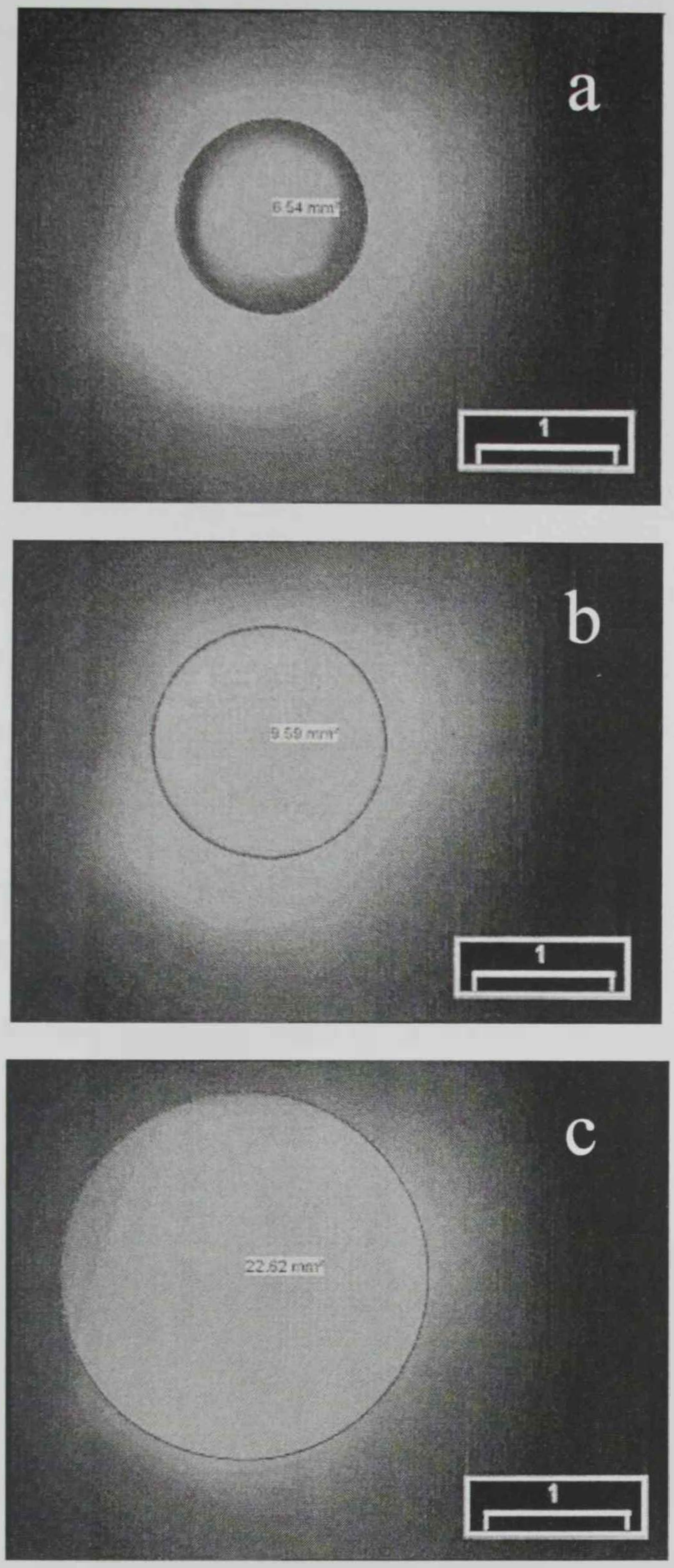


Fig. 2.22 Sample of experimental measurement of the contact droplet area for 1000 cp Silicone oil over Glass, for a) 5 sec, b) 30 sec, and c) 120 sec. The numbers present the contact area measurement in mm^2

2.3.1.1 Software & Calibration

The magnification is calibrated using calibration sample to magnification of the photo Image analysis system of software (*analySIS* 3.0 Soft Imaging System GmbH Germany March 1999)

Calibration methods

1. The Standard Calibration Sample (Micrometer) in placed on the 10X , 15X and 20X objective (as shown in Fig 2.23)

1- Acquire the focused and enhanced image from the microscope

2- Snapshot the image

3- From the image menu select *Set Input*

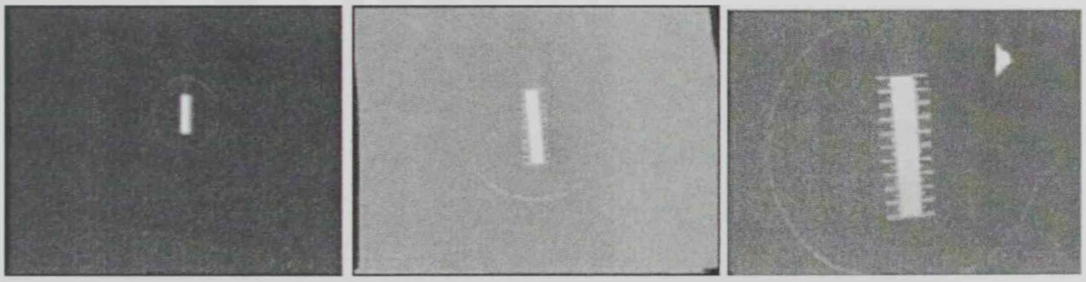
4- Click on the XY Calibration tab & Insert the required *Magnification*

5- From *Unit* define the calibration distance unit.

6- Select *Vertical* option for the calibration distance to be defined

7- Insert the *Calibration Length* according to the selected distance as defined by the calibration sample. Then Save the Calibration by clicking on *Save*

8- Add the new calibration to the Magnification table by clicking *Add* then press *OK*



10x **15X** **20X**

Fig 2.23 Shows the Magnification of three lenses. For all experiments we used 10X objective for the purpose of wide spreading area.

2.3.1.2 Spherical Cap Approximation

Contact angle is obtained from the contact area by using the correlation known as spherical cap approximation. This approach is based on the measurements of the contact area of a liquid droplet on a solid surface instead of contact angles. Results show that measurements of contact area can be converted to contact angle using spherical cap approximation. The data presented is compared to the direct measurements of contact angle.

To measure the angle from the area of circumference of droplet from the following geometric relation:

$$h = \frac{1}{2} R\theta \qquad (2.2)$$

where h, R, θ are the height of a droplet, the radius of the contact area, the contact angle respectively.

$$\frac{\pi}{2} hR^2 = V \qquad (2.3)$$

where V is the droplet volume

$$A = \frac{\pi}{4} D^2 \qquad (2.4)$$

where A, D are the contact area and the diameter of the contact area.

Time(sec)	Area (cm^2)	Deameter (cm)	Radius (cm)	Height (cm) h	Angle (θ rad)	1rad = 180/π
0	0	0	0	0	0	0
5	0.033	0.20	0.103	0.089	1.73	99.56
10	0.035	0.21	0.106	0.084	1.58	90.73
20	0.037	0.21	0.109	0.079	1.44	82.86
30	0.039	0.22	0.112	0.075	1.344	77.06
40	0.040	0.22	0.113	0.074	1.31	75.58
60	0.041	0.23	0.115	0.072	1.25	71.82
90	0.041	0.23	0.115	0.071	1.24	71.34
120	0.041	0.23	0.115	0.071	1.23	70.82
180	0.042	0.23	0.115	0.071	1.23	70.64

Table 2.8 Example of measurement contact angle using Spherical Cap approximation for Glycerine (1.5 μL) over PMMA.

2.3.1.3 Side Image of droplet

The set-up used to measure the contact area consists of digital camera type Nikon – Japan. But one of the disadvantages is depending mainly on eye estimates. So we can not use the value in our calculation later especially when the value of angle comes small ($\theta<10^{o}$) and when we compare it with approximation data the data is coming closer in value with decreasing the angle.

It is difficult to form a satisfactory profile image of a sessile drop as its contact angle approaches zero (say, is less than 5 degrees). The algorithms themselves have no inherent limitation in reaching zero if the image is satisfactory.

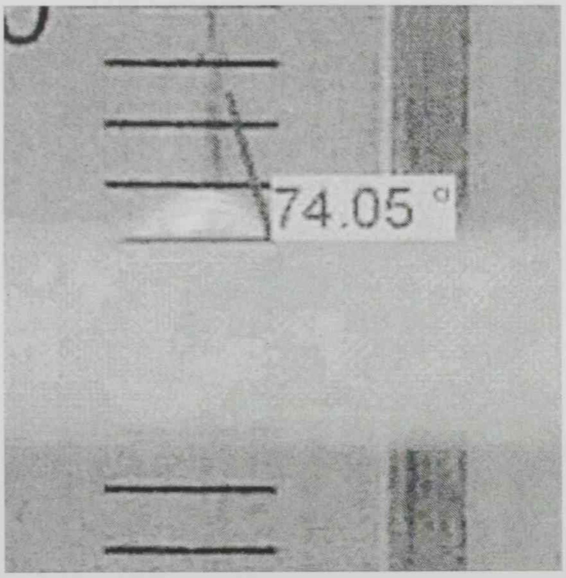


Fig 2.24 **Contact angle for 1.5μL of for Glycerin over PMMA**

2.3.1.4 Contact angle meter

The diameter of the basic and the height can be find of the droplet by using the side image. Then by using the spherical cap approximation ($h = \frac{1}{2} R\ \theta$) the data is close to the previous method. Example: Glycerin over PMMA

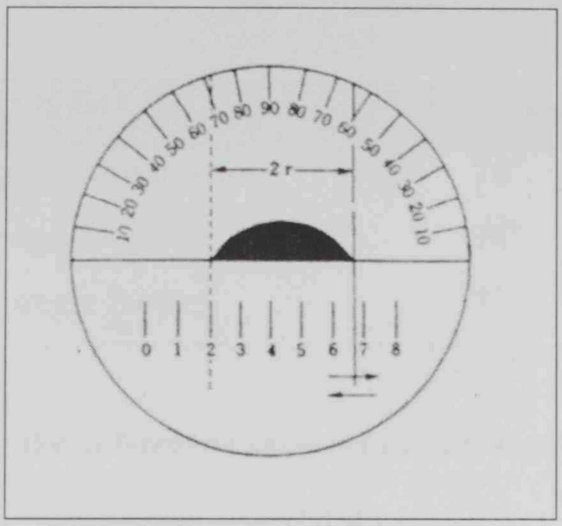


Fig 2.25 Contact angle meter

From photo: H= 0.86 mm,

R = D/2 = (2.71) / 2

$\theta = 1.26$ Red $= 72.72^{O}$

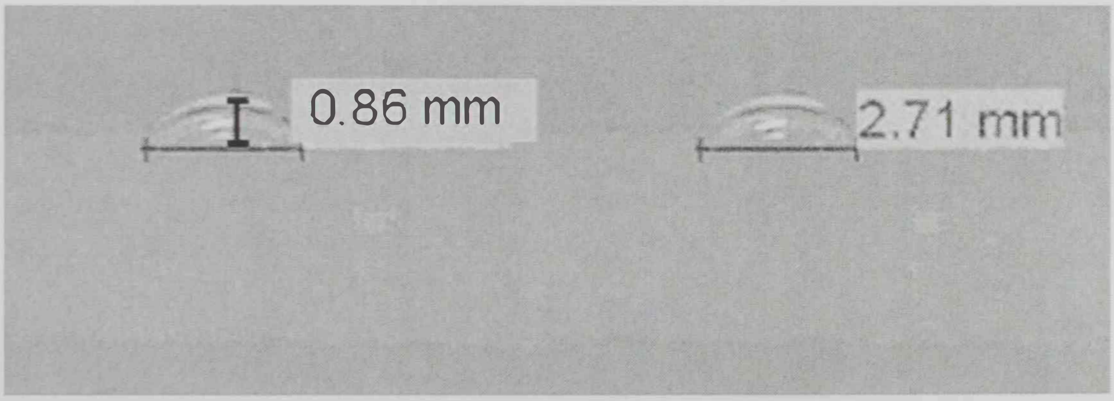


Fig 2.26 Diameter of the base and the height of the droplet

So if we comparing between three technical data for the same liquid / solid and same conduction (see table 2.9), the error percentage in measurement of the contact angle is around 2%, which can be accepted. So we prefer to use Spherical cap approximation, which is easier and more accurate.

Methods	Contact angle
Spherical cap Approximation	70°
Side Image droplet	74°
Contact angle meter	72°

Table 2.9 shows the different on values of contact angle for 1.5μL of Glycerin over PMMA

Chapter 3

Results & Discussion*

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*Part of the result is published by "Alteraifi and Sasa, "The role of Solid on the spreading kinetic of liquid droplet". In "Advance in fluid Mechanics: Computational Method in Multiphase Flow II". (2003), editor Mammoli and Brebbia, WIT press, London.

3.1 Evaporation

Before the onset of presenting results of the set of measurements is made, it is important to ascertain that droplet volume is conserved and evaporation losses are negligible.

3.1.1 Volume conservation

For incompressible fluids, the conservation of volume for the duration of the experiment was examined using the following Equation, which is based on spherical cap approximation:

$$V_i = V_f \qquad (3.1)$$

Where V_i is the initial volume and V_f is the final volume, substitute Eq. 2.2 in 3.1

$$\text{h} = \frac{1}{2} R\theta \qquad (2.2)$$

$$\frac{\pi}{2} hR_i^2 = \frac{\pi}{2} hR_f^2 \qquad (3.2)$$

Substitute Eq. 2.3 in 3.2

$$\frac{\pi}{2} hR^2 = V \qquad (2.3)$$

$$\frac{\pi}{2}(\frac{1}{2} R_i\theta_i)R_i^2 = \frac{\pi}{2}(\frac{1}{2} R_f\theta_f)R_f^2 \qquad (3.3)$$

This, $$R_i^3\theta_i = R_f^3\theta_f \qquad (3.4)$$

where R_f and θ_f are the equilibrium contact radius and equilibrium contact angle, respectively. Figure 3.1 shows cosine of the contact angle, which is obtained using spherical cap approximation, plotted versus the cosine of ($R_f^3\theta_f/R^3$), which is measured experimentally. A straight line with slope of 1 demonstrates clearly that volume of the droplet for all liquids was conserved at least for the duration of the experiment and that evaporation losses are indeed negligible.

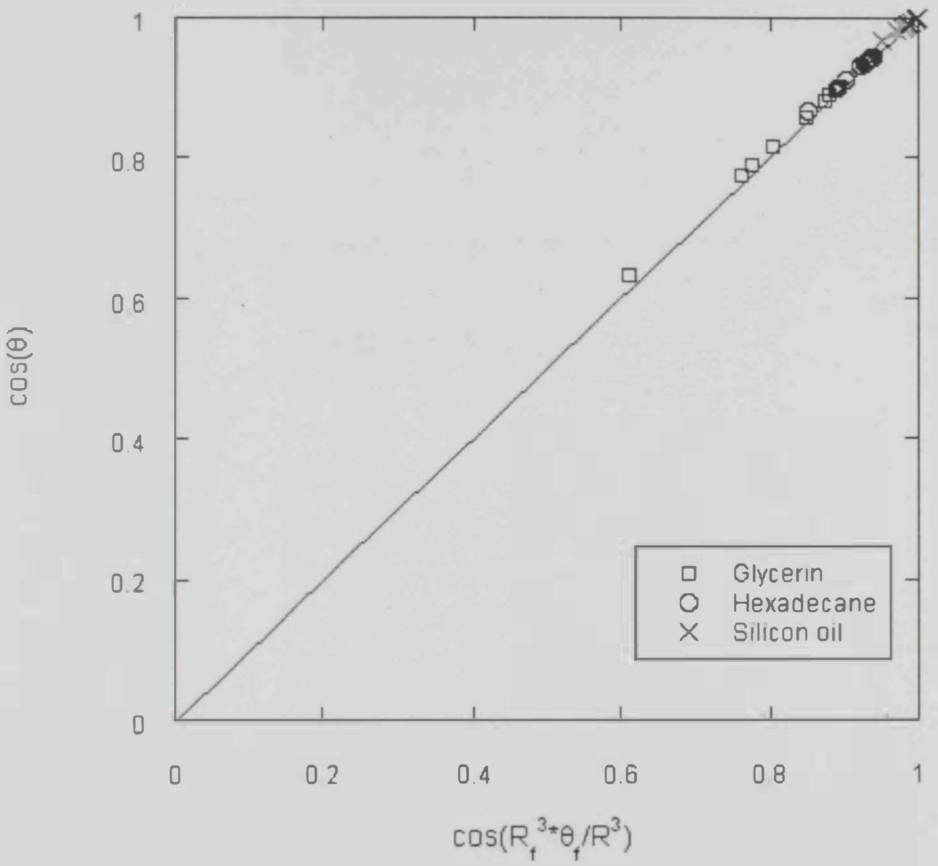

Fig. 3.1 **Volume conservation law Eq. (3.1) for three Liquids (Glycerin, Hexadecane and Silicon oil)**

3.1.2 Evaporation is negligible

For the high vapor liquids, the droplet was allowed to spread and evaporate completely. This to verify that measurements are taken when evaporation is not affecting the spreading rate to be sure there is no losses in the weight.

Fig 3.2 shows that it takes about 800 seconds for 1.5 μL water droplet to evaporation completely. Where as equilibrium spreading is reached after 100 seconds.

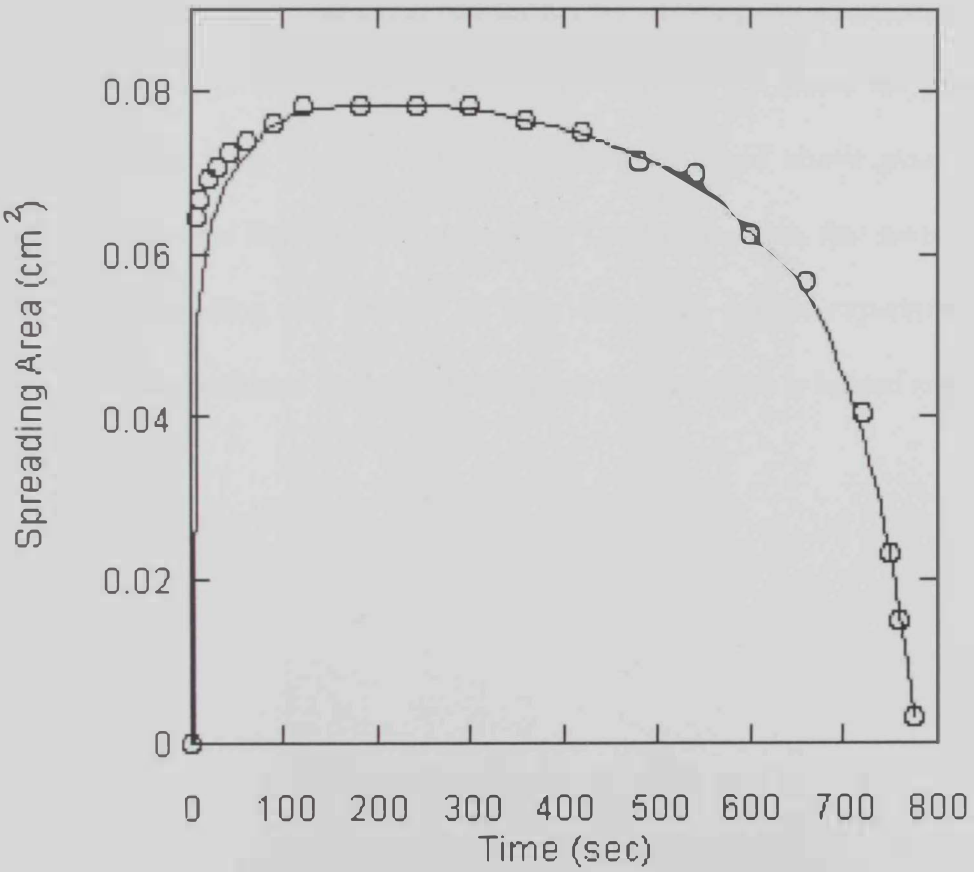

Fig 3.2 **the spreading rate for 1.5μL of water droplet on glass allowed to evaporate completely in 800 seconds**

3.2 Gravity Effect

The importance of gravity relative to capillary forces was inspected using Bond number, *Extrand (1993)*:

$$Bo = \frac{\rho g R_o^2}{\sigma} \qquad (3.5)$$

where g is the gravity acceleration, R_o is the radius of the spherical droplet before spreading and ρ is the liquid density. Bond number is found in the range between 0.115 and 0.362 for the liquids used in this study. Since $Bo < 1$, capillary forces were expected to dominate gravity.

The gravity effect was examined further by allowing the liquid drop to spread while the substrate is flipped up –side –down. Figure 3.3 shows the spreading of Si100 over Glass slide for two cases; spreading of liquid above glass slide and spreading of the same liquid below glass slide. The figure shows that measurement of the areas of spreading are similar in both case and within experimental error. Therefore. This experiment further validated that gravity effect is indeed negligible.

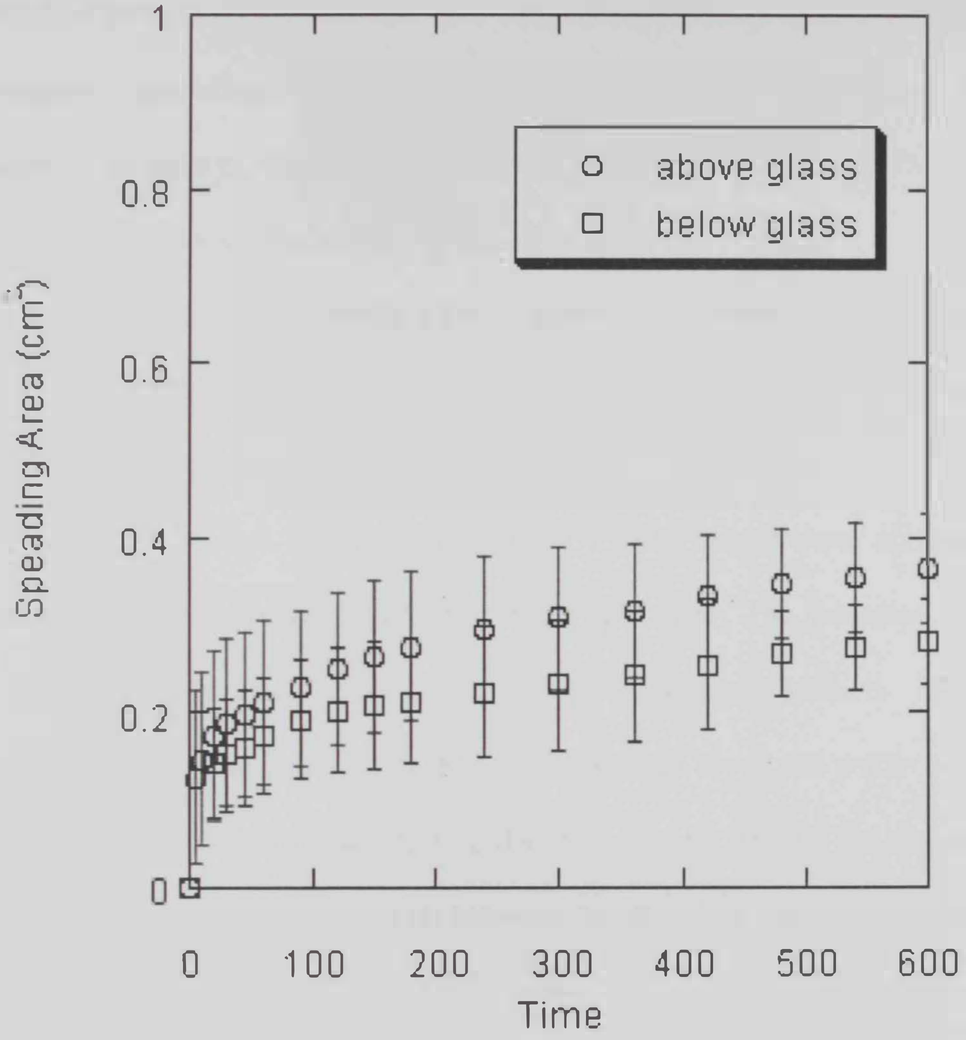

Fig 3.3 the spreading different of Silicon 100 above and below glass surface

3.3 Complete spreading

- **Silicon Oil (100cp and 1000cp)**

All liquids tested exhibited spontaneous spreading rate at the start of the process then passed through a transition zone. After transition, the droplets either continued to spread at slower rate (i.e. complete spreading) or ceased to spread (i.e., incomplete spreading). PDMS-100 and PDMS-1000 are recognized to exhibit complete spreading. Figure 3.4 shows the kinetic spreading of PDMS-1000 over Glass at 5sec, 10 sec, 60 sec and 240 sec, respectively.

Typical data representing PDMS spreading on three surfaces, namely soda-lime glass, PMMA, and PS is shown in Fig. 3.5 and Fig 3.6 for PDMS-100 for PDMS-1000, respectively.

It is noted that the spreading rate of PDMS on the three surfaces behaves similarly, in what appears to be a power law tendency. The spreading behavior on soda-lime glass is nearly identical to that on polystyrene surface. However, the spreading of the same liquid on PMMA exhibits much lower rate within both regimes, i.e., spontaneous and low rate. Noting that both PS and PMMA are organic surfaces does not explain the polarity of their behavior, yet the divergence is undeniable.

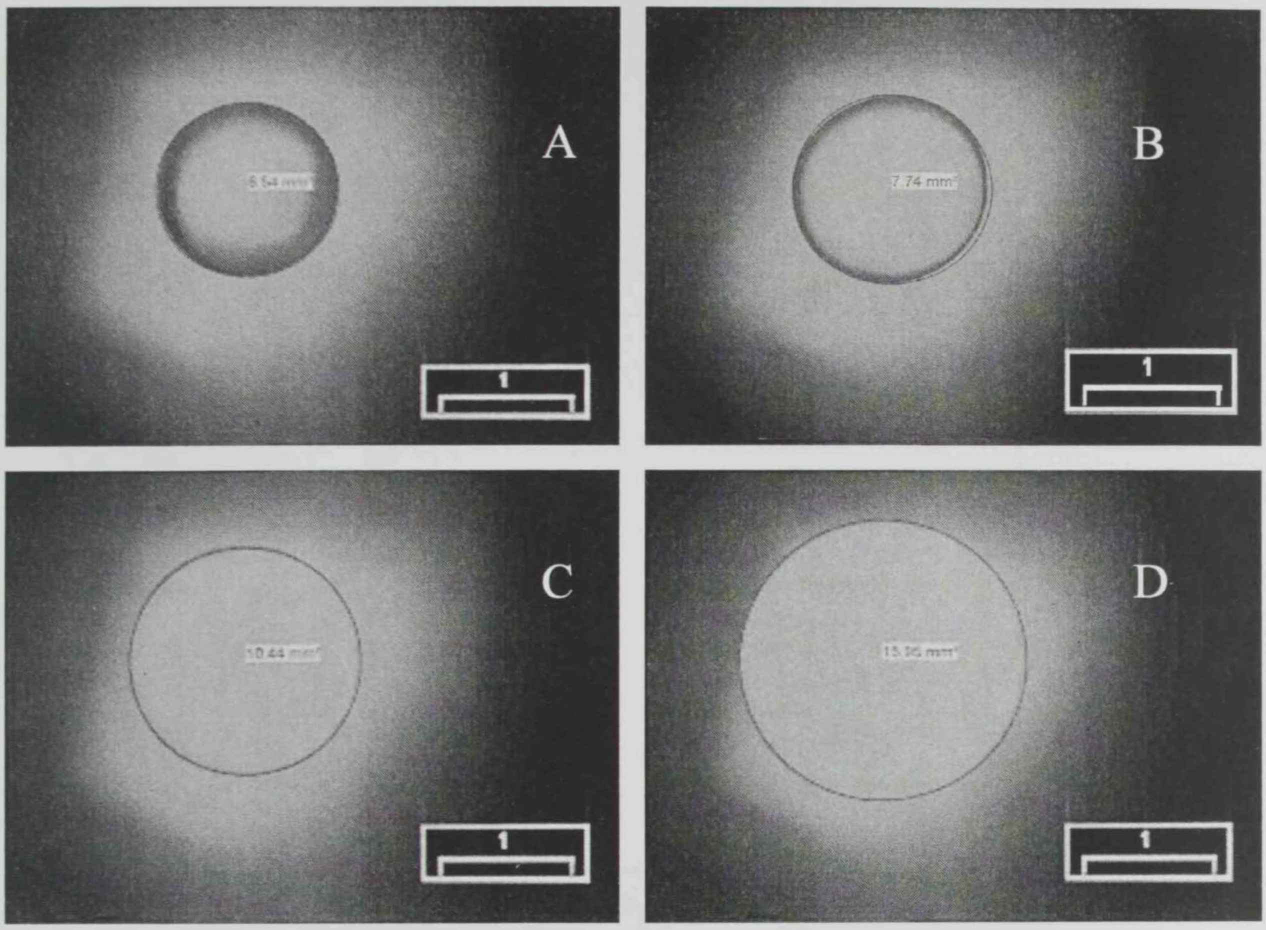

Fig 3.4 Si 1000 spreading over Glass after (a) 5 sec, (b) 10sec , (c) 60 sec and (d) 240 sec (the scale is 1mm)

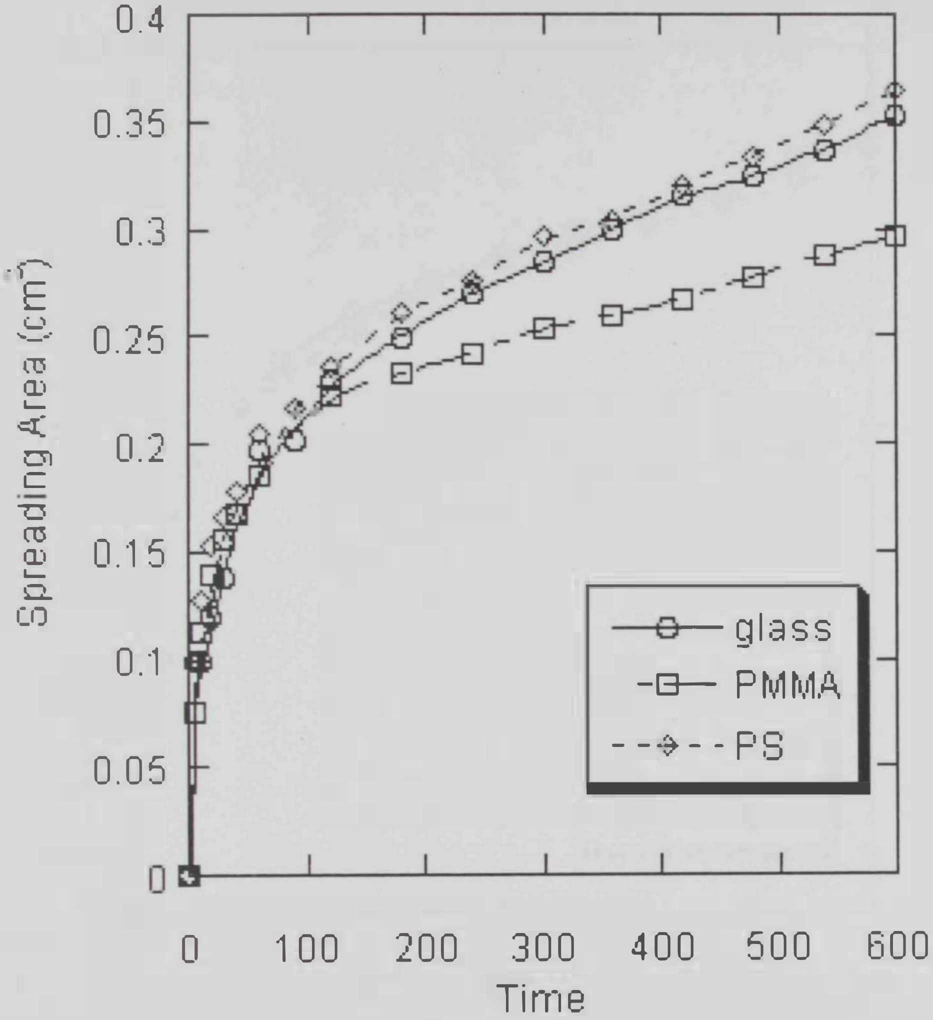

Fig 3.5 Spreading kinetics of PDMS-100 on soda-lime glass, PMMA, and PS

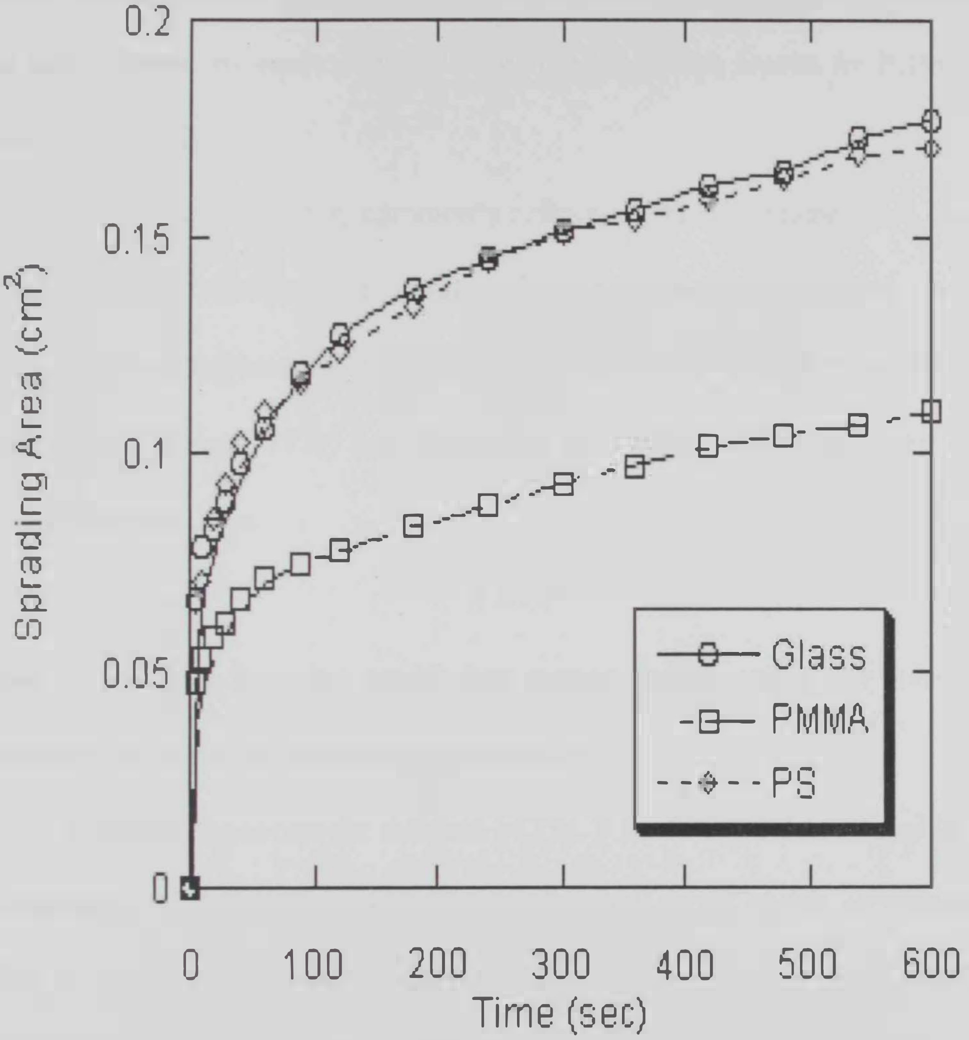

Fig 3.6 Spreading kinetics of PDMS-1000 on soda-lime glass, PMMA, and PS

In this regard, it is worthy to note several theoretical models *(de Gennes, (1985), Tanner (1979) Seaver (1994)* describe the spreading of PDMS on soda-lime glass substrate is in good agreement with the experimental measurements, These models which are derived on basis of different theoretical considerations, give rise to closely similar results, in what appears to be power law relation. It has been shown that these models are equivalent and converges to similar results for PDMS spreading *Alteraifi et al (2003).*

Considering the most commonly referenced model, Tanner law, described the kinetic data as analyzed in terms of Tanner Equation, which is based on hydrodynamic considerations accounting for the surface tension σ and the viscosity μ of the liquid, *Tanner (1979)* and *Elyousfi et al (1998).* Accordingly, the contact area A can be expressed as,

$$A = Ct^n \tag{3.7}$$

where C = kσ/μR_f, R_f is the equilibrium contact radius, and k is a non-dimensional parameter that has to be determined empirically.

Tanner's exponents for the data of Fig. 3.5 and Fig 3.6 are listed in Table 3.1. Accordingly, the behavior of PDMS on glass and on PS yields an exponent of 0.2, which is in agreement with Tanner's theory. However, identical droplets from the same liquid allowed spreading on PMMA exhibit significant departure from the norm. An appreciation of this departure may be seen directly from both curves in Fig 3.5 and 3.6. Identical PDMS droplets produced a contact area of 0.11 cm^2 within about 70 seconds on either glass or polystyrene substrate. On PMMA substrate, the same contact area was reached in 600 seconds that is a tenfold delay, *Tanner (1979).*

Table 3.1 *n* **values according to Tanner Eq. (3.7) fit, for both PDMS spreading on three solids; glass PMMA and PS**

Solids	*N*
Glass	0.20
PS	0.20
PMMA	0.18

Intuitively, one may be lead to believe that the spreading behavior of PDMS on the three different substrates ought to correlate with the critical wetting energy of the solid as defined by *Zisman (1964).* Surprisingly, comparing the three spread exponents (Table 3.1) with the corresponding values of the critical wetting energies (Table 3.2) indicate that the desired correlation does not exist. Soda-lime glass, which's critical wetting energy, is about 70 dyn/cm functions in a manner similar to that of polystyrene, an organic glass whose critical wetting energy is about 32 dyn/cm. In the meantime, polymethylmethacrylate, another organic glass, whose critical wetting energy is 39dyn/cm, departs from both.

Table 3.2 **List of surface(s) used and their critical surface tension for glass, PMMA and PS**

Surface	Surface Critical Energy σ (dyn/cm)
Glass	55-78
PMMA	39
PS	33

The above which display in no uncertain terms that the solid substrate plays a substantial role in the spreading kinetics. An attempt to rationalize the origin of this effect will be presented after examination of the role the solid substrate plays in the case of incomplete spreading. The equilibrium contact area obtained for different liquids over the three surfaces are summarized in Table 3.2 *Myers (1999)*.

3.4 Incomplete spreading

The liquids used in this study can be categorized into three groups: Alcohols groups (glycerin. Polythlenglycol and water). alkane group (hexadecane. dodecane and Undecan). and amid group (formamid and n.ndimethyformanid).

3.4.1 Alcohols groups

Alcohols group's liquids showed maximum spreading area on glass then PMMA then PS. In Fig 3.8. Fig 3.9 and Fig 3.10 show the spreading area verses time in seconds for glycerin. Polythlenglycol and water. respectively. The spreading behavior of glycerin (as example to Alcohols groups) on soda-lime glass. PMMA. and PS was examined. at equilibrium after 240 sec the spreading area are different which is shown in Fig. 3.7. for example the spreading of Glycerin on glass biggest area and PMMA area is bigger than PS spreading area.

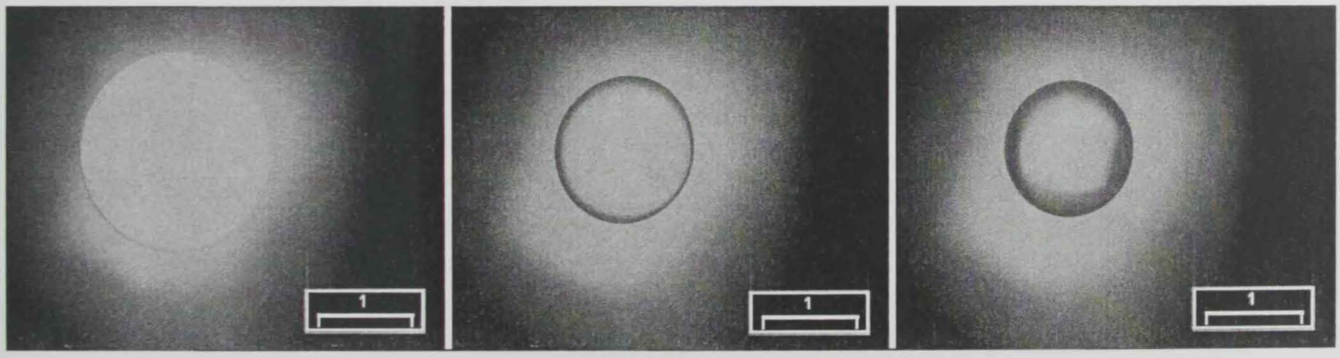

Fig 3.7 Spreading of Glycerin after 240 sec over (a) Glass, (b) PMMA and (c) PS (The scale is 1mm)

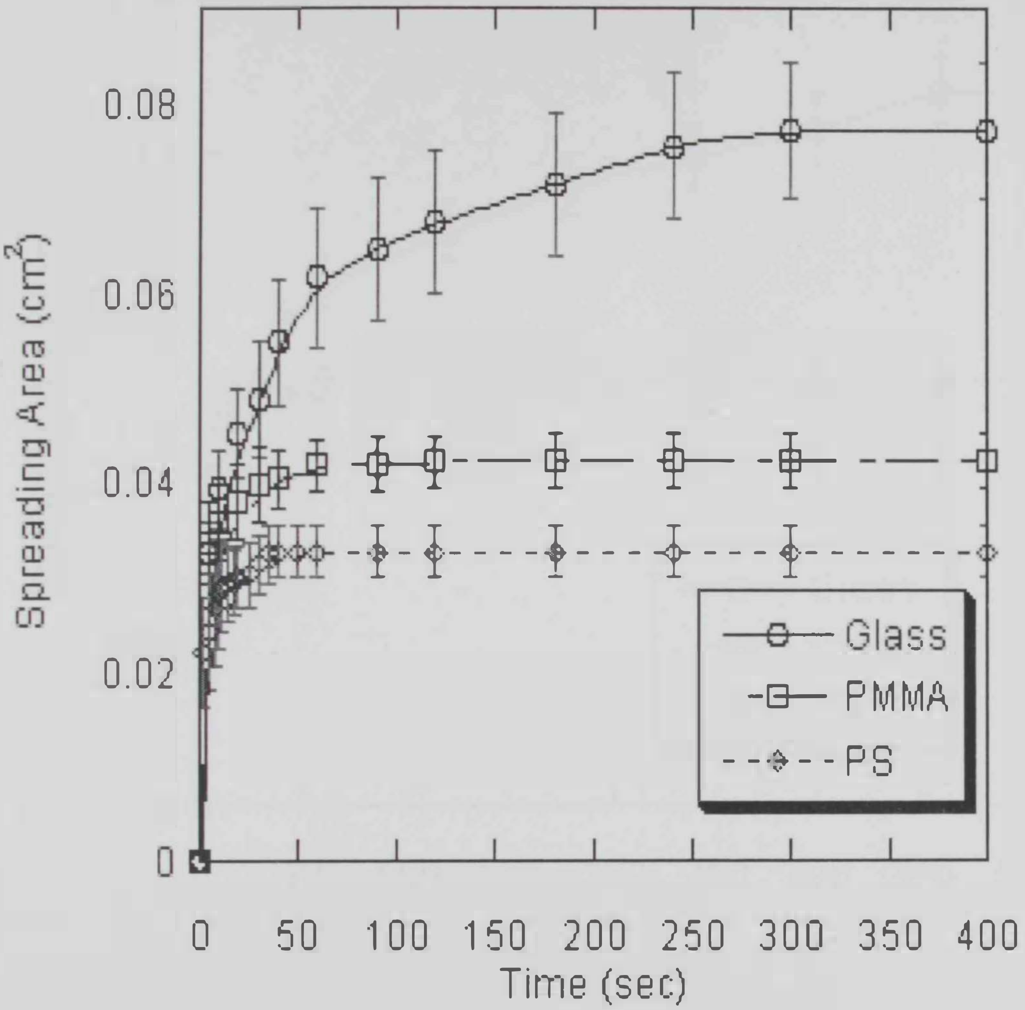

Fig 3.8 Spreading kinetics of glycerin on glass, PMMA, and PS.

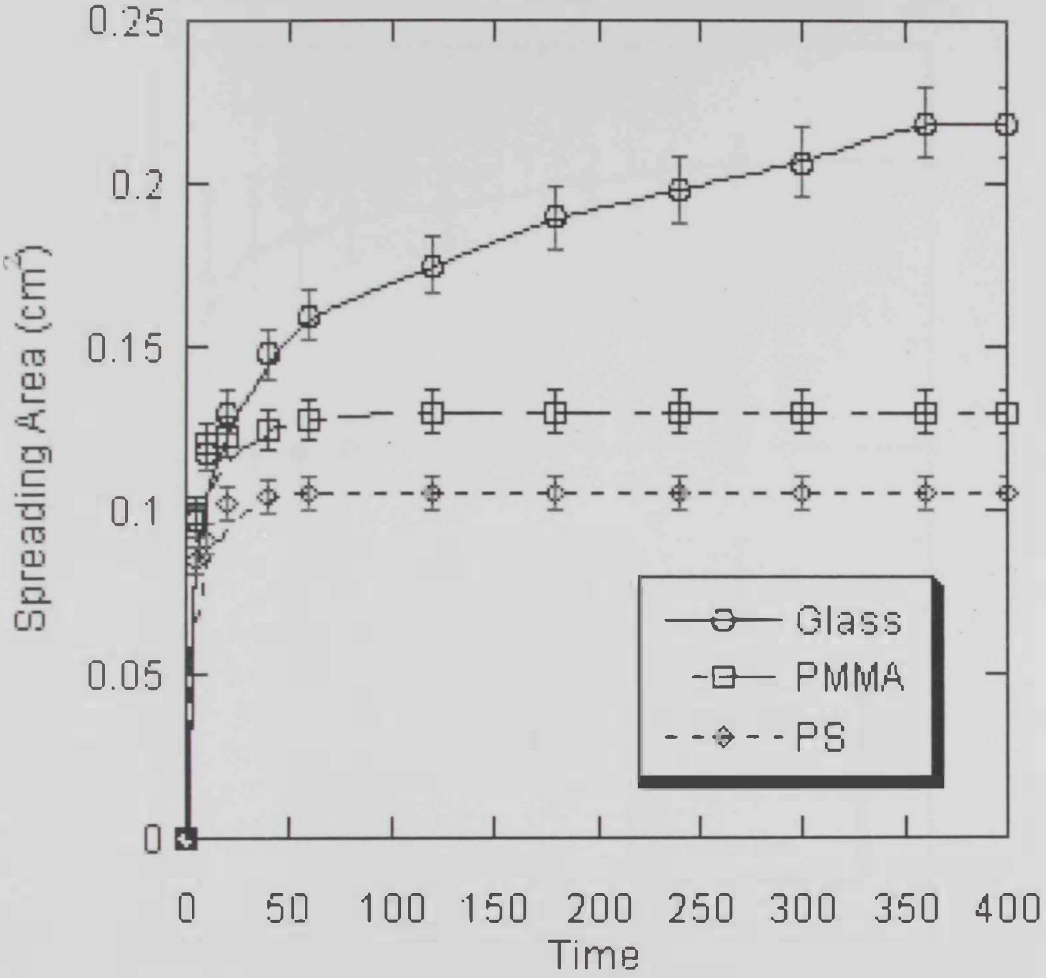

Fig 3.9 **Spreading kinetics of Polythlenglycol on glass, PMMA, and PS.**

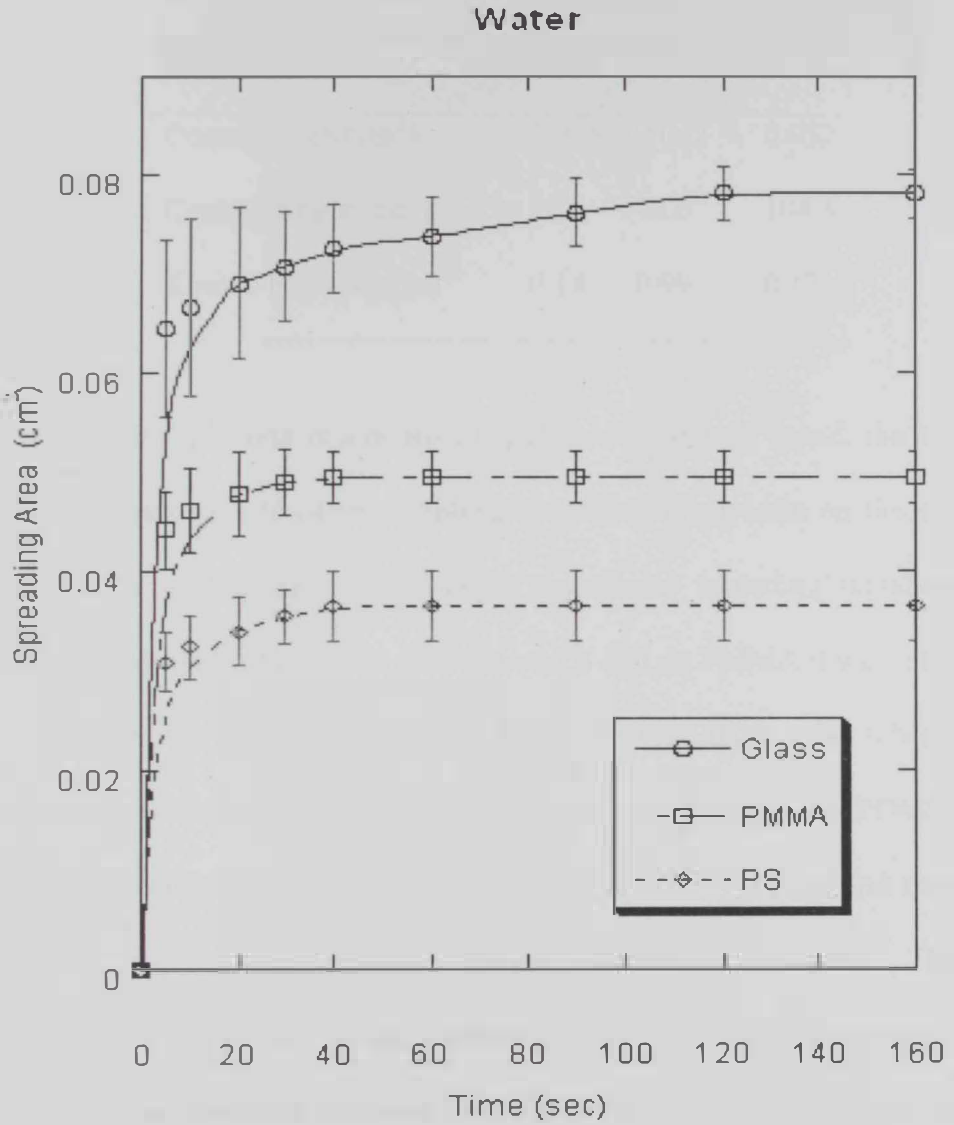

Fig 3.10 Spreading kinetics of Water on glass, PMMA, and PS.

If we consider glycerin as an example of alcohol group, the derived comparative parameters are shown in Table 3.3.

Table 3.3 Contact areas (cm^2), contact angles and n values for spreading of glycerin on glass, PMMA and PS

Solid	Glass	PMMA	PS
Contact Area (cm^2)	0.086	0.042	0.032
Contact Angle, Eq. (2.2)	26.5	70.6	104.5
Kinetic Exponent (n)	0.14	0.09	0.12

Noting that glycerin is a relatively high surface energy liquid, the axiom "like wets like" appears to rationalize equilibrial spreading of glycerin on the same set of solid substrates qualitatively. The largest equilibrial spreading (smallest contact angle) was noted to occur on glass, the least on PS and on PMMA it was intermediate.

However, the kinetic behavior of glycerin on the three solid substrates, does not follow simple energy-based rational. Again, as the case of PDMS, PMMA exhibited the lowest spreading rate as seen in Table 3.3. For a second time PMMA appears deviant as it causes further retardation to the spreading process. This may be related to the high polarity of the methacrylate moiety (particularly the carbonate group) within the chemical structure of the material, a notion that calls for further inquiry.

3.4.2 Alkanes groups (Hexadecane, Dodecane and Undecane)

Alkanes group's liquids showed maximum spreading area on PS then PMMA then glass. Fig 3.12. Fig 3.13 and Fig 3.14 show the spreading area verses time in seconds for Hexadecane. Dodecane and Undecan. respectively.

First the spreading kinetics of a low surface energy liquid on the three solid substrates was examined. Hexadecane (as example to Alkanes group) has been selected for its relatively low surface energy liquid (32 dyn/cm) and for its non-polar character. Fig 3.11 show the spreading kinetic for Hexadecane over PS. In addition. hexadecane is known to exhibit incomplete spreading on soda-lime glass.

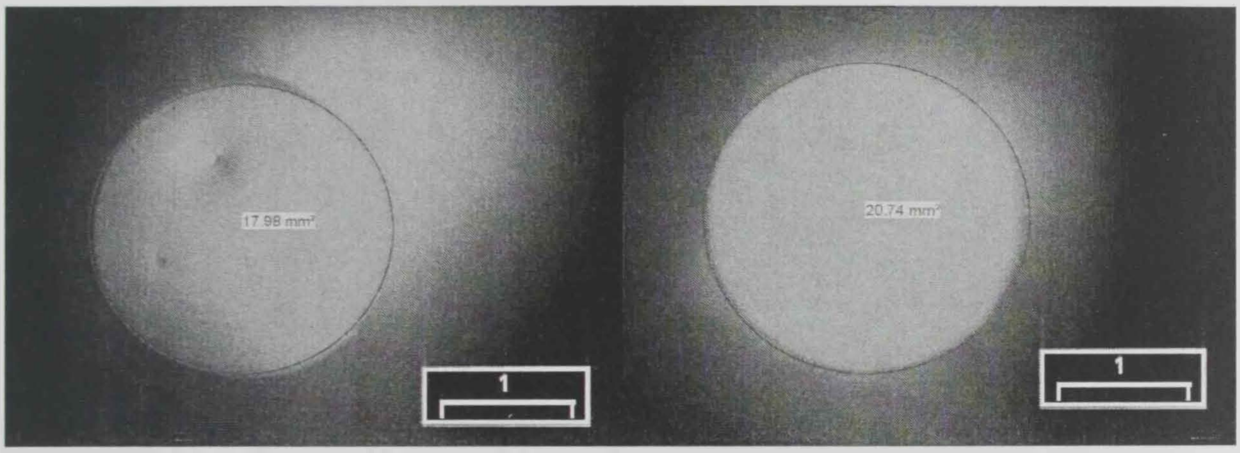

Fig 3.11 Hexadecane over PS (a) after 5 sec (b) after 60 sec (The scale is 1mm)

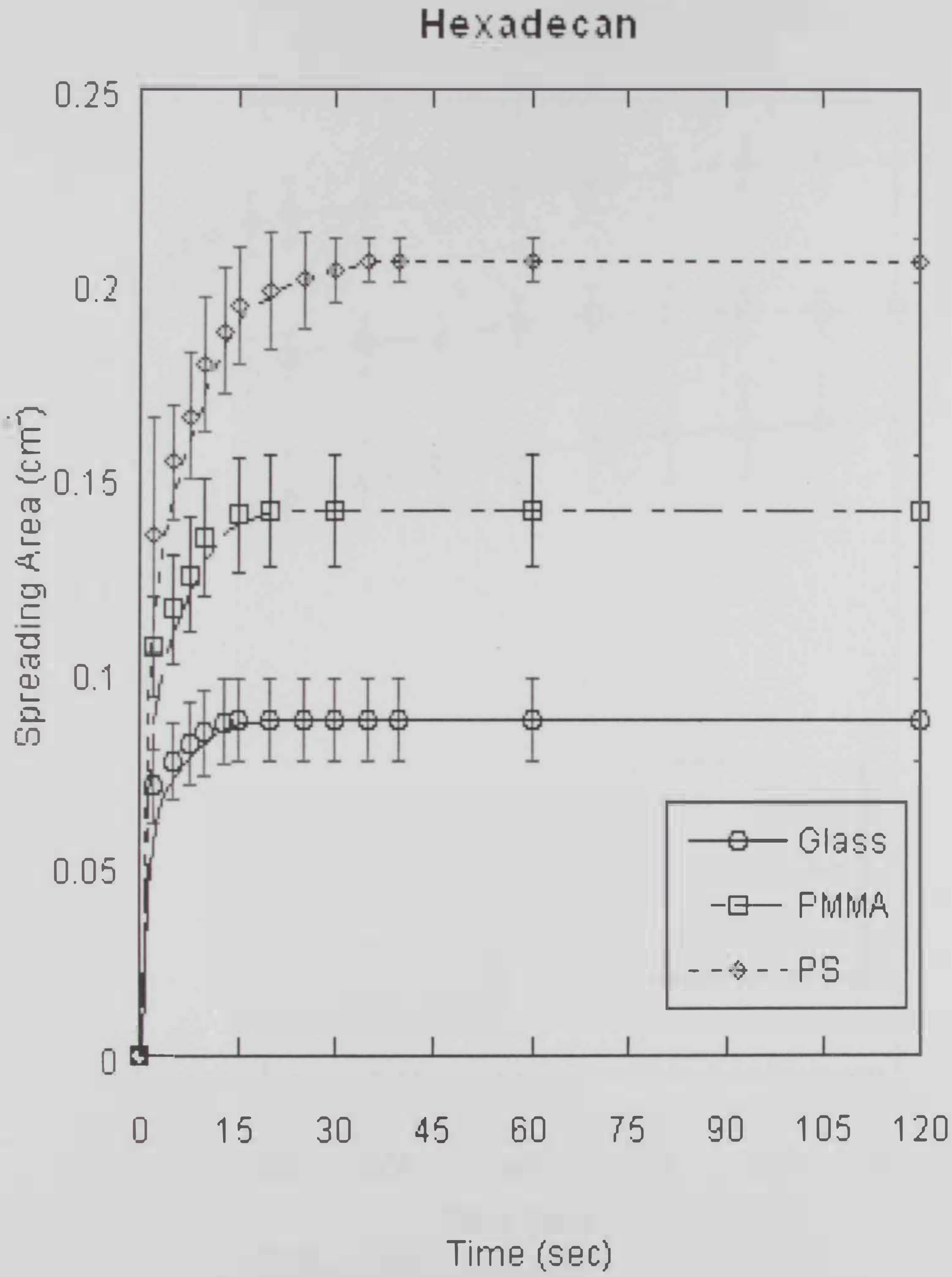

Fig 3.12 **Spreading Kinetics of Hexadecane on PS, PMMA and glass.**

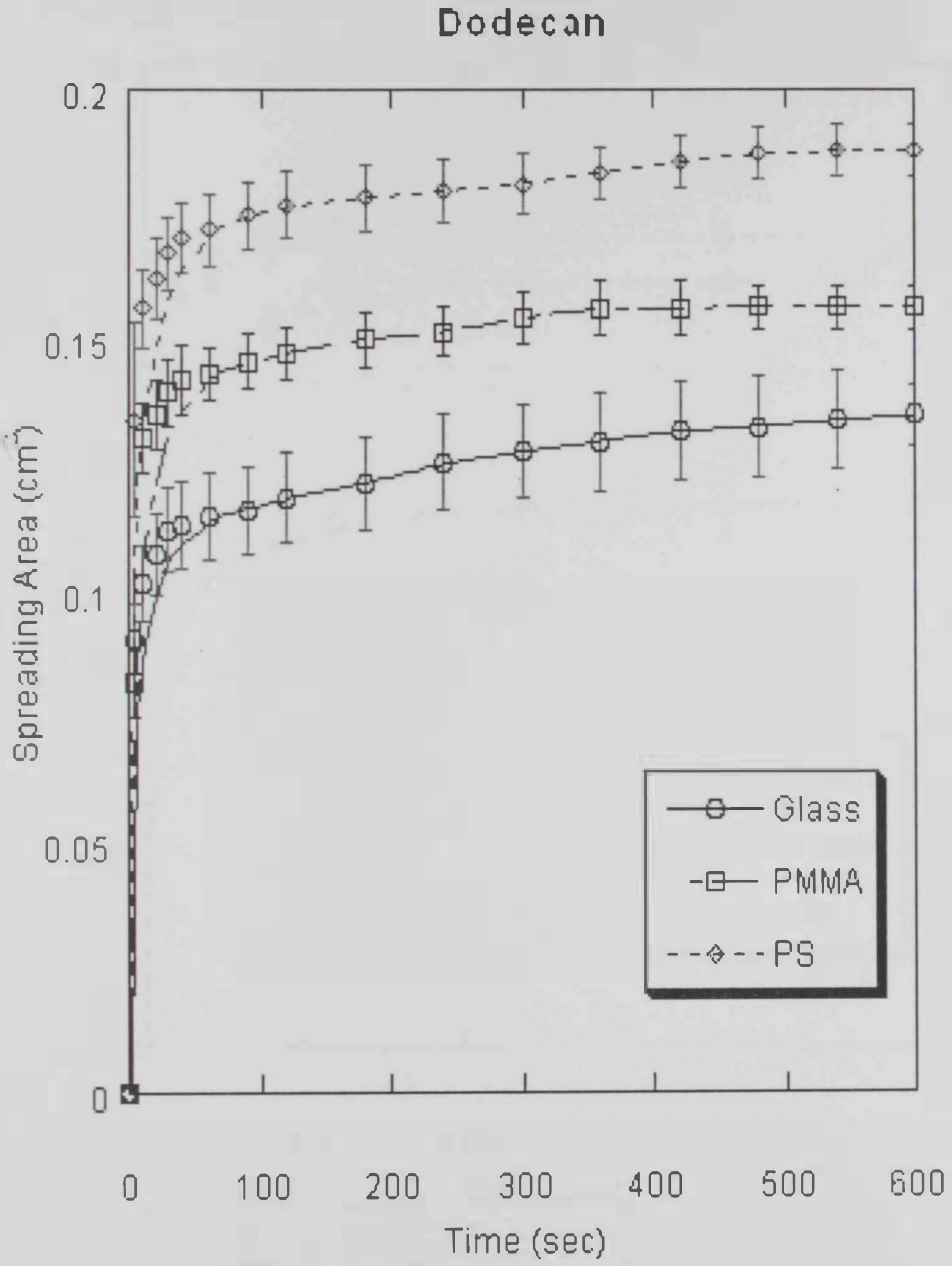

Fig 3 .13 Spreading Kinetics of Dodecane on PS, PMMA and glass.

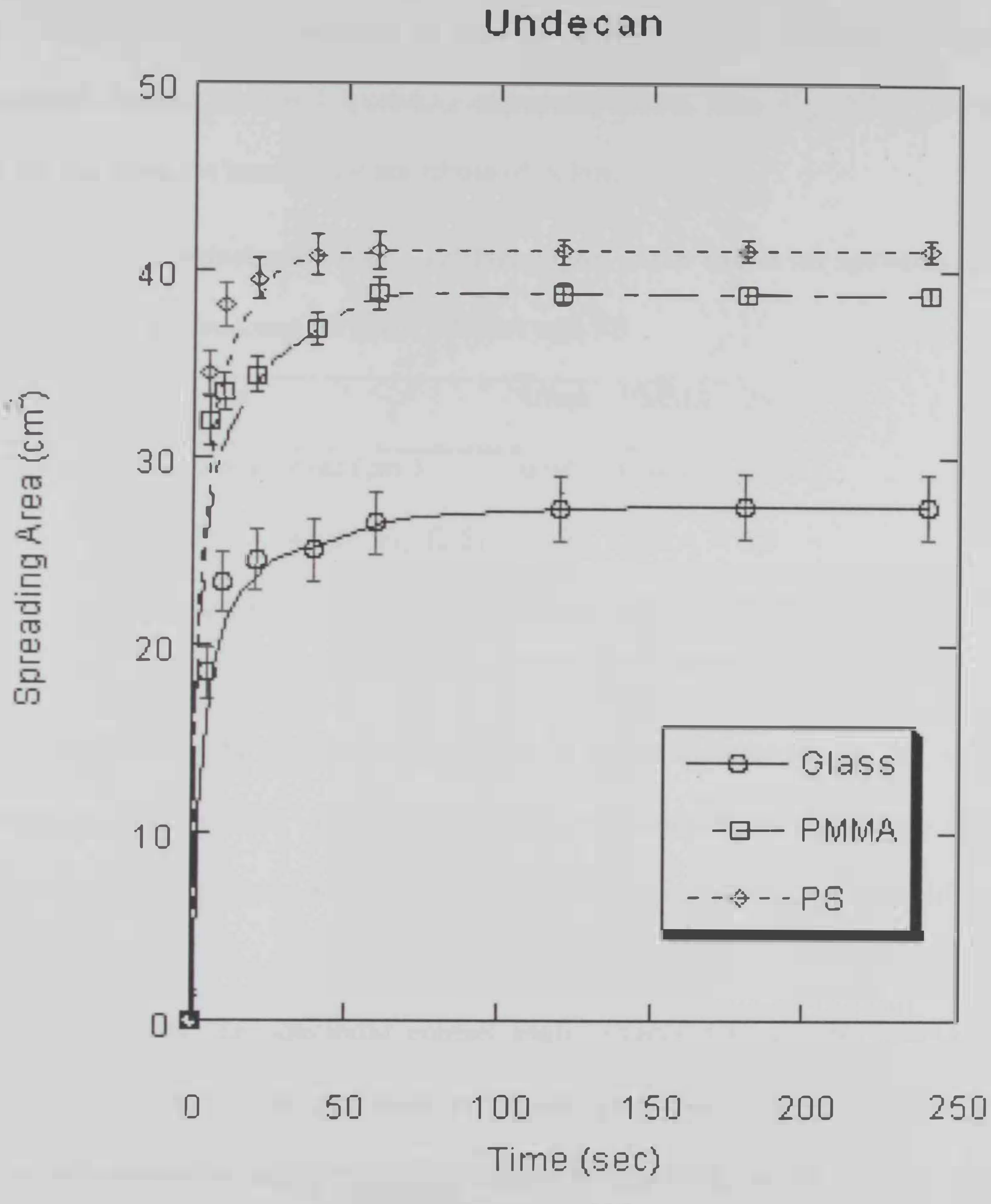

Fig 3.14 **Spreading Kinetics of Undecane on PS, PMMA and glass.**

Two attributes characterize the spreading process: its rate and its equilibrial contact area. Noting that a constant volume droplet (1.5 μl) was used in all experiments, the equilibrial contact area may be taken as a measure of wettability.

If we consider hexadecane as example of alkane group, the estimates of the equilibrial contact area and spreading exponent, drawn from Fig. 3.12 and from Tanner Equation for hexadecane are tabulated below.

Table 3.4 Contact areas (cm^2), contact angles and *n* values for spreading of hexadecane on glass, PMMA and PS

Solid	Glass	PMMA	PS
Contact Area (cm^2)	0.081	0.141	0.205
Contact Angle, Eq. (2.2)	23.9	11.5	6.5
Kinetic Exponent (*n*)	0.10	0.13	0.18

Right away the contributions of each of the solid substrates to the wetting process are unmistakable. Equal droplets from the same liquid allowed to spread under identical conditions on three different substrates produce distinctly different behaviors.

Expectedly, the equilibrial contact angles (Table 3.4) may be qualitatively ranked in accordance with the critical wetting energy of each respective solid. Glass caused hexadecane to assume the least equilibrial spreading (largest contact angle). On the other end, PS with the lowest surface energy produces the largest wetting (smallest contact angle) by hexadecane. PMMA produced intermediate effect. It is useful to bear in mind that hexadecane is a non-polar, low surface energy liquid as is the case with polystyrene. Therefore, it is reasonable to introduce the idiom: "like wets like" to rationalize the equilibrial wetting of hexadecane on the three solids.

This idiom is coined in analogy with to the famous rule "like dissolves like" in physical chemistry.

On the other hand, the kinetic behavior characterized by Tanner's exponent in Table 3.4 suggest that hexadecane spreads the fastest on PS (n = 0.18) and the slowest on soda-lime glass (n = 0.10). PMMA caused intermediate effect (n = 0.13). Clearly, for the present system, the higher the energy of the solid substrate the lower the spreading rate.

3.4.3 Primary amide (Formamid & n.ndimethyformanid)

Primary amide group's liquids showed maximum spreading area on glass then PMMA then PS. Fig 3.16 and Fig 3.17 show the spreading area verses time in seconds for Formamid and n.ndimethyformanid, respectively. The spreading behavior of Formamid (as example to Primary amide group) over Glass shown in Fig 3.15 after 5 sec, 10 sec, 20 sec and 60 sec, respectively. Where it reaches equilibrium after 60.

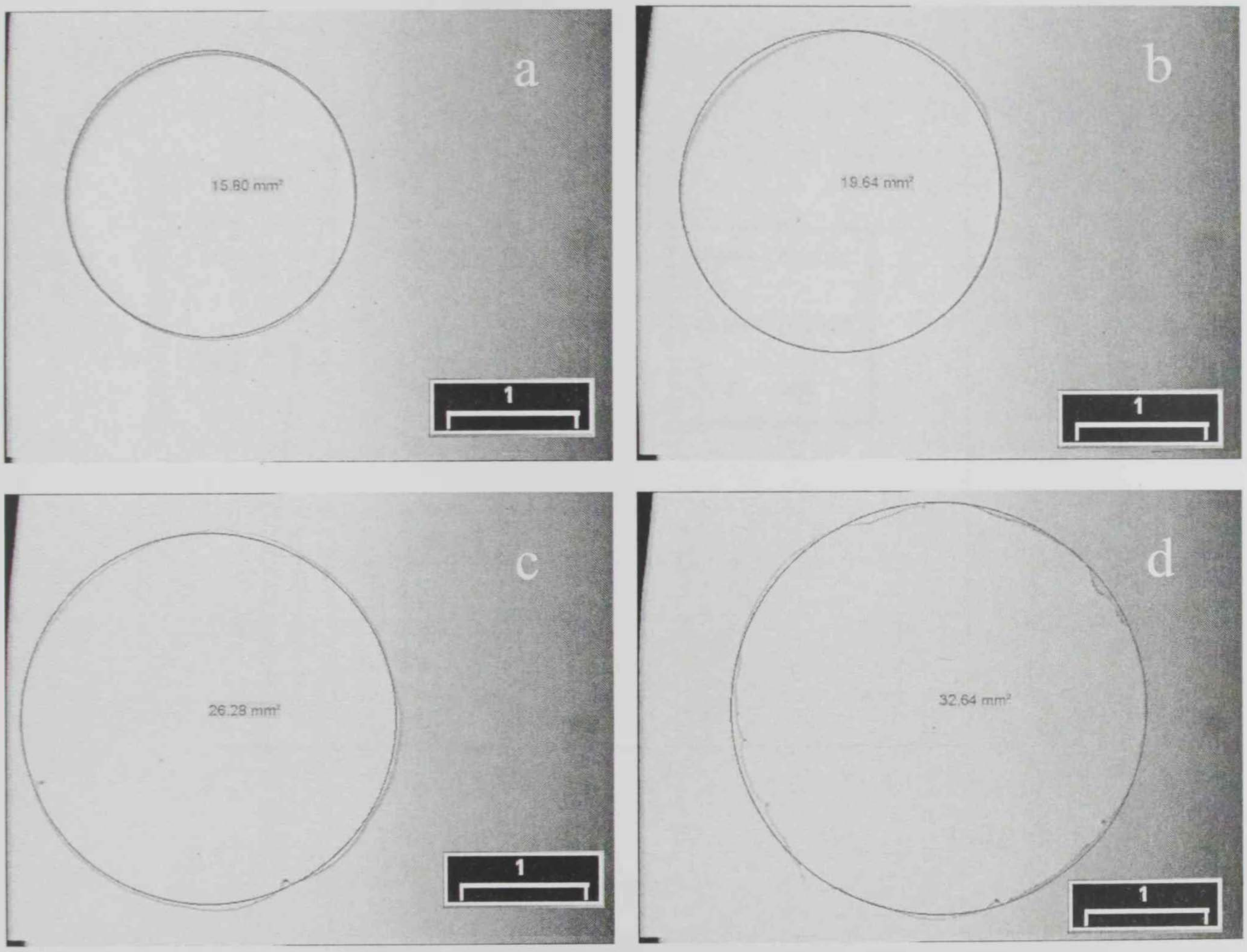

Fig 3.15 Formamid over Glass (a) 5 sec, (b) 10 sec, (c) 20 sec and (d) 60 sec

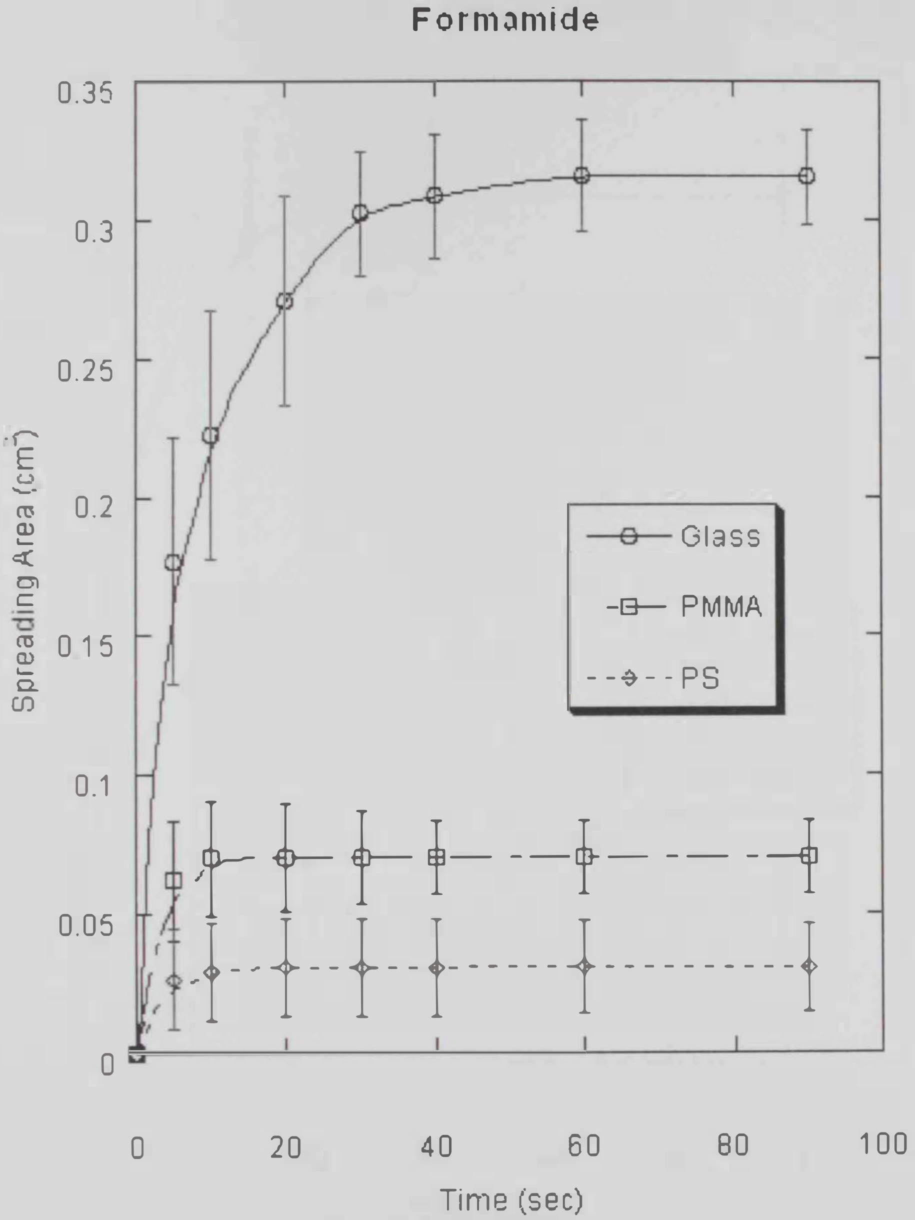

Fig 3. 16 Shows spreading Kinetics of Formamid on PS, PMMA and glass

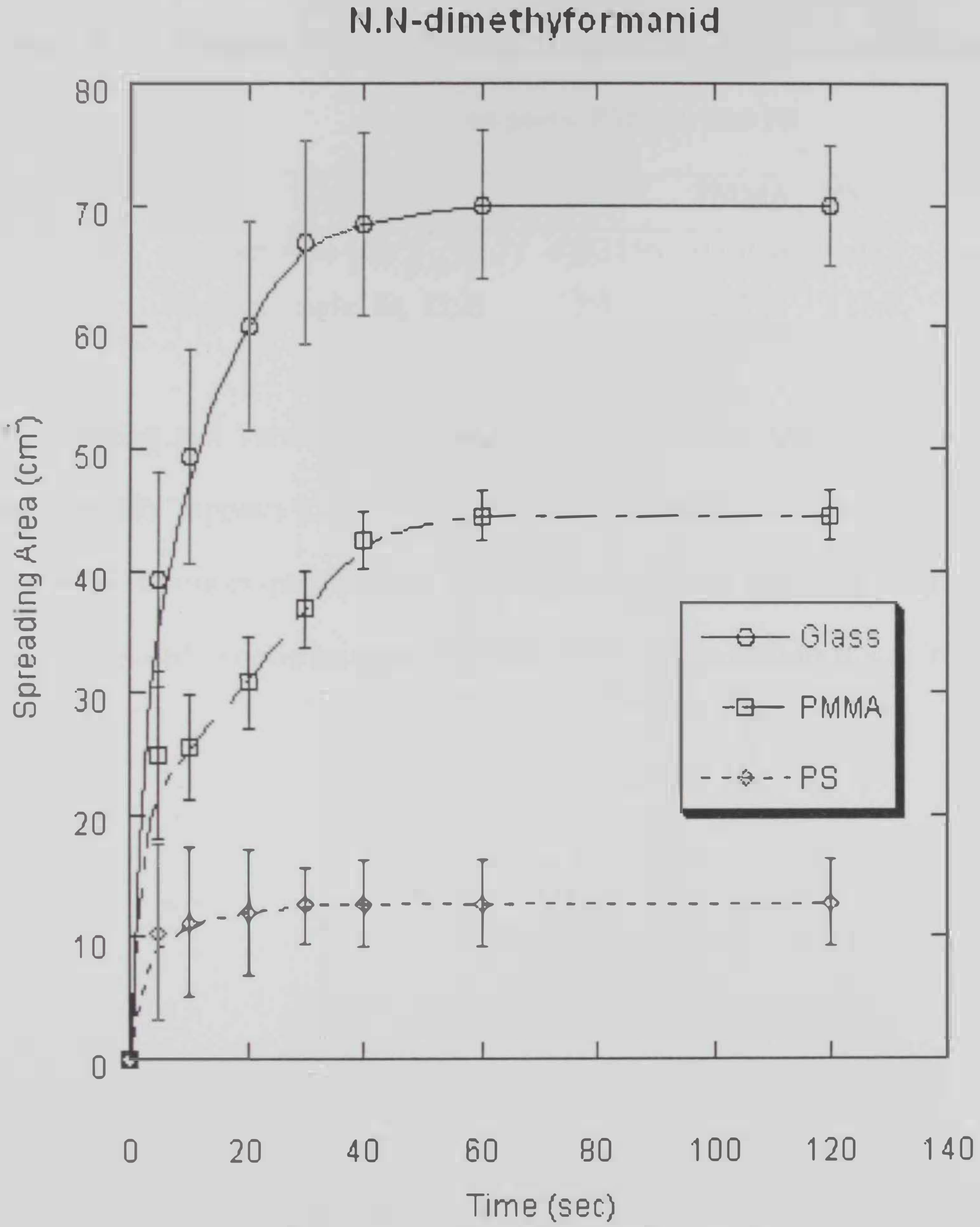

Fig 3.17 Shows spreading Kinetics of N.N-dimethyformanid on PS, PMMA and glass

If we consider Formamid as an example of Primary amide group, the derived comparative parameters are shown in Table 3.5

Table 3.5 Contact areas (cm^2) and contact angles for spreading of Formamid on glass, PMMA and PS

Solid	Glass	PMMA	PS
Contact Area (cm^2)	0.3156	0.07016	0.031
Contact Angle, Eq. (2.2)	3.4	32.7	111.6

Noting that Formamid is a relatively high surface energy liquid, the axiom "like wets like" appears to rationalize equilibrial spreading of Formamid on the same set of solid substrates qualitatively. The largest equilibrial spreading (smallest contact angle) was noted to occur on glass, the least on PS and on PMMA it was intermediate.

3.5 Attempt to explain the role of solid

Sparse evidence in the literature suggests that the solid substrate plays a key role. For example, it was noted that PDMS droplets exhibited spreading kinetics on soda lime glass that is grossly different from that on Teflon *Ogarev (1974.)*. Also in Hoffman's experiment *Hoffman (1975)* PDMS was found to spread readily on the glass surface, unlike the two other liquids; "Admix-760" and "Santicizer-405". To lure these liquids "to give a large static contact angle as desired" the glass surface was altered by vigorous chemical and thermal treatment. These experimental evidences suggest that solids indeed play an important role in the spreading kinetics of a liquid.

This role is in fact described in Young's equations in term of the solid/liquid interfacial energy. It rises from the molecular interaction between liquids and solids.

The contact angle has been widely conceived as a thermodynamic quantity. Accordingly remained to be the main focus of most theoretical and experimental investigations. The rate of change in the contact angle has been commonly used as the relevant parameter of spreading dynamics in spite of difficulties associated with contact angle measurements that are well recognized in the literature *Marmur(1983), de Gennes(1985) and Berg (1993)*. Considering that the velocity of the contact line is the pertinent quantity, it is therefore reasonable to regard the change in the contact area as the flux of the process. It is only recently that a rational link has been made between the contact angle and the contact area using spherical cap approximation *de Gennes (1985)*.

The above observations are summed up in two themes Equilibrial spreading and kinetics:

(1) PDMS is a very low surface energy liquid, which exceptionally spreads continuously on almost all solids and therefore exhibits what is called "complete"

spreading on all three solids. Therefore discussion of differences due to the substrate bares no relevance.

Hexadecane, a low surface energy liquid, was noted to exhibit equilibrial wetting that is proportional to the critical wetting energy of the solid substrate. Glycerin, a high-energy liquid, was noted to exhibit equilibrial wetting that is inversely proportional to the wetting energy of the solids. These observations are related to Young's equation, where

$$\cos\theta = (\sigma_{SV} - \sigma_{SL}) / \sigma_{LV} \qquad (3.9)$$

Provided that σ_{SV} is somehow related to Zisman's energy (the critical wetting energy). In a pragmatic sense, "Like wets like" seems to work.

(2) Spreading Kinetics: present models based on hydrodynamic theory generally relate the driving term to the surface tension of the liquid and the dissipative resistance is attributed to viscous friction, which is calculated assuming no-slip condition on the solid. The relevant parameter is the viscosity of the liquid. Our results discussed above assert the presence of additional dissipative mechanism, which must exist at the interface. We coin the term "interfacial viscosity". This agrees with the view accepted by many interfacial researchers that the interface (interphase) is a material at its own, whose properties are distinctly different from both phases.

Chapter 4

Conclusions

The complex physical processes occurring when a liquid comes into contact with a solid plays an important role in determining the spreading rate depending on the chemical processes on surface, material, position on energy line and interfacial tension between two or three phases.

A set of spreading experiments was designed to examine the validity of current models of spreading kinetics. A number of liquids having a wide range of surface tension and viscosity were used on soda-lime glass, PMMA and PS. The law advanced by *de Gennes (1985)* and by *Seaver and Berg (1994)* are found to describe the spreading behavior of silicone oil, but departed significantly in the case of other liquids. It suggested that the surface tension seemingly acts to retain the spherical geometry of the droplet surface, the difference between the solid-vapor and solid-liquid interfacial energies, on the other hand, acts to extend the contact area in approach to its equilibrial state, be it complete or incomplete. Viscous dissipation, expectedly, acts to retard the spreading rate noted in both cases, at the end of a regime of spontaneous spreading.

The present investigations provide experimental evidence that the solid substrate plays a significant role in the spreading kinetics of liquids and in determining equilibrial contact angle. The latter was found explicable on the basis of the axiom “like wets like”. Contributions of the solid substrate to the spreading kinetics are attributed to specific solid-liquid interactions, of dissipative nature, which manifest itself only at the interface. The term “interfacial viscosity” is coined to account for this phenomenon.

Future work is to explore the concept of critical surface energy to create a wide variety of surface polymers coating with known surface energy, which can be controlled and correlated the critical surface energy with polymer structure.

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