THE EFFECT OF TEMPERATURE ON POLYMETHYL METHACRYLATE ACRYLIC (PMMA)

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ABSTRACT

This research is about the effect of temperature onpolymethyl methacrylate. From the investigation of thermo-mechanical properties of polymethyl methacrylate or PMMA, the film of PMMA has been prepared. The glass transition temperature of pure PMMA sample has also been obtained in order to determine its physical state and its influence in other properties such as toughness and stiffness. An effort has also been made to study the storage modulus (E'), loss modulus (E") and Tan δ in a temperature range from 32°C to 140°C by DMA. It has been observed that storage modulus decreases with temperature due to thermal expansion of films. On the other hand Tan δ increases up to glass transition temperature beyond which it shows decreasing trend towards melting. Glass transition temperature (Tg) is found to be 82.1°C. The stress strain curves of PMMA films at room temperature and at different temperature (32°C–90°C) have been obtained. The results show that the mechanical properties i.e. Young modulus, toughness and tensile strength decrease with increasing temperature whereas the elongation at break shows increasing behavior with temperature in Table 1: PMMA on the effect of temperature. This trend in the different mechanical properties is explained on the basis of free volume theory. The references are from F.S Robert (2012). Thermal Analysis of Materials.Materials Engineering.Marcel Dekker, Inc. p. 2. ISBN 0-8247-8963-6, U.F Hans (2010). The Dynamics of Heat (2ed.).Springer.p. 211. ISBN 978-1-4419-7603-1, Kutz, Myer (2002). Handbook of Materials Selection.John Wiley & Sons.p. 341. ISBN 0-471-35924-6.

ABSTRAK

Kajian ini adalah mengenai kesan suhu ke atas 'polymethyl methacrylate acrylic' (PMMA). Dari kajian berkenaan termo-mekanikal 'polymethyl methacrylate acrylic' atau PMMA, filem daripada PMMA telah disediakan. Suhu peralihan kaca PMMA sampel tulen juga telah diperolehi untuk menentukan keadaan fizikal dan pengaruhnya lain seperti kekuatan dan ketegangan. Usaha juga telah dibuat untuk mengkaji modulus penyimpanan (E '), modulus kerugian (E '') dan Tan δ dalam pelbagai suhu dari 18° C hingga 140°C oleh DMA. Ia telah diperhatikan bahawa simpanan modulus berkurangan dengan suhu disebabkan oleh pengembangan haba filem. Sebaliknya Tan δ meningkatkan sehingga suhu peralihan kaca di luar yang ia menunjukkan trend menurun ke arah lebur. Suhu peralihan kaca (Tg) didapati 82.1°C. Tarikan tekanan filem PMMA pada suhu bilik dan suhu yang berbeza (32°C - 90°C) telah diperolehi. Keputusan menunjukkan bahawa sifat-sifat mekanikal iaitu modulus Young, kekuatan dan kekuatan tegangan menurun dengan peningkatan suhu manakala pemanjangan pada waktu rehat menunjukkan peningkatan tingkah laku dengan suhu di Jadual 1: PMMA tentang kesan suhu. Trend dalam sifat-sifat mekanikal yang berbeza dijelaskan berdasarkan 'free volume theory'. Rujukan adalah dari F.S Robert (2012). Thermal Analysis of Materials.Materials Engineering.Marcel Dekker, Inc. p. 2. ISBN 0-8247-8963-6, U.F Hans (2010). The Dynamics of Heat (2ed.).Springer.p. 211. ISBN 978-1-4419-7603-1, Kutz, Myer (2002). Handbook of Materials Selection.John Wiley & Sons.p. 341. ISBN 0-471-35924-6.

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LIST OF ABBREVIATIONS

ICI	Imperial Chemical Industries
PMMA	Polymethyl Methacrylate Acrylic
UV	Ultraviolet

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Polymethyl methacrylate (PMMA) is a synthetic resin that is produced from the polymerization of methyl methacrylate. A transparent and rigid plastic, PMMA is often used as a substitute for glass in products such as shatterproof windows, skylights, illuminated signs, and aircraft canopies. It is sold under the trademarks Plexiglas, Lucite, and Perspex. [19]

PMMA is an ester of methacrylic acid ($CH_2=C[CH_3]CO_2H$) that is belongs to the important acrylic family of resins. In the modern production it is obtained principally from propylene, a compound refined from the lighter fractions of crude oil. Propylene and benzene are react together to form cumene, or isopropyl benzene. The cumene is oxidized to cumene hydroperoxide, which is treated with acid to form acetone. The acetone is in turn converted in a three-step process to methyl methacrylate ($CH_2=C[CH_3]CO_2CH_3$), a flammable liquid. Methyl methacrylate, in bulk liquid form or suspended as fine droplets in water, is polymerized (its molecules linked together in large numbers) under the influence of free-radical initiators to form solid PMMA. The structure of the polymer repeating unit is:

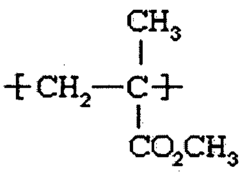

Figure 1.1: Polymethyl methacrylate structure

The presence of the pendant methyl (CH_3) groups prevents the polymer chains from packing closely in a crystalline fashion and from rotating freely around the carbon-carbon bonds. As a result, PMMA is a tough and rigid plastic. In addition, it has almost perfect transmission of visible light, and, because it retains these properties over years of exposure to ultraviolet radiation and weather, it is an ideal substitute for glass. A most successful application is in internally lighted signs for advertising and directions. PMMA is also employed in domed skylights, swimming pool enclosures, aircraft canopies, instrument panels, and luminous ceilings. For these applications the plastic is drawn into sheets that are machined or thermoformed, but it is also injection-molded into automobile lenses and lighting-fixture covers. Because PMMA displays the unusual property of keeping a beam of light reflected within its surfaces, it is frequently made into optical fibers for telecommunication or endoscopy.

Polymethyl methacrylate was discovered in the early 1930s by British chemists Rowland Hill and John Crawford at Imperial Chemical Industries (ICI) in England. ICI registered the product under the trademark Perspex. About the same time, chemist and industrialist Otto Röhm of Rohm and Haas AG in Germany attempted to produce safety glass by polymerizing methyl methacrylate between two layers of glass. The polymer separated from the glass as a clear plastic sheet, which Röhm gave the trademarked name Plexiglas. Both Perspex and Plexiglas were commercialized in the late 1930s. In the United States, E.I. du Pont de Nemours & Company (now DuPont Company) subsequently introduced its own product under the trademark Lucite. The first major application of the new plastic took place during World War II, when PMMA was made into aircraft windows and bubble canopies for gun turrets. Civilian applications followed after the war.

In this research, the aim for the effect of temperature on physical properties of polymethyl methacrylate is to determine the best effect on PMMA by different temperature on producing the material to give a great strength of PMMA. By considering the difference of temperature use, this research is also about to study the effect of temperature related to strength of PMMA. The results will be shown for the best product made of PMMA for future industries.

1.2 Problem Statement

The rising global demand for materials with a great strength and quality such as transparent glass, medical technologies and implants, and others product made by PMMA has led to the search for alternative way. The product made by PMMA has been discovered by the chemists to create an acrylic glass or organic glass. This effect of temperature on process of polymethyl methacrylate (PMMA) will be conducted leading to a new era to have a great product from PMMA materials with a high strength.

1.3 Research Objectives

The primary objective of the current research is to investigate the effect of temperature on polymethyl methacrylate (PMMA) physical properties.

1.4 Scopes of study

In order to achieve the objective of this work, the outline of research scopes for the current research are as follows:

i) To study the effect of temperature on PMMA

ii) To investigate the mechanical tensile strength of PMMA

1.5 Significance of Study

i) To apply the concept of thermal energy during heating process

ii) Analyzing the effect of temperature on PMMA by apply different temperature.

iii) Compare the strength of PMMA on the effect of temperature.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides a literature review for the current research on the effect of temperature on polymethyl methacrylate (PMMA). It is divided into four sections; the first section discusses about polymethyl methacrylate (PMMA) and its application. Second section provides the methods for mechanical testing on PMMA, while the third section is devoted for the effect of temperature on PMMA. Finally, the last section is about thermal analysis of PMMA.

2.2 Polymethyl Methacrylate (PMMA)

2.2.1 Properties of PMMA

PMMA is a strong and lightweight material. It has a density of 1.17–1.20 g/cm3, [1][2] which is less than half that of glass.[1] It also has good impact strength, higher than both glass and polystyrene; however, PMMA's impact strength is still significantly lower than polycarbonate and some engineered polymers. PMMA ignites at 460 °C (860 °F) and burns, forming carbon dioxide, water, carbon monoxide and low-molecular-weight compounds, including formaldehyde. [3]

PMMA transmits up to 92% of visible light (3 mm thickness), and gives a reflection of about 4% from each of its surfaces on account of its refractive index (1.4914 at 587.6 nm).[4] It filters ultraviolet (UV) light at wavelengths below about 300 nm (similar to ordinary window glass). Some manufacturers [5] add coatings or additives to PMMA to improve absorption in the 300–400 nm range. PMMA passes infrared light of up to 2800 nm and blocks IR of longer wavelengths up to 25000 nm. Colored PMMA varieties allow specific IR wavelengths to pass while blocking visible light(for remote control or heat sensor applications, for example).

PMMA swells and dissolves in many organic solvents; it also has poor resistance to many other chemicals on account of its easily hydrolyzed ester groups. Nevertheless, its environmental stability is superior to most other plastics such as polystyrene and polyethylene, and PMMA is therefore often the material of choice for outdoor applications. [6] PMMA has a maximum water absorption ratio of 0.3–0.4% by weight.[3] Tensile strength decreases with increased water absorption.[7] Its coefficient of thermal expansion is relatively high at (5–10)×10−5 /K.[8]

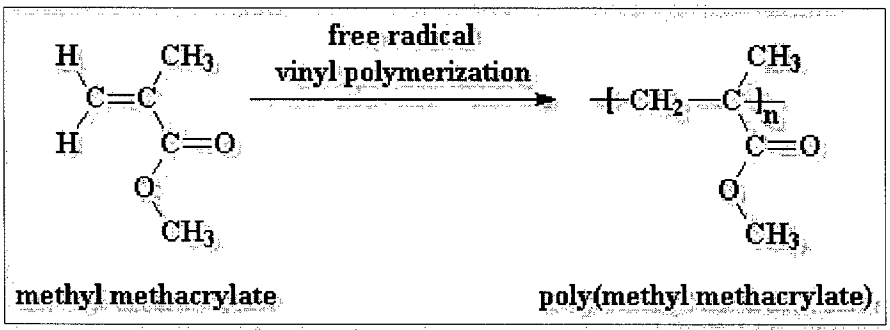

Figure 2.1: Formation of polymethyl methacrylate from methyl methacrylate

Table 2.1: Physical Properties of PMMA at 25 °C and 100kPa

Quantity	Value	Unit
Chemical formula	$(C_5O_2H_8)_n$	
Molar mass	Varies	
Melting point	160	°C
Thermal expansion	50 – 90	$e^{-6/K}$
Thermal conductivity	0.167 – 0.25	W/m.K
Specific heat	1466 – 1466	J/kg.K
Glass temperature	105 – 105	°C
Service temperature	-40 – 90	°C
Density	1170 – 1200	kg/m^3
Resistivity	1e + 19 – 0	$Ohm.mm^2/m$
Breakdown potential	16 – 30	kV/mm
Dielectric loss factor	0.04 - 0.06	
Friction coefficient	0.54 - 0.54	
Refraction index	1.492 - 1.492	
Shrinkage	0.3 - 0.8	%
Water absorption	0.3 - 0.4	%

2.2.2 Application of PMMA

PMMA is a versatile material and has been used in a wide range of fields and applications. Polymethyl methacrylate (PMMA) is a clear plastic, used as a shatterproof replacement for glass. The clear barrier at the ice rink which keeps hockey pucks from flying in the faces of hockey fans is made of PMMA. The chemical company Rohm and Haas makes windows out of it and calls it Plexiglas®. Ineos Acrylics also makes it and calls it Lucite. Lucite is used to make the surfaces of hot tubs, sinks, one-piece bathtub/shower units, among other things.

When it comes to making windows, PMMA has another advantage over glass. PMMA is more transparent than glass. When glass windows are made too thick, they become difficult to see through. But PMMA windows can be made as much as 13 inches (33 cm) thick, and they're still perfectly transparent. This makes PMMA a wonderful material for making large aquariums, with windows which must be thick in order to contain the high pressure of millions of gallons of water. In fact, the largest single window in the world, an observation window at California's Monterrey Bay Aquarium, is made of one big piece of PMMA which is 54 feet long, 18 feet high, and 13 inches thick (16.6 m long, 5.5 m high, and 33 cm thick).

PMMA is also found in paint. Acrylic "latex" paints often contain PMMA suspended in water. But PMMA is more than just plastic and paint. Often lubricating oils and hydraulic fluids tend to get really thick and even gummy when they get really cold. This is a real pain when you're trying to operate heavy construction equipment in really cold weather. But when a little bit PMMA is dissolved in these fluids it keeps them from getting thick in the cold, and machines can be operated down to -100°C (-150°F), that is, presuming the rest of the machine can take that kind of cold.

2.2.2.1 Transparent glass substitute:

PMMA acrylic glass is commonly used for constructing residential and commercial aquariums. Designers started building big aquariums when polymethyl methacrylate could be used. It is less-used in other building types due to incidents such as the Summerland disaster. Acrylic is used for viewing ports and even complete pressure hulls of submersibles, such as the Alicia submarine's viewing sphere and the window of the bathyscaphe Trieste. PMMA is used in the lenses of exterior lights of automobiles. [9] The spectator protection in ice hockey rinks is made from PMMA. Historically, PMMA was an important improvement in the design of aircraft windows, making possible such iconic designs as the bombardier's transparent nose compartment in the Boeing B-17 Flying Fortress. lPolice vehicles for riot control often have the regular glass replaced with acrylic to protect the occupants from thrown objects.Acrylic is an important material in the making of certain lighthouse lenses.[10]PMMA (under the brand name "Lucite") was used for the ceiling of the Houston Astrodome.

2.2.2.2 Medical technologies and implants

PMMA has a good degree of compatibility with human tissue, and can be used for replacement intraocular lenses in the eye when the original lens has been removed in the treatment of cataracts. This compatibility was discovered in WWII RAF pilots, whose eyes had been riddled with PMMA splinters coming from the side windows of their Supermarine Spitfire fighters – the plastic scarcely caused any rejection, compared to glass splinters coming from aircraft such as the Hawker Hurricane.[11] Historically, hard contact lenses were frequently made of this material. Soft contact lenses are often made of a related polymer, where acrylate monomers containing one or more hydroxyl groups make them hydrophilic.

In orthopedic surgery, PMMA bone cement is used to affix implants and to remodel lost bone. It is supplied as a powder with liquid methyl methacrylate (MMA). When mixed these yield a dough-like cement that gradually hardens. Surgeons can judge the curing of the PMMA bone cement by pressing their thumb on it. Although PMMA is biologically compatible, MMA is considered to be an irritant and a possible carcinogen. PMMA has also been linked to cardiopulmonary events in the operating room due to hypotension.[12] Bone cement acts like a grout and not so much like a glue in arthroplasty. Although sticky, it does not bond to either the bone or the implant, it primarily fills the spaces between the prosthesis and the bone preventing motion. A disadvantage of this bone cement is that it heats up to 82.5 °C (160.5° F) while setting that may cause thermal necrosis of neighboring tissue. A careful balance of initiators and monomers is needed to reduce the rate of polymerization, and thus the heat generated. A major consideration when using PMMA cement is the effect of stress shielding. Since PMMA has a Young's modulus greater than that of natural bone, the stresses are loaded into the cement and so the bone no longer receives the mechanical signals to continue bone remodeling and so resorption will occur.[13]

Emerging biotechnology and Biomedical research uses PMMA to create microfluidic lab-on-a-chip devices, which require 100 micrometre-wide geometries for routing liquids. These small geometries are amenable to using PMMA in a biochip fabrication process and offers moderate biocompatibility. Bioprocess chromatography columns use cast acrylic tubes as an alternative to glass and stainless steel. These are pressure rated and satisfy stringent requirements of materials for biocompatibility, toxicity and extractable.

2.2.2.3 Artistic and aesthetic uses

Acrylic paint essentially consists of PMMA suspended in water; however since PMMA is hydrophobic, a substance with both hydrophobic and hydrophilic groups needs to be added to facilitate the suspension.Modern furniture makers, especially in the 1960s and 1970s, seeking to give their products a space age aesthetic, incorporated Lucite and other PMMA products into their designs, especially office chairs. Many other products (for example, guitars) are sometimes made with acrylic glass to make the commonly opaque objects translucent.

Perspex has been used as a surface to paint on, for example by Salvador Dalí.Diasec is a process which uses acrylic glass as a substitute for normal glass in picture framing. This is done for its relatively low cost, light weight, shatter-resistance, aesthetics and because it can be ordered in larger sizes than standard picture framing glass.From approximately the 1960s onward, sculptors and glass artists such as Leroy Lamis began using acrylics, especially taking advantage of the material's flexibility, light weight, cost and its capacity to refract and filter light.

In the 1950s and 1960s, Lucite was an extremely popular material for jewellery, with several companies specialized in creating high-quality pieces from this material. Lucite beads and ornaments are still sold by jewelry suppliers.Acrylic Sheets are produced in dozens of standard colors, most commonly sold using color numbers developed by Rohm & Haas in the 1950's.

2.3 The Effect Of Temperature

The effect of temperature onprocess is refer to the basic concept of thermal energy because of the thermal energy is the portion of the thermodynamic or internal energy of a system that is responsible for the temperature of the system.[14][15] The thermal energy of a system scales with its size and is therefore an extensive property. It is not a state function of the system unless the system has been constructed so that all changes in internal energy are due to changes in thermal energy, as a result of heat transfer (not work). Otherwise thermal energy is dependent on the way or method by which the system attained its temperature.

From a macroscopic thermodynamic description, the thermal energy of a system is given by its constant volume specific heat capacity *C(T)*, a temperature coefficient also called thermal capacity, at any given absolute temperature (*T*):

$$U_{thermal} = C(T) \cdot T.$$

The heat capacity is a function of temperature itself, and is typically measured and specified for certain standard conditions and a specific amount of substance (molar heat capacity) or mass units (specific heat capacity). At constant volume (V), C_V it is the temperature coefficient of energy.[16] In practice, given a narrow temperature range, for example the operational range of a heat engine, the heat capacity of a system is often constant, and thus thermal energy changes are conveniently measured as temperature fluctuations in the system.In the microscopical description of statistical physics, the thermal energy is identified with the mechanical kinetic energy of the constituent particles or other forms of kinetic energy associated with quantum-mechanical microstates.

2.4 Tensile Testing

A tensile test, also known as tension test, is probably the most fundamental type of mechanical test which can be performed perform on material. Tensile tests are simple, relatively inexpensive, and fully standardized. By pulling on something, you will very quickly determine how the material will react to forces being applied in tension. As the material is being pulled, you will find its strength along with how much it will elongate. [20]

2.4.1 Hooke's Law

For most tensile testing of materials, you will notice that in the initial portion of the test, the relationship between the applied force, or load, and the elongation the specimen exhibits is linear. In this linear region, the line obeys the relationship defined as "Hooke's Law" where the ratio of stress to strain is a constant, or $\frac{\sigma}{\varepsilon} = E$. E is the slope of the line in this region where stress (σ) is proportional to strain (ε) and is called the "Modulus of Elasticity" or "Young's Modulus".

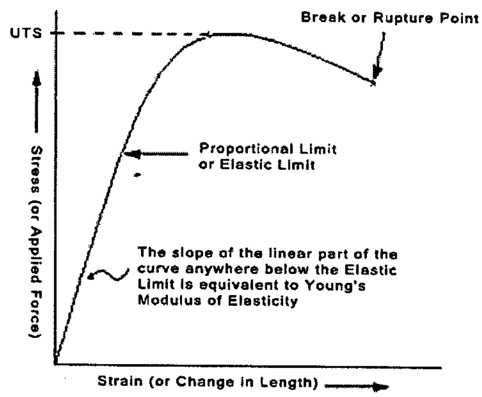

Figure 2.2: Tensile Testing Curve (a)

2.4.2 Modulus of Elasticity

The modulus of elasticity is a measure of the stiffness of the material, but it only applies in the linear region of the curve. If a specimen is loaded within this linear region, the material will return to its exact same condition if the load is removed. At the point that the curve is no longer linear and deviates from the straight-line relationship, Hooke's Law no longer applies and some permanent deformation occurs in the specimen. This point is called the "elastic, or proportional, limit". From this point on in the tensile test, the material reacts plastically to any further increase in load or stress. It will not return to its original, unstressed condition if the load were removed. [20]

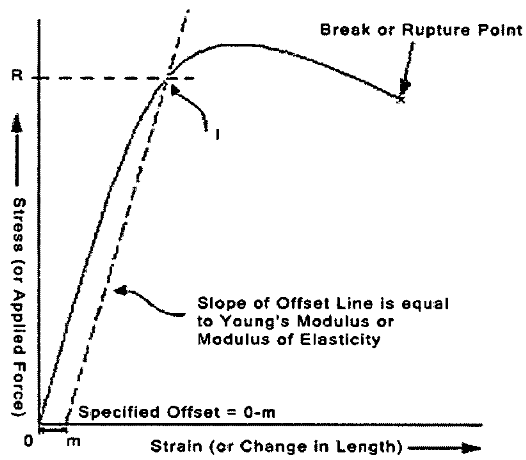

Figure 2.3: Tensile Testing Curve (b)

CHAPTER 3

MATERIALS AND METHODS

3.1 Overview

This paper presents, the result of this evaluation as optimum operating condition such as operating temperature at atmospheric condition and tensile testing of materials. The evaluation of this scenario for PMMA product will give high quality of strength and flexible on surrounding. By considering the effect of surrounding temperature makes the research being compared from 3 times on the same temperature to give a better reading of maximum stress of sample.

3.2 Materials

- Polymethyl methacrylate acrylic (PMMA) sample.

3.3 Equipment

- Universal Tensile Machine (Autograph AG-X Series)

Control system with high performance and safety. The software connects to the unit under test and the connector. Test results of high quality. Have a resolution up to 1/1000 times the load cell. Machines with a wide selection of accessories. Meet the needs of users. Sort the results of ongoing work. The spacious living area. Confident with Over-stroke limit and Emergency-stop. moving the direction switch. Not exceed the defined range. Quick and easy data transfers whether by internet or thumb drive.

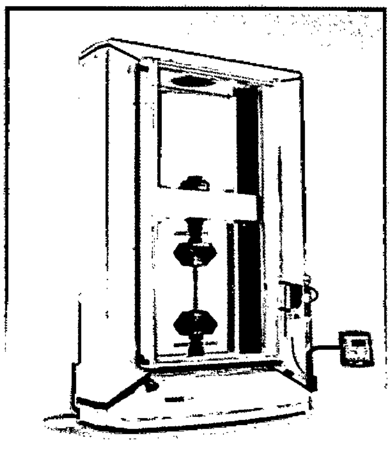

Figure 3.1: Universal Tensile Machine (Autograph AG-X Series)

- IR Thermometer (Lutron Infrared Thermometer - TM-919AL)
- Oven

3.4 Experiment Procedure

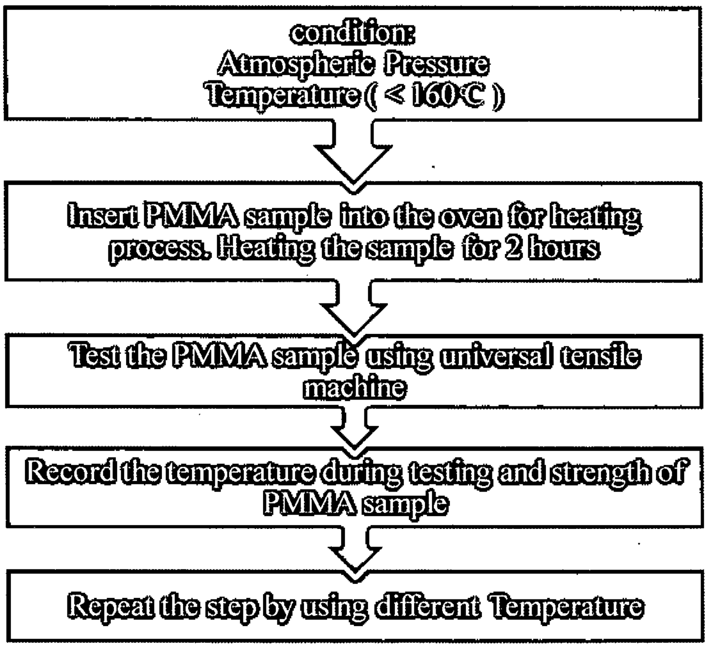

Figure 3.2: Process Flow of Experiment

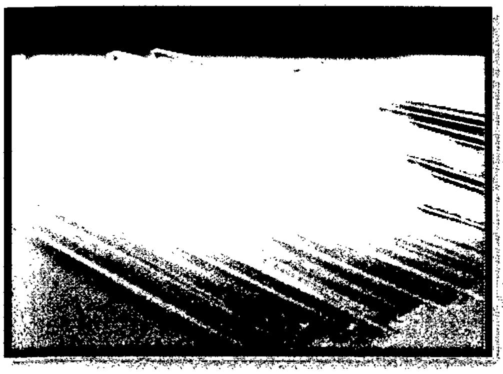

Figure 3.3: PMMA Sample

Figure 3.4: IR Thermometer

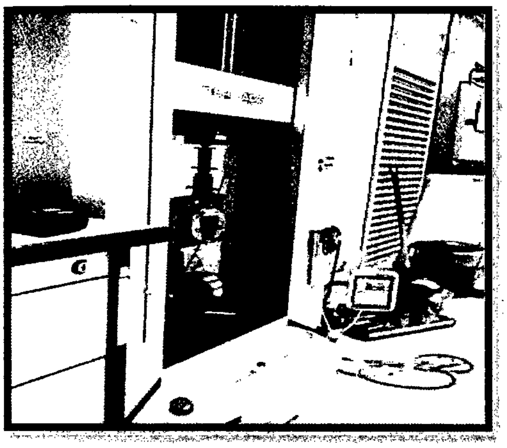

Figure 3.5: Universal Tensile Machine

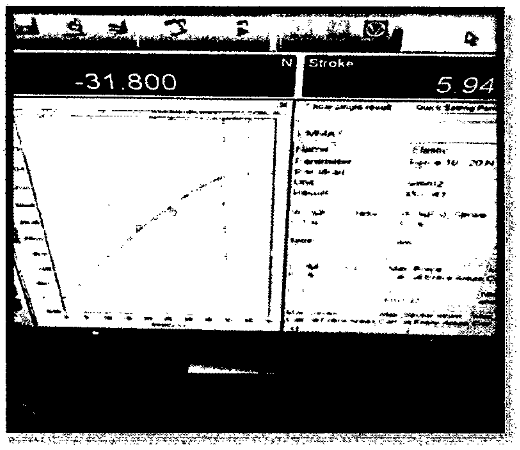

Figure 3.6: Trapezium-X Software

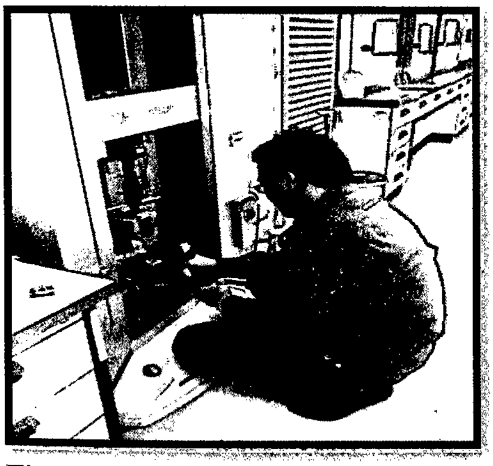

Figure 3.7: During Experiment

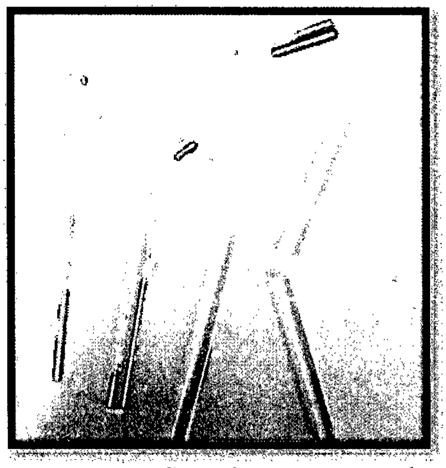

Figure 3.8: Sample PMMA Broken