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DETERMINATION OF MECHANICAL PROPERTIES
OF SODA-LIME GLASS
BY VARIOUS MECHANICAL TESTS

M.Sc. Thesis by
Elsen Ayşe ERORTA, B.Sc
(506991401)

T.C. YÜKSEKÖĞRETİM KURULU
DOKÜMAN YÖNETİM MERKEZİ

Date of submission : 13 May 2002

Date of defence examination: 30 May 2002

Supervisor : Prof. Dr. Eyüp Sabri KAYALI

S. Kayalı

Members of the Examining Committee : Prof.Dr. Hüseyin ÇİMENÖĞLU (ITU)

H. Çimenöğlü

Prof.Dr. Mehmet KOZ (MU)

M. Koz

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JUNE 2002

PREFACE

Without doubt, glass has been one of the most important materials in industrial and daily life of the human being. Because of the reason that glass-making is the one of the oldest technologies, glass material has always been a great interest. Among its decorative use since the early times, nowadays, it has a wide application area in high technology. As a result of its advantages, in the intervening years there has been much active research on glasses.

The general aim of this study is to examine and to compare the various methods that are commonly used in industry to investigate mechanical properties of the glass material.

First of all I would like to express my acknowledgements to Prof. Dr. Eyüp Sabri Kayalı for his valuable guidance in all the steps of this study, to Research Assistant Gökhan Başman and to metallography laboratory technician Mızrap Canıbeyaz.

I want to thank my friends, Ceren Şahin, Bora Alpaslan, Ayça Algün and Tolga Tavşanoğlu for being near me before and during this study and for the joy they bring to my life.

I am grateful to my family for supporting me with an endless positive aspect in all my decisions and especially to my father, the greatest idol in my life, for his effort in the name of making me courageous against all the hard periods in my life including this thesis.

Finally I would like to give my great thanks to my husband François Alain Bourcier for his great patience and love that strongly motivates me in my studies.

June, 2002

Elsen Ayşe ERORTA

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DETERMINATION OF MECHANICAL PROPERTIES OF SODA-LIME GLASS BY VARIOUS MECHANICAL TESTS

SUMMARY

Nowadays, soda-lime glass is considered as one of the most important engineering materials due to its wide application possibilities such as decorative purposes, automotive industry, food containers and architectural glazing.

The advantages of glass material can be listed as, its natural brightness, its resistance against wear, its hardness, its chemical durability, its light transmitting qualities, its chemical inertness and its ability of being easily formed.

Mechanical properties of soda-lime glass (elastic modulus, hardness, fracture toughness and maximum bending strength) are investigated in this study by comparing various test methods (Ball on the ring test, three point bending, Vickers indentation, Knoop indentation, and ultra microhardness test) in order to determine suitable test method for the so-called mechanical properties.

During this study, four groups of glass specimens which have different thicknesses (1st group $t = 0,214$ cm, 2nd group $t = 0,386$ cm, 3rd group $t = 0,794$ cm, 4th group $t = 0,643$ cm) are examined by the test methods that are mentioned above. As a result of the experimental studies, the test results for the glass specimens are compared according to the parameters of the test methods.

To obtain elastic modulus for the glass specimens, Knoop indentation and Ultra microhardness tests are found the most suitable ones. Hardness values are determined veritably from Vickers indentation and Knoop indentation test results for the glass specimens. Hardness values (HV_1 and HV_2) that are calculated from plastic energy (W_p) in Ultra microhardness test; are found independent from plastic indentation depth (h_p). Maximum fracture stress, σ_{max} , values that are calculated from the ball on the ring and three point bending of the beam test method have shown thickness depended variation. For the Vickers cracks, $P/c^{3/2}$ ratio found constant over the range of investigated indentation loads. This result also supports that Vickers indentation test is suitable for investigating K_c values for the glass specimens. Both K_c values of Vickers indentation test (the one that is obtained according to the H/E ratio in Knoop indentation and the other one that is obtained according to the elastic modulus (E) values in ultra microhardness test) are found approximately similar and they match the predicted values for the literature. This result shows K_c calculation for the glass specimens in Vickers indentation by using the both ways; is veritable.

SODA-LIME CAMLARININ MEKANİK ÖZELLİKLERİNİN FARKLI MEKANİK TESTLERLE BELİRLENMESİ

ÖZET

Günümüzde, soda-lime camları dekoratif uygulamalar, otomotiv endüstrisi, gıda endüstrisi ve mimari uygulamalar gibi geniş çaplı kullanım alanları göz önüne alınırsa mühendislik malzemelerin en önemlilerinden biridir.

Bu denli yaygın kullanım alanına sahip olan cam malzemelerin avantajları, doğal parlaklıkları, aşınma dirençleri, sertlikleri, kimyasal kararlılıkları, geçirgenlik özellikleri ve kolay şekil alabilirlikleri olarak sıralanabilir.

Soda-lime camlarının mekanik özellikleri (elastik modül, sertlik, kırılma tokluğu, maksimum eğme mukavemeti) farklı mekanik test metodları yardımıyla (Çift halka iki eksenli eğme deneyi, Üç nokta eğme deneyi, Vickers indentasyonu, Knoop indentasyonu ve Ultra mikrosertlik testi) tespit edilmiştir. Böylelikle soda-lime camlarının mekanik özelliklerinin belirlenmesinde, her özelliğe uygun test metodu saptanmıştır.

Bu çalışmada, farklı kalınlıklardaki (1. grup $t = 0,214$ cm, 2. group $t = 0,386$ cm, 3. group $t = 0,794$ cm, 4. group $t = 0,643$ cm) dört grup cam numune yukarıda adı geçen test metodlarıyla incelenmiştir. Deneysel çalışmaların sonucunda cam numunelerden elde edilen değerler kullanılan test metodlarının parametrelerine göre karşılaştırılmıştır ve aşağıda sıralanan sonuçlar elde edilmiştir.

Knoop indentasyonu ve Ultra mikrosertlik testlerinin, soda-lime camlarında elastik modül saptanmasında en elverişli metodlar olduğu görülmüştür. Literatüre en uygun sertlik değerleri, Vickers indentasyonu ve Knoop indentasyonu kullanılarak bulunmuştur. Ultra mikrosertlik testinde, plastik enerjiden, (W_p), yola çıkılarak hesaplanan sertlik değerlerinin, (HV_1 and HV_2), plastik batma derinliğinden, (h_p), bağımsız olduğu saptanmıştır. Çift halka iki eksenli eğme deneyi ve üç nokta eğme deneyleri kullanılarak bulunan maksimum eğme mukavemeti değerleri, σ_{max} , kalınlıktan bağımsız bir değişim sergilemiştir. Vickers indentasyonu ile elde edilen çatlaklar için, $P/c^{3/2}$ oranın; uygulanan yük aralığında sabit kaldığı görülmüştür. Bu sonuç ayrıca Vickers indentasyonu yardımıyla, kullanılan cam numuneler için kırılma tokluğu hesabı yapılabileceğini doğrulamaktadır. Vickers indentasyonunda, Ultra mikrosertlik ve Knoop indentasyonundan elde edilen elastik modül değerleri kullanılarak hesaplanan kırılma tokluğu değerleri birbirine yakın bulunmuştur. Bu değerler literatürdeki kırılma tokluğu değerlerine uygundur. Bu sonuç, Vickers indentasyonunda cam numuneler için kırılma tokluğu değerlerine her iki yöntemden de elde edilen elastik modül değerleri kullanılarak ulaşılabileceğini göstermektedir.

1. INTRODUCTION

The term glass is commonly used to mean the fusion product of inorganic materials that have been cooled to a rigid condition without crystallizing. This generally means the ordinary silicate glasses, each with its characteristic properties and chemical composition, have been made and these do not necessarily consist of inorganic materials [1].

In general meaning, commercial glasses can be defined as a hard, transparent and an artificial material. Besides the importance of traditional use of glass, nowadays it is so much used in computer industry, communication industry, and medicine. In addition to that it is also used for producing high-technological products [2].

In fact, the original use of glass was for decorative purposes. Next glass was used for containers, and this use is still the most important today. The production of flat glass, chiefly for windows in buildings and vehicles, is now the second largest item of glass manufacture. Lamp envelopes are another major area of use. It is important to mention that when glass is enhanced with coatings and films it can be used to serve the needs of human which can be listed as food containers, transportation or automotive industry and architectural glazing.

There are many special applications of glass, some in small quantity, most of which have been developed over the past few decades. Some of these applications are glass ceramics and surface-strengthened glass for higher strength, fiberglass, mirror blanks of fused silica, glass electrodes for alkali ions, and glass lasers [3]. The advantages of glass material can be listed as, its natural brightness, its resistance against wear, its hardness, its chemical durability, its light transmitting qualities, its chemical inertness and its ability of being easily formed.

The general aim of this study is to compare the results of the various test methods (Ball on the ring test, three point bending, Vickers indentation, Knoop indentation, and ultra microhardness test) and to investigate mechanical properties such as elastic modulus, hardness, fracture toughness and maximum bending strength of the soda-lime glass.

2. LITERARY PART

2.1. History of Glass

Glass is probably the oldest man-made material, used without interruption since the beginning of recorded history [4]. During the formation of the earth, highly siliceous melts of rocks occasionally froze to natural glasses such as obsidian. Water, dissolved homogeneously under high pressure, evaporated rapidly if such melts penetrated the surface, e.g., in a volcanic eruption; and when cooled quickly, the foaming melt became solid natural glass foam, since high viscosity prevented the escape of bubbles. Modern industrial technologies may be considered variations of this basic process [5].

It is not known exactly when glass was first discovered. The oldest finds date to 7000_{B.C.} in the Neolithic period. It is an amorphous substance produced by heating a mixture of such materials as sand, soda (sodium carbonate) and limestone to a temperature of about 1300 °C. Temperatures only slightly lower than this can be achieved with a wood fire, which was the traditional fuel for melting. Today, glass is made continuously in large tanks. Raw materials are fed in at one end, and a molten ribbon of glass emerges at the other end. The glass is heated by oil or gas flames over the melt, but, since these fuels were becoming more expensive, the electrical glass-melting process, which employs metal electrodes in the melt to generate heat, is becoming more widely used. Substances called fluxes are added to the mix to make it melt at lower temperatures. Windows, containers, light bulbs, optical instruments, and any specialty items of glass are an essential part of modern life [4].

Glass was first used in Egypt for decorative objects before 3000_{B.C.} mainly as a colored glaze on stone, pottery, and beads. The art of making glass was perfected about 1500_{B.C.} in Egypt and the Near East. In 1490_{B.C.} a craftsman dipped the form attached to a rod into molten glass, and the first usable hollowware was created [4].

Dating from 669-629_{B.C.}, the clay tablet library of Assyrian King Ashurbanipal contains cuneiform texts with glass formulas, the oldest of which reads, approximately: "Take 60 parts of sand, 180 parts of sea plants, 50 parts of chalk-and you will get the glass." This glass composition contains, essentially, all the materials used in today's formulations, although not in the same proportions. Glassblowing, in 50_{B.C.}, in Phoenicia greatly extended the type of objects that could be made of glass. It also made them easier to fabricate and more transparent [4].

For many centuries after the fall of the Roman Empire, glass making decreased in importance in Western Europe, as did many technologies and arts and artistic glass disappeared. In Byzantium, however, Greek and Syrian glass centers continued to prosper. In 79_{B.C.}, fine glass cups were replacing precious metals as a status symbol among the rich Romans [4].

The Phoenicians were the first to create small glass mirrors with a thin underlay. However, since the glass did not have a level surface, glass did not develop for this purpose. It was not until the thirteenth century in Germany, when the backside of a flat piece of glass was coated with a lead-antimony layer that a quality mirror was made of a glass. Later Venetian artisans improved upon the process, as we know it today. Only after discovering of the plate pouring process in 1688 in France, under Louis XIV, could large-surface mirrors be created [4].

Beginning in the eleventh century, several new centers of glass making arose in Western Europe. In Bohemia, ash from plants (potash, which is high in potassium) was used as a raw material to make glass with a low melting point. The most important European center of glass making, developed near Venice, where new compositions, colors, forming techniques, and artistic skills developed [4].

The Venetians added manganese, in the form of the mineral pyrolucite, to oxidize iron impurities in glass and remove the green and brown tint caused by the reduced state of iron. By adding lead, borate, and more soda to glass, they increased its working temperature range and were able to make more intricate shapes, thinner brown glass, and finer enamels. Special additives were also used to color glass [4].

Glass making in the city reached its peak between the fifteenth and seventeenth centuries. Venetian glassware designers were strongly influenced by many aspects of Islamic art [4].

About 1675, so-called crystal glass was developed to compete with Venetian glass. Purer materials, oxidation of iron, and the addition of lead gave a more transparent glass, this transparency, together with the higher index of refraction resulting from the addition of lead, gave a sparkle to faceted cut glass, resulting in a heavier, more desirable glass. Flat glass for windows was still rare during much of the seventeenth and eighteenth centuries. At the end of seventeenth century, the French learned how to grind and polish cast glass to produce plate glass [4].

For a long time, systematic studies of relation of composition to properties and the development of new glasses remained inhibited by the inability to produce glass of sufficient homogeneity. For this reason, the first significant process waited until about 1800, when Guinand and Fraunhofer devised special stirring methods. The correlations between glass composition and light reflection could be systematically and scientifically studied for the first time. The English pastor Harcourt and the famous physicist Stokes, consequently laid the foundation of a "chemistry of glasses" in 1834. Around the end of the seventeenth century, flint glass, an alkali lead silicate glass, was discovered and produced in England [5].

Shortly before 1900, an American, Michael Owens (1859-1923), invented automatic bottle blowing machine, which was introduced in Europe after the turn of the century. In 1900, glass making was not essentially different from what it had been 300 years previously. Somewhat later, the process for mechanical production of flat glass became available, without which the quickly rising demand for architectural glass could not have been met. In 1916, Michael Owens was to make an indelible mark in the glassmakers' struggle to bring mechanization to the industry. He mechanized the production of glass containers, and then perfected the world's first machine for flat drawn window glass, an act which did more in a few years to revolutionize the art of flat glass making than anything had done for thousands of years previously. It set the stage for the great achievements we know today [4].

2.2. General Approach to Glass

Glass is an amorphous solid. A material is amorphous when it has no long-range order, that is, when there is no regularity in the arrangement of its molecular constituents on a scale larger than a few times the size of these groups [3].

Many glass technologists object to the above definition of a glass. Earlier writers insist on this criterion: "A glass is a material, formed by cooling from the normal liquid state, which has shown no discontinuous change...at any temperature, but has become more or less rigid through a progressive increase in its viscosity," according to Jones (G.O. Jones, *Glass*, Methuen, London, 1956), or, more succinctly, "glass is an inorganic product of fusion which has been cooled to a rigid condition without crystallization" as taken from the ASTM Standards for Glass. The difficulty with this view is that glasses can be prepared without cooling from the liquid state. Glass coatings are deposited from the vapor or liquid solution, sometimes with chemical reactions [3].

2.3. Chemical Definition of Glass

Traditional glasses have been made of inorganic materials such as silica sand, sodium, and calcium carbonates, feldspars, borates, and phosphates that react to form metallic oxides in the final glass [3].

A batch of commercial glass consists of a mixture seven to twelve individual ingredients. The bulk of the batch is made up of four to six ingredients, chosen from such materials as sand, limestone, dolomite, soda ash, boric acid, borax, feldspathic materials, and lead and barium compounds [4].

What materials can be glasses? In principle, any substance can be made into a glass by cooling it from the liquid state fast enough to prevent crystallization. The final temperature must be so low that molecules move too slowly to rearrange to the more stable crystalline form. Alternatively, one can imagine building up the material onto a substrate, either by deposition or chemical reaction from the vapor, the substrate being so cold that rearrangement cannot take place [3].

In actual practice, glass formation has been achieved with a relatively limited number of substances. After substances that have been made into glasses are listed, the question of why so few substances are amenable to glass formation is considered in subsequent sections [3].

Materials that have been made into glasses are listed in Table 2.1 and 2.2. Undoubtedly these lists will be extended as new methods of more rapidly cooling melts and of deposition from vapor or solution are devised [3].

Table 2.1 Glasses formed by cooling from the liquid.

Elements
S, Se
Te(?)
P
Oxides
B_2O_3 , SiO_2 , GeO_2 , P_2O_5 , As_2O_3 , Sb_2O_3 , In_2O_3 , Tl_2O_3 , SnO_2 , PbO_2 , SeO_2 , "Conditional" TeO_2 , SiO_2 , MoO_3 , WO_3 , Bi_2O_3 , Al_2O_3 , Ba_3O_3 , V_2O_5 , SiO_2 , Nb_2O_5
Sulfides
As_2S_3 , Sb_2S_3 Various compounds of B, Ga, In, Te, Ge, Sn N, P, Bi CS_2 B_2S_3 - Li_2S , P_2S_5 - Li_2S
Selenides
Various compounds of Tl, Sn, Pb, As, Sb, Bi, Si, P
Tellurides
Various compounds of Tl, Sn, Pb, As, Sb, Bi, Ge
Halides
$ZnCl_2$, multicomponent chlorides based on $ZnCl_2$, $CdCl_2$, $BiCl_3$ and $TbCl_4$ BeF_2 , AlF_3 , ZrF_4 , HfF_4 , SrF_2 , TiF_4 as glass- formers and many other ions as intermediates and modifiers AgI , AgF , AlF_3 Sb_2S_3 , Ag_2S , Sb_2S_3 , AgI , Sb_2S_3 , Ag_2S - AgI $CuCl$, Br , I
Acetates
Pb-K acetate, Ca-K acetate
Nitrates
KNO_3 , $Ca(NO_3)_2$ and many other binary mixtures containing alkali and alkaline earths nitrates
Sulfates
$KHSO_4$ and other binary and ternary mixtures
Carbonates
K_2CO_3 - $MgCO_3$

Table 2.1 (continued)

Simple organic compounds
<i>O</i> -Terphenyl, toluene, 3-methyl hexane, 2,3-dimethyl ketone, diethyl ether, isobutyl bromide, ethylene glycol, methyl alcohol, ethyl alcohol, glycerol, glucose
As droplets only: <i>m</i> -xylene, cyclopentane, <i>n</i> -heptane, methylene chloride
Polymeric organic compounds
Example, polyethylene (CH_2) _n , and many others
Aqueous solutions
Acids, bases, chlorides, nitrates, and others
Metallic alloys by "Splat Cooling"
Au ₄ Si, Pd ₄ Si
Te ₅ -Cu ₂₄ -Au ₅

The materials in Table 2.1 can be placed in several categories. The oxides are by far the most important commercially. Multicomponent oxide glass results from mixing of other oxides with the main "glass formers" SiO₂, B₂O₃, GeO₂, and P₂O₅. The "conditional" glass forming oxides in Table 2.1 do not form glasses alone, but can do so in binary or multicomponent mixtures with other oxides [3].

Table 2.2 Glasses formed by deposition or reaction from the vapor, and not included in Table 2.1.

Elements
Boron
Silicon, Germanium
Bismuth, Gallium
Oxides
Aluminum(?)
Tantalum
Niobium
Water(?)
Metals and alloys
Other compounds
Silicon carbide
Indium antimonide
Various combinations of silicon, or germanium, with oxygen, sulfur, selenium, and tellurium
Magnesium with antimony or bismuth
Nickel, cobalt, or iron with phosphorous or sulfur

A second category is the chalcogenide glasses based on sulfur, selenium, or tellurium. In chemistry, the term chalcogenide refers to compounds containing oxygen, sulfur, selenium, or tellurium; thus its use to describe glasses of these elements, excluding oxides, is unfortunate. The root chalco- comes from a Greek word for copper, and the chalcogenide elements have traditionally been those that form strong compounds with copper. These glasses are primarily interesting because some are electronic conductors (semiconductors). They also soften at relatively low temperatures and transmit infrared radiation well [3].

Another category is ionic glasses- halides, nitrates, sulfates, and carbonates. The latter three are quite similar because they form glasses only as binary or multicomponent mixtures. Other categories are the simple organic compounds, the organic polymers, the aqueous solutions, and metallic alloys [3].

2.3.1. Chemical and Physical Properties of Raw Materials

The major raw materials used in glass making may be divided into three categories [4]:

1. Mined or quarried materials that are milled and beneficiated in some manner after extraction to render them suitable for the market.
2. Manufactured chemicals, as soda ash, borax, boric acid, aluminum hydrate, etc.
3. By-product materials. Cullet, or scrap glass, and beneficiated blast furnace slags are the most important current materials in this class.

Raw materials used for the manufacture of glass may vary considerably in their degree of purity, and the type of a particular raw material is commonly indicative of the degree of analytical control it will provide [4].

2.3.2. Description of Glass Making Materials

Alumina (Al_2O_3). Although this oxide does not represent a large part of the composition of most glasses, it is an important one.

Feldspar. For a number of reasons, it is one of the most important sources of alumina. The mineral can be obtained in a state of sufficient purity free from iron and other objectionable elements.

Feldspars are represented by the formula $R_2O \cdot Al_2O_3 \cdot 6SiO_2$, in which R_2O represents an alkali oxide, K_2O in microcline and Na_2O in albite. Two other feldspathic minerals are widely used as sources of alumina: nepheline syenite and aplite.

Alumina hydrate ($Al_2O_3 \cdot 3H_2O$). Alumina hydrate is a manufacture product prepared by a precipitation process from minerals, such as bauxite, dissolved as sodium aluminate.

Kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). It is feasible to use some of the purer grades of kaolin as a source of alumina.

Kyanite and sillimanite ($Al_2O_3 \cdot SiO_2$). These minerals do not have the low iron content of feldspars, but have higher alumina content and may offer some cost advantage.

Slag. Blast furnace slags, beneficiated and milled to a condition suitable for use in glass batches as a source of alumina, silica, lime, and magnesia, offer a readily soluble source of Al_2O_3 . Raw slags are not very suitable in production of glass from either a physical or chemical quality standpoint.

Antimony oxide (Sb_2O_3). The principal mineral source is stibnite (Sb_2S_3). Antimony trioxide is formed when the metallic antimony is heated in the air or treated with nitric acid. Its role in glass composition is not clearly understood, but it is used in concentrations up to 1%, and it appears to make the glass more easily meltable and workable.

Arsenious oxide (As_2O_3). Arsenious oxide is a by-product of copper metallurgy. It collects as a fume in smelter flues and is refined by sublimation. It volatilizes at red heat without melting and condenses in fine crystals. It acts as an oxidizing agent toward ferrous oxide and also toward sulfur and carbon.

Barium oxide (BaO). Barium oxide is usually furnished by the compound barium carbonate ($BaCO_3$). It occurs naturally as the mineral witherite, but rarely pure enough for use in the glass batch.

Boric oxide (B_2O_3). Boron, or more specifically boric acid, is supplied to the glass batch in a variety of forms.

Lime: calcium oxide and magnesium oxide, CaO and MgO , respectively. This oxide is readily obtained from calcium carbonate ($CaCO_3$), available as quite pure high-calcium carbonates (whiting). Burnt lime, formed by the complete calcinations of limestone in limekilns, is another source of calcium for the glass batch. Burnt lime offers a few advantages. It is already calcined, reacts quickly with silica with evolution of heat, contains no carbonaceous matter, and presents a minimum of weight and bulk. Hydrated lime or slaked lime is obtained by mixing burnt lime with water in the proper proportions. Slaked lime contains about %75 CaO , and is preferred by some glassmakers as a source of CaO .

Gypsum ($CaSO_4 \cdot 2H_2O$). Gypsum, or anhydrite or dead-burnt gypsum ($CaSO_4$), Offers possibilities as a substitute for salt cake in glass melting and, at the same time, furnishes some CaO .

In the melting process, calcium sulfate must react with sodium carbonate and yield lime and sodium sulfate. Gypsum is stored quite easily.

Iron oxide (FeO and Fe_2O_3). Iron oxide is the principal source of iron for some green glasses and for glasses used to absorb ultraviolet radiation.

Lead oxide (PbO). Lead oxide may be supplied to the glass batch in a number of ways. An early and common method was to use red lead (Pb_3O_4) and many still prefer its use as a raw material.

Potassium oxide (K_2O). Potassium oxide is often supplied by the hydrated carbonate of potash, ($K_2CO_3 \cdot 1\frac{1}{2}H_2O$) known as pearl-ash. It is manufactured from potassium chloride.

Potassium carbonate (K_2CO_3). Potassium carbonate, also known as calcined carbonate of potash, is a material preferred by glass makers.

It is somewhat dusty when freshly calcined and is apt to become lumpy from hydrating in a humid atmosphere.

Saltpeter, niter (KNO_3). Saltpeter is used when the oxidizing action of a nitrate is desired.

Silica (SiO_2). Silica, also called silicon dioxide, is the most important constituent in common commercial glasses because it is the principal glass-forming oxide. The chief source of silica sand, commonly called glass sand, consists essentially of quartz granules.

Sodium oxide (Na_2O). Sodium carbonate (soda ash) is the most common source of sodium oxide in the glass batch. It is readily available as a natural mineral or a manufactured product.

Fluorine (F_2). Fluorine is unique among the active elements in that it forms no stable oxides. It occurs in nature and in glasses, glazes, and enamels as fluorides.

Phosphate compounds. Apatite is a phosphate compound occurring as natural phosphate rock.

Titania (TiO_2). Titania is refined from rutile and ilmenite ores. It is marketed as a fine, white powder.

Lithia (Li_2O). Lithium carbonate (Li_2CO_3), manufactured from silicate minerals containing lithia, is the principal means of introducing Li_2O directly.

Zinc oxide (ZnO). This oxide is produced by direct oxidation of zinc and subsequent purification by sublimation. It is prepared in several grades based on color, particle size, and smoothness.

Zirconium oxide (ZrO_2). This material is usually introduced as zirconium oxide (ZrO_2). As a component of soda-lime glasses, it tends to increase viscosity, refractive index, and resistance to weathering. Its application is quite limited [4].

2.3.3. Types of Glasses

Pure silica glass

SiO₂: 99.5%+

Chiefly used for its low thermal expansion, high service temperature, and, when very pure, for its transparency to a wide range of wavelengths in the electromagnetic spectrum and to sound waves. It also has good chemical, electrical, and dielectric resistance. Its disadvantage is very high temperature needed for manufacture, although it can be by hydrolysis of SiCl₄; in either case, it is expensive. It is used for lightweight mirrors for satellite-borne telescopes, laser beam reflectors, special crucibles for the manufacture of pure single crystals of silica for transistors, and as a molecular sieve that lets hydrogen and helium through [4].

96% silica glass

SiO₂: 96%

B₂O₃: 3%

Made by forming an article, larger than the required size, from a special borosilicate glass, leaching out the no silicate ingredients with acid, and treating at high temperature to shrink the article and close pores. Good thermal properties; service temperature higher and expansion coefficient lower than borosilicate glass. Used for missile nose cones, windows of space vehicles, and some laboratory glassware where exceptional heat resistance is needed [4].

Soda-lime-silica glass

SiO₂: 70%

Na₂O: 15%

CaO: 10%

The addition of soda (Na₂O) and sometimes potash (K₂O) to silica lowers the softening point by 800-900°C. Lime (CaO) and sometimes magnesia (MgO) and alumina (Al₂O₃) are added to improve chemical resistance. Electrical properties can vary quite widely with composition. This is the most common of all glasses, used in quantities for plate

and sheet (including windows), containers, and light bulbs. "Crown" glass is of this type, although modern optical crown glass usually contains barium oxide instead of lime [4].

Lead-alkali-silicate glass

SiO_2 : 30-70%

PbO : 18-65%

Na_2O and/or K_2O : 5-20%

Lead oxide reduces the softening point even more than lime and also increases the refractive index and dispersive power [4].

"Flint" glass for optical purposes and "crystal" glass for tableware are both lead glasses. They are also used for thermometer tubes, parts of electric lamps, and neon sign tubes [4].

Borosilicate glass

SiO_2 : 60-80%

B_2O_3 : 10-25%

Al_2O_3 : 1-4%

Has low thermal expansion, about one-third that of soda-lime glass, can be made with good chemical resistance and high dielectric strength, and is used where combinations of these are needed [4].

Its high softening temperature makes it harder to work than soda lime or lead glasses. Used for laboratory glassware, industrial piping, high-temperature thermometers, large telescope mirrors, household cooking ware, such as "Pyrex", enclosures for very hot lamps, and electronic tubes of high wattage [4].

Aluminosilicate glass

SiO_2 : 5-60%

Al_2O_3 : 20-40%

CaO : 5-50%

B_2O_3 : 0-10%

Another low-expansion, chemically resistant glass that has a higher service temperature than borosilicate glass but is correspondingly harder to fabricate. It is used for high-performance military power tubes, traveling wave tubes, and many applications similar to those of borosilicate glass. Aluminosilicate glass without any boron is especially resistant to alkalis. Nearly all laboratory glassware is made from borosilicate glass, aluminosilicate glass, or a glass called aluminoborosilicate, which contains roughly equal amounts of Al_2O_3 and B_2O_3 . The choice depends on the application; thus, aluminosilicate glass is used for high-temperature applications or alkali-resistant glass. Aluminoborosilicate glass is slightly better than borosilicate for chemical resistance but has slightly greater thermal expansion [4].

Colored glasses

The color glass is simply the consequence of the absorption and emission of the electron clouds of its constituent ions. In other words: If a glass is irradiated by white light, mobile electrons of the outer electron shells of certain ions accept energy of certain wavelength, while the remaining light, now deficient in certain components, no longer passes as white, but rather as colored residual light [5].

A portion of the incident light is converted to thermal vibration; another part, however, contributes to the passing light by emission. This emission is caused by the return of excited electrons to the original level [5].

This part does not conform exactly to the wavelength of the light absorbed. By introducing 3d elements into the base glasses, e.g., Fe, Mn, Ni, Cu, Co, Cr, etc., the simplest type of colored glasses can be obtained [5].

Green	Iron oxide, chromium oxide	
Blue	Cobalt oxide, copper oxide	
Violet	Manganese oxide	
Amber	Sulphur and carbon	
Red	Selenium and cadmium sulphide	
Opal glass	Fluorine compounds, e.g. cryolite	[5]

Optical glasses

Light barium crown glass

SiO₂: 45-50%
B₂O₃: 3-5%
Na₂: 1%
K₂O: 7%
BaO: 20-30%
ZnO: 10-15%
PbO: 0-5% [4]

Dense barium crown glass

SiO₂: 30-40%
B₂O₃: 10-15%
BaO: 10-15%
ZnO: 0-10%
Al₂O₃: 10% [4]

Very light flint glass

SiO₂: 60%
K₂O: 8%
PbO: 27% [4]

Very dense flint glass

SiO₂: 20-40%
K₂O: 0-10%
PbO: 50-80% [4]

Special glasses

Silicon-free glass for sodium vapor discharge lamps

B₂O₃: 36%
Al₂O₃: 27%
BaO: 27%

MgO: 10% [4]

Phosphate glass with high resistance to HF

P₂O₅: 72%

Al₂O₃: 18%

ZnO: 10% [4]

“Soft-solder” glass with transformation temperature below 752°F (400°C)

SiO₂: 5%

B₂O₃: 15%

PbO: 64%

ZnO: 16% [4]

“Lindemann” glass with low X-ray absorption. All metal atoms have low atomic numbers.

B₂O₃: 83%

BeO: 2%

Li₂O: 15% [4]

Neutron-absorbing glass with high cadmium content

SiO₂: 26%

Al₂O₃: 2%

CdO: 64%

CaF₂: 8% [4]

High-lead-content glass for absorbing gamma rays or X-rays; also, a very dense flint glass

SiO₂: 20%

PbO: 80% [4]

Tellurite glass of very high refractive index and dielectric constant

TeO₂: 80%

PbO: 14%

BaO: 6% [4]

Optical glass with high refraction and low dispersion

La₂O₃: 20%

B₂O₃: 40%

Tm₂O₃: 20%

BaO: 20% [4]

Semiconducting vanadate glass

V₂O₅: 85%

P₂O₅: 10%

BaO: 5% [4]

Semiconducting chalcogenide glass transparent to infrared

As: 44%

Te: 24%

I: 32% [4]

Two-dielectric chalcogenide glass transparent to infrared

(1) As₂S₃: 100%

(2) As: 40%

Ti: 20%

S: 40% [4]

Elemental glass (consisting of a pure element)

S: 100% [4]

Photosensitive gold ruby glass

SiO₂: 72%

Na₂O: 17%

CaO: 11%

Au: 0.02%

Se: 0.04% [4]

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DOKÜMANTASYON MERKEZİ**

Photochromic glass

SiO₂: 60%

Na₂O₃: 10%

Al₂O₃: 10%

B₂O₃: 20%

Ag: 0.6%

Cl: 0.3%

LiO₂: 0.9% [4]

2.3.4. Phase Transformations of Glass

The phase formation in glass is given in the following Fig.2.1.

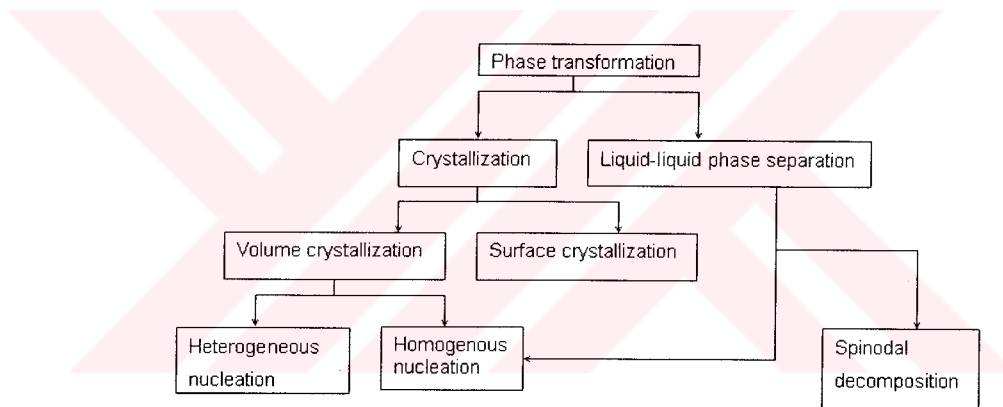


Fig. 2.1 Phase formations in glasses [1]

The following types of phase transformations are usually observed in glass [1]:

Crystallization: The growth of a crystalline phase(s) that may or may not have the same composition as the original liquid.

Surface crystallization: Crystal growth begins (i.e. nucleates) from the glass-atmosphere interface, and usually grow perpendicular to this interface.

Volume crystallization: Here crystal growth begins from 'nucleation sites' within the body of the material. The initiating site for crystallization may be a substance foreign to

the bulk of the material, when it is called heterogenous nucleation, but if the nucleus is the same as the bulk material it is called homogenous nucleation.

Liquid-liquid phase separation: The growth of non-crystalline phases which will have a different composition from the original phase.

Spinodal decomposition: Within a region which separates into two liquid phases there will be a region where there is no energy barrier to nucleation and phase separation is, therefore, limited by diffusion only [1].

2.3.5. The Transformation Temperature of Glass

The peculiar type of freezing is of great importance in glass technology and in the theoretical understanding of glass. The effect of this “freezing” is not to alter the structure of the glass but to change the way it expands and contracts with changes in temperature [4].

When a liquid is cooled below its freezing point, crystallization occurs by the growth of crystals at a finite rate from a finite number of nuclei. Glass formation may be attributed to a low rate of crystal growth, a low rate of nuclei formation or combination of both [1].

The heat energy in a liquid or a solid appears as motion of the atoms or molecules of the material. In a crystalline solid, the molecules occupy fixed positions relative to one another, and the molecular motions are vibratory motions around this fixed position. In a liquid, these vibratory motions occur, but there is some random movement of the molecules so that some intermolecular bonds are constantly being broken and new bonds formed [4].

In both liquids and solids, part of the vibratory motion because of heat is motion along axis of the interatomic bonds in the material, so that the distance between two neighboring atoms varies slightly as these atoms vibrate. In general, the higher the temperature, the greater the amplitude of the vibration [4].

Interatomic bonds may be formed in a number of different ways but always involve a balance of attractive and repulsive forces. At the normal interatomic spacing, these

forces balance and the net force between two atomic nuclei is zero. It is almost always true, however, that, at this normal interatomic spacing, it is easier to pull two atoms a little further apart than to compress them further together. The result is that the thermal vibration has the effect of slightly increasing the interatomic spacing [4].

Therefore, most materials expand slightly as the temperature rises and, correspondingly, contract when it falls. This normal thermal expansion involves no rearrangement of interatomic or intermolecular bonds but merely changes the effective average spacing between atoms [4].

Glass undergoes normal thermal expansion and contraction, but, above a temperature, called the transformation temperature, it undergoes a second kind of expansion or contraction as the temperature changes. Glass has an “open” structure; the network of silicon and oxygen atoms (in a common glass) is not densely packed. As the temperature decreases, however, the structure becomes more dense. The change in the volume of a given weight of glass, as the glass is cooled, is shown in Fig.2.2 [4].

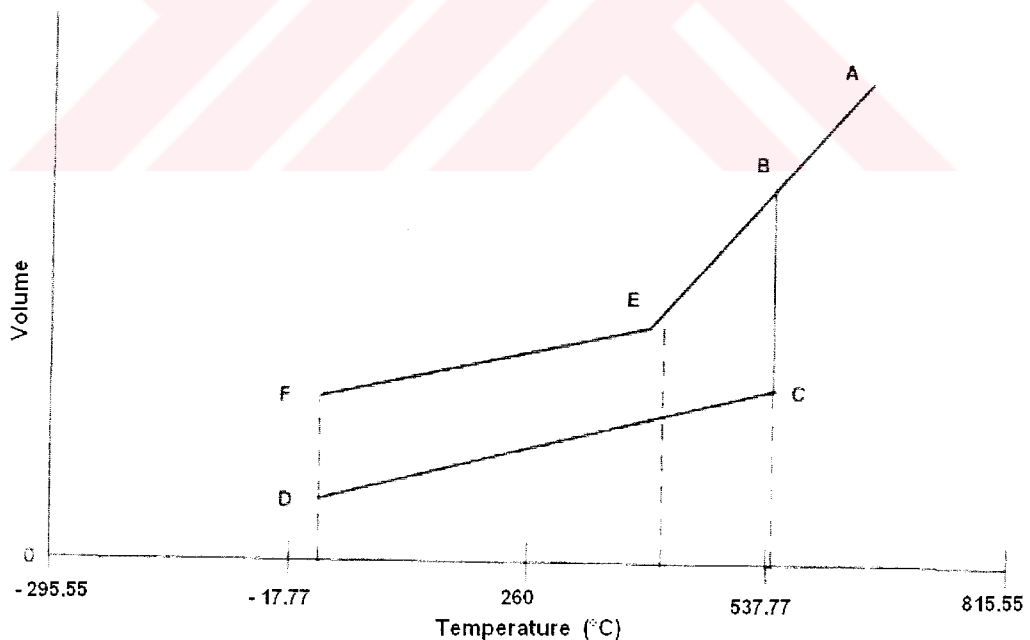


Fig. 2.2 Changes in glass volume on cooling [4]

Beginning at A, with the glass as a normal liquid (that is, above the melting point of the glass-forming materials), it is cooled to B, the theoretical freezing point. If the material crystallizes, there is a sharp decrease in volume to C, after which the crystalline material continues to shrink as temperature falls, but at a slower rate (per degree of cooling), to D, the volume at room temperature. From A to B, the liquid has contracted by two processes, normal thermal contraction and configurational contraction because of less open structure [4].

From C to D, the crystal, which undergoes no configurational change, shrinks only by normal thermal contraction. (It should be mentioned that most materials shrink when crystallizing. The increase in volume when ice formed from liquid water is the exception, not the rule) [4].

At a particular point, however, the rate of contraction slows and, below that point, continues from E to F at the rate previously discussed for the crystal. Apparently, the configurational shrinkage has stopped at E, and, from E to F, the glass, although still a liquid, is shrinking only by normal thermal contraction. The temperature at which this occurs (the transformation temperature) is not a sharply defined point, but rather a range of about 500°C, as the bend in the curve suggests [4].

At the transformation temperature, the glass has become viscous that the configurational changes necessary for the denser structure no longer have time to occur. These changes involve rearrangement of the intermolecular bonds, and, when the glass has reached a particular viscosity, the necessary changes can no longer keep pace with the rate at which the temperature is falling [4].

The interesting point is that the viscosity at which this occurs, for practical cooling rates, is roughly the same for all glasses, 10^{13} poises, although the temperature involved may range from -89°C for glycerin to over 1000°C for pure silica glass [4].

In fact there are two properties of glass that change at the transformation temperature. The first is the rate of thermal expansion, as already discussed. The second, reasonably enough, is the specific heat of the glass, that is, the amount of heat energy required to raise the temperature of 1 gram of glass 1°C [4].

Below the transformation temperature, all the heat supplied goes only into the molecular vibrations, as no appreciable configurational change is occurring; above the transformation temperature, the individual molecules can also move about somewhat in the material, and some of the heat energy goes into this motion and into the vibratory motion of the molecules. Accordingly, the specific heat may increase appreciably as the transformation temperature is exceeded [4].

The temperature at which a particular piece of glass effectively ceases to undergo configurational change, when cooling, is sometimes called fictive temperature of the glass. This is the temperature at which the glass is thermodynamically stable, that is, has no spontaneous tendency to change to a denser or less dense structure. The fictive temperature of common glass is in the neighborhood of 500°C, and it follows that the glass is not in thermodynamic equilibrium at the room temperature [4].

In principle, it is slowly shrinking, because configurational change will continue until the fictive temperature reaches the actual temperature. For glass at room temperature, however, the process goes forward so slowly that millions of years would be required [4].

Because rates (of cooling and of configurational shrinkage) are involved, it would seem that the temperature at which this transformation occurs should depend on the rate of cooling. This is, indeed, the case. As shown in Fig.2.2, if the cooling rate is high, the configurational change falls behind at a higher temperature; if it is very low, the transformation temperature is correspondingly lower [4].

Thus, we may obtain glass of the same composition, but of different densities because of different fictive temperatures according to the rate at which glass is cooled. Also within the same piece of glass, the density may vary if the exterior part of the glass has cooled more rapidly than interior. Finally, the glass may change in dimensions after it has cooled, because of continued configurational shrinkage [4].

Now, it can be restated the definition of a glass in somewhat more formal terms. A glass is a material obtained by supercooling a liquid to a temperature, where the viscosity of the liquid exceeds 10^{13} poises, does not incur discontinuous changes in viscosity or structure, and retains the organization and internal structure of a liquid [4].

As the preceding discussion has implied, cooling beyond the temperature where this viscosity is reached will have little effect on the internal structure of the material, except to increase the viscosity further; the viscosity of common glass at room temperature exceeds 10^{20} poises, and, over the time periods interests people, the material behaves as an ideal elastic solid [4].

2.3.6. Glass Formation

The rates of nucleation and growth of crystals in the liquid, together with cooling rate, determine whether a glass is formed. Uhlmann and co-workers have treated the kinetics of glass formation in terms of the Avrami equations for the volume fraction V_c / V crystallized, where V_c is the volume of the crystalline material in a total volume V , and their treatment is followed here. The general transformation equation includes the possibility of time dependent rates of nucleation and crystallization [3].

A simplification is to assume that these rates are functions of temperature only and not time. The result is

$$V_c / V = 1 - \exp(-\pi u^3 I t^4 / 3) \quad [2.1]$$

Where I is the rate of nucleation of crystals per unit volume, u is the rate of crystallization (m/s), and t the time. The exponential form in Eq.1.1 allows for the possibility of impingement of growing crystals; at short times, V_c / V is proportional to the term $\pi u^3 I t^4 / 3$ [3].

If the rate of nucleation and crystallization are known as a function of temperature, the volume fraction of crystals at a particular temperature can be calculated as a function of time. It is assumed that crystallization is detectable at a certain fraction V_c / V ; then the time for detection as a function of temperature can be found. The resulting temperature-log time plot is called a time-temperature-transformation (TTT) curve, as shown in Fig.2.3 for anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), with $V_c / V = 10^{-3}$. The position of the curve is only weakly dependent on the value assumed for V_c / V [3].

The rates of nucleation and growth are a maximum at a certain temperature; the result is that the TTT curves have one or more minimum times, as shown in Fig.2.3. This minimum results because of two opposing factors [3].

As the temperature of the liquid is lowered below the melting temperature, the driving force for both nucleation and growth increases, leading to increased rates. Opposed to this increased is the decreased in transport rates (diffusion or viscosity) as the temperature is lowered, which decreases the rate of nucleation and growth. The result is maximum in these rates and a minimum time for appreciable crystallization, as shown in Fig.2.3. The cooling rate to avoid crystallization and thus form a glass must be high enough to avoid the “nose” in the TTT curve. A rough estimate of this critical cooling rate R_c can be found by considering the temperature range over which the crystallization rate is appreciable [3].

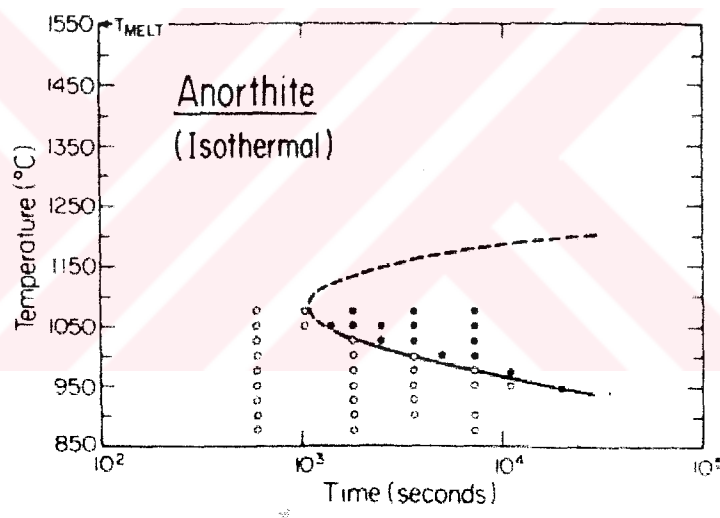


Fig. 2.3 Experimental isothermal time-temperature-transformation (T-T-T) diagram

For the curve in Fig.2.3, this temperature range is about 100°C at $2(10)^3$ /s, so $R_c \approx 100/2(10)^3 = 0.05^\circ/\text{s}$. A cooling rate faster than this in the fast crystallization temperature range should prevent a crystallization volume fraction of more than 10^{-3} from being formed. Often measured nucleation and crystallization rates are not available. In that circumstance, it would be useful to be able to estimate nucleation and growth rates of crystals in a liquid to allow calculation of critical cooling rates and the tendency to glass formation. Uhlmann and Yinnon describe some estimation techniques; in some materials, estimation of critical cooling rates within an order of magnitude was possible.

Ruckenstein and Ihm have also calculated critical cooling rates for glass formation from nucleation and crystallization equations. Crystallization rates are easier to measure than nucleation rates, and have been determined for many glass-forming systems. Maximum crystallization velocities as listed in Table 2.3. The rates of crystallization are lowest for substances easily cooled to glasses, such as silica and germania, whereas they are higher for alkali and alkaline earth compounds, which must be cooled more rapidly to avoid crystallization [3].

Table. 2.3 Crystallization velocities and viscosities of glass-forming liquids.

Material	Melting Point (°C)	Max Cryst Velocity (cm/s)	Temp of Max η (°C)	Log Viscosity at max η (P)
Vitreous silica, SiO_2	1734	$2.2(10)^{-7}$	1674	7.36
Vitreous germania, GeO_2	1116	$4.2(10)^{-8}$	1020	5.5
Phosphorous pentoxide, P_2O_5	580	$1.5(10)^{-5}$	561	6.7
Sodium disilicate, $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$	878	$1.5(10)^{-4}$	762	5.8
Potassium disilicate, $\text{K}_2\text{O} \cdot 2\text{SiO}_2$	1040	$3.6(10)^{-4}$	930	
Barium diborate, $\text{BaO} \cdot 2\text{B}_2\text{O}_3$	916	$4.3(10)^{-4}$	849	1.7
Lead diborate, $\text{PbO} \cdot 2\text{B}_2\text{O}_3$	774	$1.9(10)^{-4}$	705	1.6
1,2-Diphenylbenzene	55.5	$2.5(10)^{-3}$	38	-0.46
1,2,3,4-tetra-naphthylbenzene	197	$9.3(10)^{-3}$	175	-0.34
Glycerol	18.3	$1.8(10)^{-4}$	-6.7	1.0
Salol	41	$6.4(10)^{-4}$	20	
Polyethylene adipate	55	$9.5(10)^{-3}$	26	
Toluene	95	>0.5		
Ethyl ether	116	>0.15		
Methyl alcohol	98	>0.09		

From the table, one might guess that an upper limit for the crystallization rate of a material easily formed as a glass by cooling the liquid would be about 10^{-4} cm/s [3].

With this rate, it is necessary to cool the glass through the temperature range of maximum crystallization rate in less than 0.001 s to prevent growth of crystals larger than 100 Å in diameter [3].

This time is too short for most practical conditions, so the nucleation rates for materials with maximum crystallization rates above 10^{-4} cm/s must be low. For the glasses such as silica, this low rate is enough to ensure glass formation for a wide range of cooling rates [3].

The velocity of crystallization of cristobalite from fused silica is shown as a function of temperature in Fig.2.4, from the work of Wagstaff [3].

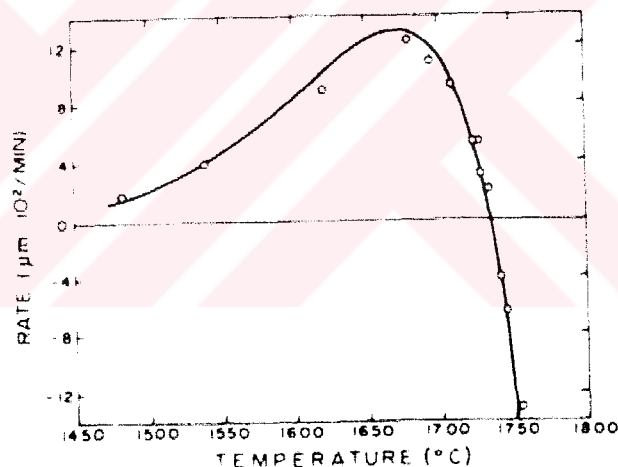


Fig. 2.4 The rate of crystallization of cristobalite from fused silica as a function of temperature

As the silica is cooled below the melting point of cristobalite, the rate of crystallization rises to a maximum value and then decreases. At much lower temperatures (below about 900°C for pure vitreous silica) the rate of crystallization is so slow that even for long holding times, no appreciable amount of crystalline material is formed [3].

Thus, if the silica is cooled rapidly enough from above the melting point to below 900°C, no appreciable amount of crystalline cristobalite is formed, and the silica becomes a stable glass [3].

Uhlmann and Yinnon have summarized the relationship between liquid properties and the tendency to glass formation. The factors that favor glass formation are [3]:

1. High viscosity at the nose of TTT curve, since low transport rates lead to low rates of nucleation and crystallization;
2. Absence of heterogenous nucleation sites;
3. A large crystal-liquid interfacial energy, which reduces the nucleation rate;
4. In multicomponent systems, a large concentration change between liquid and crystal.

In these multicomponent systems, it is often found that glass formation is favored by a “deep-eutectic”, because liquid compositions in low-temperature eutectics have higher viscosities and therefore lower nucleation and crystallization rates than at higher temperatures [3].

2.3.7. Chemical Durability of Glass

The term ‘chemical durability’ has been used conventionally to express the resistance offered by a glass towards attack by aqueous solutions and atmospheric agents. There is no absolute or explicit measure of chemical durability and glasses are usually graded relative to one another after subjecting them to similar experimental conditions; the nature of the experiment usually determines the relative order [1].

Because of its chemical inertness, the chemical durability of glasses is concerned almost entirely with their reactivity with liquid water, aqueous solutions, and water vapor, all of which are extremely slow [3].

A series of different processes can take place when liquid water reacts with glass:

1. Dissolution of the glass into the water with the concentration ratios in the dry glass (congruent dissolution).

2. Ion exchange between alkali, and to some extent alkaline earth, ions in the glass with hydrogen-bearing ions from the water.
3. Diffusion of molecular water into the glass.
4. Formation of layers of reaction products on the glass surface. Included are preferential adsorption or precipitation of glass or solution constituents onto the glass surface or into a surface layer.
5. Reaction of water with the silicon-oxygen network [3].

In contact with water vapor process 2-5 are possible.

The relative importance of these processes depends upon factors such as temperature, solution composition, especially pH, and glass composition. One goal of this discussion is to clarify conditions under which these various processes are significant [3].

Soda-silicate glass, for example, is quite soluble in water, and, this “water glass” has very limited applications. Nonetheless, by proper choice of materials, glasses of very great chemical durability can be prepared [4].

Pure silica is attacked by alkaline solutions, however, and thus common (soda-lime-silica) glasses contain the seeds of their own chemical destruction. When these glasses are exposed to water, the water dissolves sodium ions from the surface of the glass to form alkaline sodium hydroxide [4].

This in turn attacks the silica. Newly formed or freshly broken glass surfaces are rapidly attacked in this fashion. Workers of glass surfaces have put this effect to good use by wetting a glass before scribing it for “cutting”. The chemical attack on the surfaces exposed by the scribe initiates regular cracks that assist in getting a clean break [4].

The chemical durability of a formed glass article can be improved by lowering the alkali content of the surface of the article before use. Such a reduction can be achieved by heating the articles in an atmosphere of SO_2 or by adding various chemicals to the glass surface which react with alkali diffusing to the surface at high temperature ($\sim 650^\circ\text{C}$), forming an alkali compound such as Na_2SO_4 . The sulphate can then be rinsed off thus reducing concentration of alkali at the glass surface [1].

2.4. Physical Properties of Glass

The physical properties of glass will be discussed in several subtitles which are density, viscosity, thermal expansion, surface tension and electrical conductivity.

In Table 2.4, the general physical properties of glass have shown.

Table 2.4 Physical properties of some commercial glasses [1].

Type of glass	Viscosity data			Coefficient of linear thermal expansion $\times 10^{-6}$ (0-300°C)	Refractive index (n_D)	Log(volume resistance) (ohm-cm at 250°C)	Power factor	Dielectric constant (1 Mc., 20°C)
	Strain point* (°C)	Annealing point† (°C)	Softening point‡ (°C)					
Fused silica	1070	1140	1667	5.5	1.458	12.0	0.0002	3.78
96% silica glass	820	910	1500	8.0	1.458	9.7	0.0005	3.80
						11.2	0.00024	3.8
						11.7	0.00019	3.8
Soda-lime sheet glass	505	548	730	85	1.510	6.5	0.004	7.0
Soda-lime plate glass	510	553	735	87	1.510	6.7	0.011	7.4
Soda-lime container glass	505	548	730	85	1.520	7.0	0.011	7.6
Soda-lime bulb glass	470	510	696	92	1.512	6.4	0.009	7.2
Lead alkali silicate (elc.)	395	430	626	91	1.539	8.9	0.0016	6.6
		435	630	89	1.560	10.1	0.0016	6.66
High lead alkali silicate	390	430	580	91	1.639	11.8	0.0009	9.5
Alumino silicate	670	715	915	42	1.534	11.4	0.0037	6.3
	540	580	795	49	1.490	6.9	0.010	5.6
Low expansion borosilicate	520	565	820	32	1.474	8.1	0.0046	4.6
Low electrical loss Borosil	455	495	—	32	1.469	11.2	0.0006	4.0
Borosilicate for tungsten seal	485	525	755	36	1.487	8.8	0.0027	4.7
Borosilicate for Kovar seal	435	480	708	46	1.484	9.2	0.0026	5.1

* Strain point corresponds to a viscosity of 10^{14} poises and represents a temperature, usually 35.45°C below the annealing point.
† Annealing point corresponds to a viscosity of 10^1 poises and represents a temperature at which internal strains are reduced to an acceptable limit in 15 minutes.
‡ Softening point corresponds to a viscosity of 10^{-3} to 10^0 poises.

2.4.1. Density of Glass

Density is the most frequently measured property of glass. It can be measured quickly and accurately (up to three places of decimals even in a moderately equipped laboratory), and is quite often used in the quality control of commercial glass manufacture [1].

Systematic studies of the variation of the properties of simpler glasses with composition have produced large amounts of data, which it was hoped would provide information pertinent to the problem of the constitution of glass. This hope has not always been justified [1].

Density may be treated as an additive property over some compositional ranges. The first relation to composition, established empirically by Winkelmann and Schott, describes a linear dependence. In some cases this relation is applicable; in other cases it does not even cover the entire glass-formation region of a simple system. Just consider the crossing density curves of binary alkali silicate systems, or the turning points in the density curves of simple borate glasses [5].

2.4.2. Viscosity of Glass

The viscosity of a glass is one of its most important technological properties. It determines the melting conditions, the temperatures of working and annealing, fining behavior (removal of bubbles from the melt), upper temperature of use, and devitrification rate. The viscosities of different glasses vary enormously with composition and are strong functions of temperature [3].

When a shearing force is applied to a liquid, it flows and the viscosity is a measure of the ratio between the force and rate of flow. If two parallel planes of area A , a distance d apart, are subjected to a tangential force difference F , the viscosity η is defined as

$$\eta = \frac{Fd}{Av} \quad [2.2]$$

where v is the relative velocity of the two planes. The most common viscosity unit is the poise (P), which is a dyne-second per square centimeter or a gram per centimeter per second. In most literature, viscosity is reported in poises [3].

The SI unit of viscosity is the pascal-second or Pa-s; 1 Pa-s = 10 P. The viscosity of most common fluids such as water and organic liquids is about one hundredth of a poise at room temperature [3].

Table 2.5 shows that the viscosity at the feeder is 10 to 100 times that at the melting end, and that when the glass is removed from the mould a few seconds later, the viscosity is 100 000 times greater than at the melting end [1].

Within the general limits set forth above, the ease with which glass can be worked into a variety of forms depends upon the length of the temperature interval between minimum and maximum viscosities at which it can be shaped [1].

Table 2.5 Range of glass viscosities.

Operation	Temperature ($^{\circ}\text{C}$)	$\log \eta$ (poise)
Melting	1575	2.0
Automatic feeder	1300 – 1100	3.0 – 4.0
Gathering in mould	1000	4.5
Removal from mould	780	7.0
Annealing	580 – 555	13.0 – 13.5
Maximum service temperature	500 – 450	14.6 – 15.5

Viscosity also plays an important role in melting conditions, refining behavior (removal of bubbles and seeds from the melt), upper temperature of use, and devitrification rate of glasses [1]. The viscosities of some commercially important silicate glasses are shown in Fig.2.5 as a function of temperature [3].

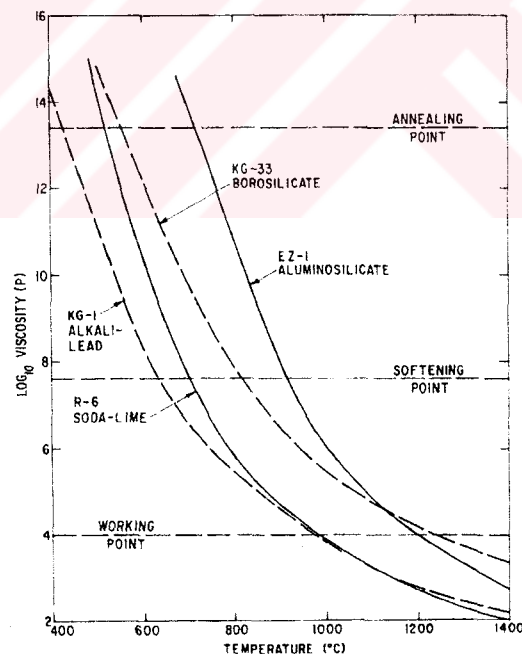


Fig.2.5 Viscosity of some commercial silicate glasses [3]

2.4.2.1. Variation of Viscosity with Time

As early as 1925, Stott, Irvine and Turner reported that heat-treatment of several hours was required to reach a constant condition when the viscosity of glass was as high as $10^{16.5}$ poises [1].

Lillie made a systematic study of the change of viscosity with time in the annealing range, and found that the time required to reach a constant viscosity characteristic of a given temperature increased as the heat-treatment temperature was lowered. Some of the results are shown in Fig.2.6. The upper curve of Fig.2.6 is for a sample previously held at 477.8°C for 64 hours, a time sufficient for attainment of 'equilibrium viscosity', and the lower curve is for a newly drawn fibre [1].

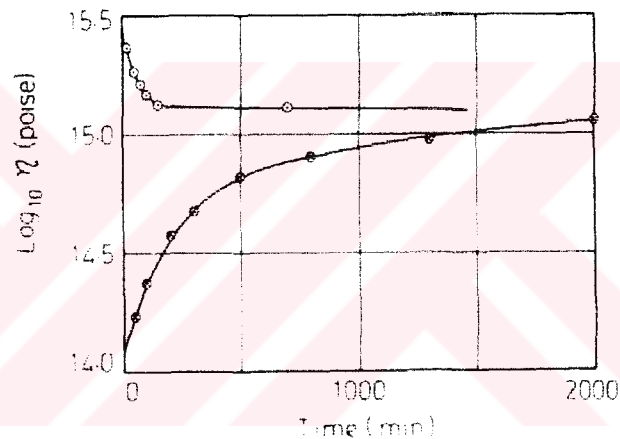


Fig. 2.6 Viscosity-time curves for two samples of a glass at 486.7°C [1]

The initial viscosity for the two samples is different by a factor of more than ten, but they approach the same final viscosity. It has been found that at higher temperatures less time is required, and at lower temperatures longer times, until it becomes practically impossible to reach the equilibrium viscosity [1].

2.4.3. Thermal Expansion of Glass

The linear coefficient of thermal expansion is the fraction of original length at 0°C by which material increases per degree centigrade rise in temperature. For glass, values range from 5.5×10^{-7} (5.5 parts per 10 million) for pure silica to as much as 125×10^{-7} for most glass [4].

At temperatures over the transformation temperature of glass, the coefficients may increase as much as 50 percent, because configuration changes and normal thermal expansion occur [4].

Glass is a poor conductor of heat, and glass exposed to sudden changes in temperature may develop dangerous stresses, leading to fracture resulting from the temperature difference between the surface and the interior [4, 6].

This property of glass which is considered as a disadvantage in such cases, can be achieved if the tensile strength is increased by tempering and if the temperature difference between the two surfaces is decreased, and most of all if a glass material that has a low thermal expansion value is used [6].

For fairly obvious reasons, sudden heating which puts the glass surface in compression is less dangerous than sudden cooling, which puts the surface in tension [4, 6].

For applications where thermal shock is anticipated, toughened glass offers some advantage, because the surface is already under compression. The problem is usually attacked more directly, however, by using glasses with low coefficients of thermal expansion. Pure silica is ordinarily too expensive (because it is so difficult to fabricate), but 96% silica glass has a coefficient of thermal expansion of only 8×10^{-7} , compared to 5.5×10^{-7} for pure silica, but, say, 90×10^{-7} for ordinary glass. For less demanding service, borosilicate glasses with a coefficient of 32×10^{-7} are satisfactory, and these are the basis of the well-known Pyrex brand of heat-resistant glassware. Where excellent corrosion resistance is to be combined with thermal shock resistance, aluminoborosilicate glass (42×10^{-7}) is used [4].

2.4.4. Surface Tension of Glass

A molecule in the interior of a liquid is completely surrounded by other molecules, and so, on average, it is attracted equally in all directions. A molecule in the surface, however, is subject to a net inwards attraction, because the number of molecules per unit volume is greater in the bulk of the liquid than in the vapour [1].

The surface of a liquid will always, therefore, tend to contract to the smallest possible area. In order to extend the area of the surface it is obviously necessary to do work to bring the molecules from the bulk of the liquid into the surface against inward attraction force. The work required to increase the area by 1 cm² is called the free surface energy [1].

As a result of the tendency to contract, a surface behaves as if it were in a state of tension, and it is possible to ascribe a definite value to this surface tension, which is the same at every point and in all directions along the surface of the liquid. It is given the symbol γ , and may be defined as the force in dynes acting at right angles to any line of 1 cm length in the surface. The work done in extending the area of a surface by 1 cm² is equal to the surface tension, which is the force per centimeter opposing the increase, multiplied by 1 cm, the distance through which the point of application of the force is moved [1].

The surface energy γ at temperature T and pressure p can be defined as the reversible work dW_r to form a surface area dA [3].

$$\gamma = -(dW_r / dA)_{T, p} \quad [2.3]$$

For a liquid, surface energy and surface tension are equal. The units of surface energy are joules per square meter; $10^3 \text{ dyn/cm} = 1 \text{ J/m}^2$. The surface energy decreases as the temperature increases; for most silicate glass melts this change is quite small (less than 10%) from 1200 to 1500°C [3].

The influence of composition on surface energy is about 0.3 J/m² at 1200°C, and this value is a reasonable approximation for the surface energy of most sodium-containing silicate glasses at this temperature. The surface energy of a molten zirconium-barium-lanthanum fluoride glass at 550°C was found to be $0.174 \pm 0.005 \text{ J/m}^2$ by a solidified pendant drop technique [3].

Boric oxide (B₂O₃) has the low surface tension of about 0.085 J/m² at 800°C, and addition of alkali oxides raises the surface tension sharply [3].

These measurements of surface energy of melts refer to surfaces that have reacted with ambient water form SiOH groups on the outer surface. The energy of a freshly fractured glass surface is much higher; for example, for a soda-lime glass it is about 3.4 J/m². A fresh surface of this energy reacts very rapidly with low concentrations of water vapor to form SiOH groups and a much lower surface energy. Segregation of impurities to surfaces and interfaces is usually favored because it lowers the surface energy [3].

2.4.5. Electrical Conductivity of Glass

Among electrical properties, electrical conductivity is the property of greatest practical importance. On the one hand, it controls the use of the glass in electrical engineering applications at ambient temperature. On the other hand, high-temperature conductivity is important for contemporary methods of electrical melting of glass based on corrosion-resistant electrodes submerged in the melt and utilizing the electrical resistance of the melt itself [5].

Electrical conduction is based on the transport of electrons or ions. The “specific electrical conductivity” K is defined as the conductivity of a cylindrical body with a cross section of 1 cm² and a length of 1 cm. The “specific electrical resistance ρ ” is defined as the reciprocal value of the electrical conductivity [5].

$$\rho = 1 / K \text{ (K in } \Omega^{-1} \cdot \text{cm}^{-1}) \quad [2.4]$$

At ambient temperature, conventional glass has a very small electrical conductivity due to the structural features of the silicate network. A long time ago, Gehlhoff and Thomas characterized the conductivity by the temperature at which the specific conductivity has the value $K = 100 \cdot 10^{-10} \text{ (}\Omega^{-1} \cdot \text{cm}^{-1}\text{)}$, the so-called “ T_{K-100} value.” For a soda-lime (window) glass, T_{K-100} would be 150-200°C [5].

This value was to be listed for the technical glasses. Of great interest is the strong change in the specific electrical conductivity over large temperature ranges. For this reason, attempts at a mathematical formulation have been made (e.g., as early as 1908 by Rasch and Hinrichsen) as below. Here, A and B are constants [5].

$$\log K = A - (B/T) \quad [2.5]$$

On a more theoretical basis, Stevels obtained the similar relation [5]:

$$\ln K = A - (\phi / RT) \quad [2.6]$$

The value of A changes with both temperature and composition. The activation energy ϕ is a function of composition. The activation energy is about 84×10^3 J/mol for conventional glasses and is nearly constant between 50°C and the glass-transition temperature T_g [5].

2.5. Mechanical Properties of Glass

In bulk, glass appears almost completely rigid, but in thin sheets or fibers, it is quite pliable, provided that the radius of curvature is large compared to the thickness of the glass [4].

When it is considered that, the silicon-oxygen bond is very strong; so that glass should be a very strong material. In principle, it is true. Newly formed, fine glass fibers will support stresses greater than 70.000 kg/cm^2 (7×10^3 MPa). This value is twice as much as steel could support even in theory [4].

2.5.1. Elasticity of Glass

A mass is generally deformed under the effect of external mechanical forces. If the deformation of the mass disappears completely on discontinuation of the mechanical force, the body is considered to be perfectly elastic. Glass (below t_g) is perfectly elastic, provided the force applied is relatively short-term in nature. Elastic bodies observe Hook's law: there is a proportional relationship between strain e and the acting deforming stress σ [7]:

$$\sigma = M.e \quad [2.7]$$

The proportionality constant M is generally called modulus in this relationship. The following modulus are distinguished according to the types of deformation [7]:

- modulus of elasticity in tension, E , also called Young's modulus, which is considered whenever elongation of a body results from tensile stressing;
- modulus of elasticity in shear, also called the torsional modulus, G , which is considered when a body is subject to lateral tangential stress;
- modulus of elasticity in compression, K , when a body is stressed from all sides by compression.

The reciprocal value of the modulus of elasticity in compression is called compressibility, k [7].

Tensile stressing of a glass rod brings its elongation and at the same time its transverse narrowing [6].

The relation between tensile stressing and strain (which can occur as narrowing or elongation) can be defined by the help of Fig.2.7.

By calculating the slope from Fig.2.7, it is possible to reach the value of elastic modulus in tension, E [8].

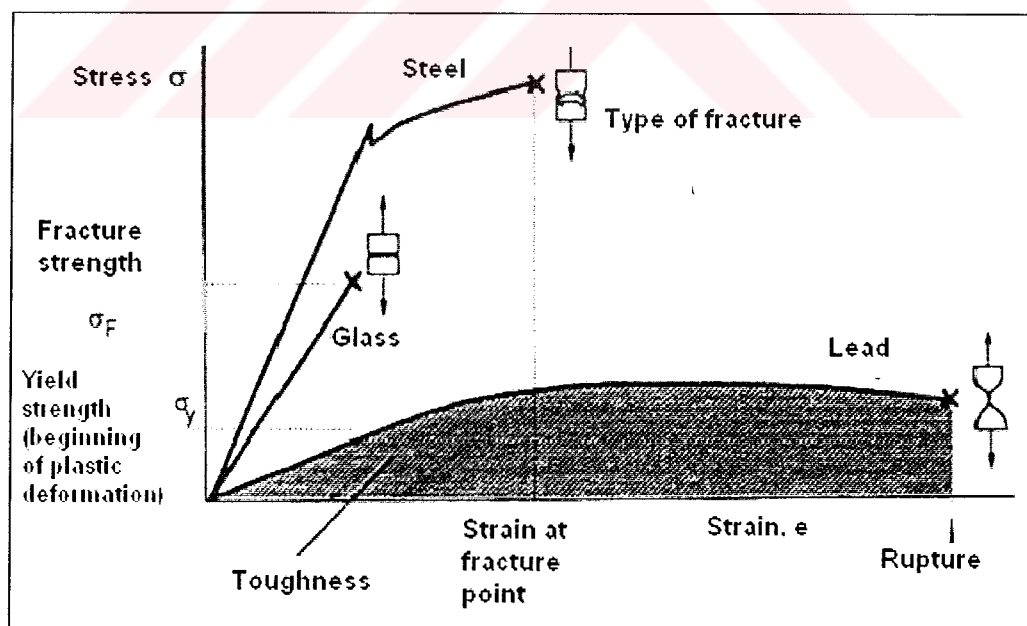


Fig.2.7 Stress-strain diagram for different materials [8]

If the relative narrowing is $\Delta d / d$ and the relative elongation is $\Delta l / l$, the ratio of the two deformations, is called Poisson's ratio or Poisson's number, μ . Poisson's ratio is a dimensionless quantity [7].

The three modulus mentioned above and Poisson's ratio are mutually related as [7]:

$$E = 2(1 + \mu)G = 3(1 - 2\mu)K \quad [2.8]$$

From the Eq.[2.8] it is possible to derive the following combined equations [7]:

$$E = \frac{9KG}{3K + G} = 3K(1 - 2\mu) = 2G(1 + \mu) \quad [2.9]$$

$$G = \frac{3EK}{9K - E} = \frac{E}{2(1 + \mu)} = \frac{3K(1 - 2\mu)}{2(1 + \mu)} \quad [2.10]$$

$$K = \frac{EG}{9G - 3E} = \frac{E}{3(1 - 2\mu)} = \frac{2G(1 + \mu)}{3(1 - 2\mu)} \quad [2.11]$$

$$\mu = \frac{3K - E}{6K} = \frac{K - 2G}{2G} = \frac{3K - 2G}{6K + 2G} \quad [2.12]$$

Eq.[2.8] through Eq.[2.12] are referred to as Graf's equations. Compressibility k , as the reciprocal value of the modulus of elasticity in compression, is defined by the Eq.[2.13] [7].

$$k = \frac{3(1 - 2\mu)}{E} \quad [2.13]$$

With glasses, only the modulus of elasticity in tension, E , and Poisson's ratio, μ , are usually specified. The other modulus can be calculated from the combined Eq.[2.9] through Eq.[2.13] [7].

The two quantities E and μ are encountered in technical calculations of the resistance to thermal shock, in the calculation of annealing schedules and in the technology of glass-to-glass, glass-to-metals, and glass-to-ceramics fusion technologies [7].

And the Table 2.6 below shows the factors for calculating Young's modulus from chemical composition [1].

Table 2.6 Factors for calculating Young's modulus from chemical composition.

	<i>Winkelmann and Schott (94)</i>			<i>Clarke and Turner (96)</i>
SiO_2	6.9	6.9	6.9	3.9
B_2O_3		5.9	2.5	
Na_2O	6.0	9.8	6.9	10.8
K_2O	3.9	6.9	2.9	
CaO	6.9	6.9		23.5
BaO		6.9	2.9	
ZnO	5.1	9.8		
PbO	4.5		5.4	
MgO		3.9	2.9	29.4
Al_2O_3	17.6	14.7	12.7	11.8
Fe_2O_3				11.8
P_2O_5			6.9	
As_2O_5	3.9	3.9	3.9	

It is possible to observe the values of elastic modulus and Poisson's ratio for some glasses in the Table 2.7 below [1].

Table 2.7 The values of elastic modulus and Poisson's ratio for some glasses.

<i>Glass type</i>	<i>Young's modulus (GPa)</i>	<i>Poisson ratio</i>
Fused silica	70	0.16
Soda-lime silica (GE type 008)	69	0.22
Corning type 7740 borosilicate	63	0.20
Corning type 7052 borosilicate	57	0.22
Corning type 1720 aluminosilicate	85	0.24
GE type 001 potash soda lead silicate	62	0.21

2.5.2. Strength of Glass

Glass is characterized by great brittleness and very low strength. What are the limits of its technical applicability? The dependence of strength on chemical composition and structure is controversial. The only general rule that can be made is that the oxides increasing chemical durability and the modulus of elasticity in tension contribute favorably to mechanical strength [7].

The strength of glass is first of all a function of the state of the surface, its defects, and its interaction with moisture, gases and impurities (e.g., dust). There is no standard criterion for the point where fracture of glass occurs. The strength of glass is therefore not regarded as a physical material property [7].

Three types of strength are distinguished; tensile strength, bending strength and compression strength. On taking tensile strength as equal to unity, the bending strength is approximately twice as high, and compression strength is at least ten times as high [7].

It is well known that the measured mechanical strength of glass is much lower than the theoretical strength; various workers, using several methods to calculate the theoretical strength, have agreed on a figure of the order of 6895MPa. In practice, however, strengths may be as low as 5 MPa [9].

Griffith first propounded the theory that the difference was largely due to minute surface flaws or 'Griffith cracks' acting as stress concentrators, and this view is still widely accepted. No one has ever succeeded in definitely identifying these micro cracks, although attempts have been made to render them visible, chiefly by Andrade and Tsien, Ernsberger, and Hillig [9].

Many experiments indicate that glass with a "normal" surface usually fails from the surface and that flaws are responsible for its ordinary strength. The contemporary view is that Griffith's theory correctly describes the strength of glass having significant surface flaws. However, glass can be prepared without surface flaws (having so-called "pristine" surface) and then has very high strength [10].

Carefully prepared silica fibers have strengths as high as 14 GPa (2 million psi), which is about $E/5$ with $E = 70$ GPa. Applying the Griffith-Irwin fracture mechanics with $K_{Ic} = 0.81 \text{ MPa}\cdot\text{m}^{1/2}$ as determined from experiments with the cracks requires a crack length of 1 nm to account for a strength of 14 GPa. Such a short crack is probably outside the range of validity of the Griffith-Irwin theory as 14 GPa is thought to be the theoretical strength of silica [10].

The researches showed large variation of mechanical strength of float glass produced under different technological conditions. The analysis of the literature data indicates that there are inconsistencies in the methods employed for the strength analysis of sheet glass. All methods described are based on two main statistical approaches, namely those of Weibull and Gauss. The application of the Weibull statistics is convenient to define the physical nature of glass failure and is based on the following failure function [11].

$$F = 1 - \exp \left[- \left(\frac{\sigma}{\sigma_0} \right)^m \right] \quad [2.14]$$

Where, F is the failure probability, σ_0 and m are the Weibull parameters [11].

In industrial practice it is preferred to use the average mechanical strength (σ_{av}) and its standard deviation (s) as the main parameters of the sheet glass strength (σ) based on Gaussian (normal) statistics for n measures [11]:

$$F(x) = \frac{1}{\sqrt{2\pi}s^2} \exp \left[-\frac{1}{2} \frac{(\sigma - \sigma_{av})^2}{s^2} \right] \quad [2.15]$$

$$\sigma_{av} = \frac{\sum \sigma_i}{n} \quad [2.16]$$

$$s = \sqrt{\frac{n \sum \sigma_i^2 - (\sum \sigma_i)^2}{n(n-1)}} \quad [2.17]$$

Fracture occurs at the point where the glass has been subject to concentrated tensile stressing. In a glass rod being bent, the tensile stress is situated at the outer side from the bend. When a heated glass vessel is cooled, it always cracks starting from the side on which it has been cooled, because tensile stressing results from contraction at the cooled surface. Strength is mostly related to micro cracks. The micro cracks in glass, which is an amorphous material, propagate in a way different from crack development in ductile materials (e.g. metals). They are peculiar in that they “grow” slowly even at rest, without the effects of any external mechanical forces. The micro cracks act as stress concentrators [7].

The mean size of the micro cracks and thus also the mechanical strength will be affected by the microstructure of the glass-ceramic material. Table 2.8 depicts the effect of the crystal size on the strength during bending of several types of glass-ceramic materials [12].

Table 2.8 The effect of crystal size on the strength of glass-ceramic materials using various nucleators.

Composition (wt.%)														Crystal size (μm)	Bending strength (MPa)
Main components						Nucleators									
SiO ₂	Li ₂ O	Na ₂ O	K ₂ O	ZnO	Al ₂ O ₃	P ₂ O ₅	TiO ₂	MoO ₃	WO ₃	V ₂ O ₅	Au	Ag	Pt		
80.6	16.7					2.7								1-3	404
81.0	12.5		2.5		4.0						0.027			5	260
78.5	12.1		2.5		3.9	3.0								5	274
59.0	9.0		2.0	27.3		2.7								5	175
59.0	9.0		2.0	27.3				2.7						5	247
71.2	19.8				6.0	3.0								5-10	210
63.5	5.7		4.2	5.3	18.9	2.4								10	86
62.5	5.6		4.2	5.3	18.5				3.9					10	109
61.0	5.6		4.1	5.2	18.2	2.4			3.5					10	166
61.7	5.7		4.2	5.3	18.5	2.4		2.2						10	193
62.5	5.7		4.2	5.3	18.5	2.4				1.4				10	162
62.5	5.7		4.2	5.3	18.6	2.4	1.3							10	116
83.0	17.0													15	23
83.0	17.0										0.027			15	34
63.4	5.7		4.2	5.3	18.9	2.4						0.1		15	29
63.5	5.7		4.2	5.3	18.9	2.4							0.001	15	39
72.0	20.0	2.0			6.0									10-20	64
61.0	9.2		2.0	27.8										20	2
59.0	9.0		2.0	27.3			2.7							20	2
57.7	8.8		1.9	26.6			5.0							20	2

The cracks are mostly situated at the edges of products, where the glass contracts at a higher rate on cooling. Large objects have more cracks on their surface than small ones and are thus less mechanically and thermally durable.

In principle, the strength of glass can be increased in two ways:

- 1) by preventing access of water or moisture to the glass surface (silicone-coating),
- 2) by creating a compressive stress in the glass surface.

When not taking into account surface exchange of ions having the same charge but a different ionic radius (which can be used for strengthening glass only in some instances) toughening is the technique used for increasing the strength of glass products (but not for strengthening glass as a material). The purpose of toughening is to create a compression stress in the surface layer of the wall.

The cracks “close” under compression and do not propagate deeper under mechanical or thermal loading. Toughening is carried out by instantaneous cooling down in a stream of cold air or by immersion in an oil bath [7].

2.5.3. Strain of Glass

Strain in glass may either be a source of severe disturbances and lead to fracture, or, if controlled, facilitate entirely novel uses, just as in the case of crystallization phenomena. Thermal and chemical strengthening, the development of new high-strength glass-ceramics are based on deliberately produced strain in glass [5].

Homogeneous glass is characterized by its perfect isotropy. Mechanical loading leads to density differences in the direction of pressure, as well as densification, leading to strain which can be followed and measured via the appearance of birefringence. This provides some analogy to the structure and optical behavior of crystals [5].

Time dependence of mechanical behavior is often termed delayed elasticity (or elastic after-effect). In glasses, the delayed response arises in part due to a viscous flow (because the structure of glasses is thought to be liquid-like) and in part due to rearrangement of network modifying cations under the influence of stress [1].

The viscous flow in glass increases with temperature, and hence the overall behavior can be sketched as shown in Fig.2.8 [1].

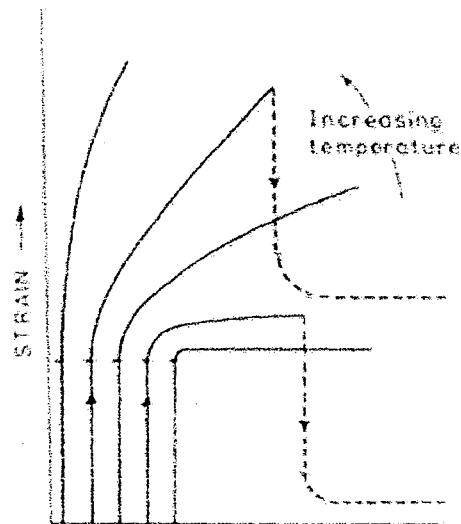


Fig. 2.8 Strain-time relationships under constant stress at varying temperatures [1]

2.5.4. Fatigue in Glass

Fatigue in glass results when its strength deteriorates while it is stressed in an atmosphere containing water. This fatigue requires design strengths three or four times lower than if they retained their initial strength [3].

If a fresh glass surface is violated, e.g., by a diamond, and subsequently subjected to a small load of long duration in a normal atmosphere, a final strength test yields a noticeably smaller strength value than obtained without preloading. It must be assumed that the fissure is kept open under this small load and water enters, leading to gel formation and swelling, assisting fracture. Fatigue is an important factor in predicting failure. Testing for reliable predictions requires the separation of bulk properties, flaw structure, and flaw reactions with the environment [5].

2.5.5. Tempered Glass

Tempered glass, also known as toughened glass, is produced by heat-annealed glass to approximately 650°C, at which point it begins to soften. Its outer surfaces are then cooled rapidly, creating high compression in them (Fig.2.9) [4].

Its strength is usually increased by a factor of four or five times that of annealed glass, embodying safety and strength, as well as beauty [4].

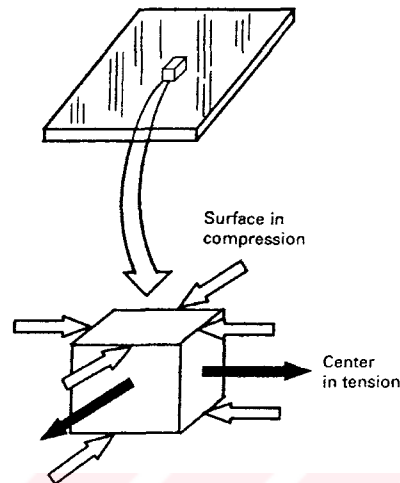


Fig.2.9 Heat-treated glass [4]

Tempering also imparts a unique safety characteristic, so that when fully tempered glass breaks, it fractures into relatively harmless fragments. Tempered glass can resist temperature differences up to $\approx 175^{\circ}\text{C}$, which would cause ordinary glass to crack. The heat treatment process introduces surface compressions in heat-strengthened and fully tempered glass as shown in Fig.2.9. Tempered glass must be handled and installed with the same care as ordinary glasses to prevent damage to the edges or surfaces [4].

2.5.6. Heat-Strengthened Glass

Heat strength glass is defined in ASTM C 1048 as having residual surface compression greater than 24 MPa and less than 69 MPa or edge compression greater than 34 MPa and less than 67 MPa [4].

When broken, the appearance of the break pattern will vary widely depending on the amount of compression and the surface quality. At the lower portion of the surface compression range, there will be a large, open pattern reminiscent of annealed glass but generally without the sharp-pointed shards. In the midrange of 31 to 48 MPa, the pattern becomes increasingly smaller, or more closed, with more fragments [4].

At the high end above 48 MPa, it becomes smaller and smaller until, above 62 MPa, it is often difficult to determine if the lite was heat-strengthened or tempered [4].

2.5.7. Hardness of Glass

Hardness is a complex property, which has not as yet received a satisfactory theoretical treatment. Because of consequent uncertainty, the experimental methods proposed give results, which are discordant, which are expressed in arbitrary and unrelated units, and which do not necessarily measure the property usually meant by the term hardness [13].

The fundamental idea associated with hardness is that when we feel a substance, or press it with our fingers, it does not deform. The term “hard” is similar to many other technical terms, which are also a part of every-day speech in that the usual and qualitative meaning is familiar and useful, but the quantitative specification in terms capable of measurement is difficult if not impossible [13].

The most generally used criterion of relative hardness is the ability of a harder substance to scratch a softer one, and this criterion forms the basis of the well-known Mohs' scale, widely used in mineralogy. In this scale, glass occupies a position intermediate between apatite and quartz, some glasses being scratched by, others scratching, orthoclase [13].

Auerbach, however, found some flints to be softer than apatite, and a borosilicate crown harder than quartz. The matter is further complicated by the fact that the scratching test is not decisive, as Auerbach found that each one of a series of glasses ranging from the softest flints to the hardest borosilicate crown scratched every other one [13].

The method of Auerbach, based on a theoretical investigation by Herz, is typical of the more elaborate methods of hardness determination. If two surfaces in contact, one spherical, the other plane, both of the same composition and isotropic, are subjected to a pressure P , the surface contact will be a portion of a sphere of radius $2r$, where r is the radius of the original sphere [13].

The boundary of the surface of contact is a circle of diameter d , determined by the relation $E' = \frac{E}{(1 - \mu^2)} = \frac{12Pr}{d^3}$ in which μ and E are Poisson's ratio and Young's modulus, respectively. The ratio $E / (1 - \mu^2)$ is evidently a constant for a given glass, and Auerbach named it the indentation modulus, denoted by E' . The ratio Pr / d^3 involve quantities which can be determined by experiment. The method of experiment used by Auerbach was to press a lens of known curvature against a plane-polished piece of the same glass, and to measure with a microscope equipped with a micrometer eyepiece the diameter of the circle of contact, which is seen as a round black spot [13].

The indentation modulus is essentially dependent on Young's modulus, was not found to bear any simple relation to the hardness, as determined by the scratching test. In carrying out the experiments, it was found that the limiting pressure that could be applied to the lens without the formation of a crack was proportional to the radius of curvature ρ , and thus was a characteristic constant of the glass. This constant was denoted by F' , and if the limiting pressure be denoted by P' , it is determined by the relation below [13].

$$F' = P' / \rho \quad [2.18]$$

It was further empirically found that, though this new quantity itself bore no relation to the hardness, the latter was represented by the given equation.

$$H = \frac{1}{\pi} \sqrt[3]{\frac{3}{2} (E')^2 F'} \quad [2.19]$$

In fact, hardness is not an essential characteristic of a material, but rather it is a complex function of a number of physical properties that are combined in differing degrees depending on the method of the test. In a sense, we can equate the hardness of a material with its resistance to abrasion or wear and this characteristic is of practical interest since it may determine the durability of a material during normal use and it may also decide the suitability of the material for special applications where abrasion resistance is of prime importance. Thus, the resistance of the material to abrasion under closely specified conditions may be taken as one measure of hardness [14].

The resistance of scratching of the material by other materials represents another measure of its hardness, and the depth of penetration of a loaded pyramid (usually a diamond) into the material under specified conditions represents yet another measure of hardness [15].

All of these methods are empirical and, although any one of hardness may differ according to the method employed. For this reason care must be taken to select test methods which represent the closest approximation to the practical conditions of use whenever possible [14,15].

One of these test methods that has been described above, is the scratching test, which forms the basis of the Mohs' scale and the method of Auerbach.

Scratch hardness has the merit of being relatively simple to carry out but the results are often of uncertain value. Attempts have been made to devise more reliable scratch hardness tests than that proposed by Mohs, such methods are based on studying the effects of drawing a diamond scribe across the glass under specified conditions [15].

Indentation hardness has been widely applied in the metallurgical field and this method has also been applied to glasses and similar materials. A number of indentation hardness test methods, such as Vickers, Rockwell and Knoop hardness test methods, are available, and they will be discussed in further headlines.

2.6. Fracture Mechanics

The principles of fracture mechanics have been used to analyze the fracture surfaces of brittle materials for many years. Basically, fracture mechanics gives us a way of separating the properties of the material from the flaw distribution in the structure. Flaws in glass can be either extrinsic, e.g., due to machining or handling, or can be intrinsic, e.g., bubbles and striae. In essence, fracture mechanics involves introducing a large crack into a material and determining the resistance of the material to the propagation of this crack under different environmental and stressing conditions. Knowledge of the crack propagation parameters and behavior can then be combined with information regarding flaw severity to provide a means for predicting strength and/or lifetime of a particular structure [16].

2.6.1. Fracture Definition

Fracture can be defined as separations of the material into two or more pieces under stress. New surfaces are obtained when a material is broken. Mainly, fracture consists of two phases, which are crack initiation and crack propagation. The crack propagation that occurs at any part of material causes fracture [17].

In the structures, which have been designed by avoiding the plastic deformation and the elastic deformation over a certain value; such as ships, bridges, pressure tanks, and pipelines; fracture can occur unexpectedly [17].

The reason of the fracture in that kind of structures is generally, the unsuitable welding technique that have applied or the welding that have done wrongly which causes crack initiation and crack propagation in the structure [17].

2.6.2. Types of Fracture

The character of fracture alters depending on temperature, deformation speed and the stress applied on the body [17].

Fracture types can be classified by regarding the criterions as given in Fig.2.10 [17].

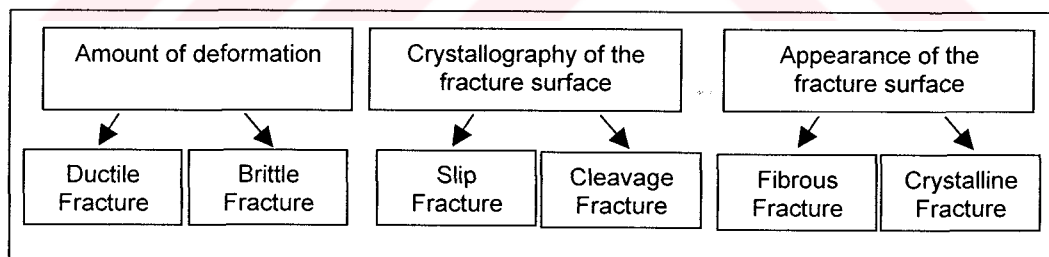


Fig.2.10 Types of fracture

2.6.3. Fracture Types of Glass

Glasses are brittle materials. It is related to the cleavage fracture. Thus, the types of fracture that can be observed in glass materials can be given as brittle fracture and cleavage fracture.

2.6.3.1. Brittle Fracture

- Little or no visible plastic deformation precedes the fracture.
- The fracture is generally flat and perpendicular to the surface of the component.
- The fracture may appear granular or crystalline and is often highly reflective to the light. Facets may also be observed, particularly in coarse-grain steels.
- Chevron patterns may be present.
- Cracks grow rapidly, often accompanied by a loud noise [18].

2.6.3.2. Cleavage Fracture

Cleavage fracture occurs, as a result of the rupture of the bonds, which are vertical to the fracture plane. The exterior tensile forces that are applied to the material, cause cleavage crack to traverse through the material that undergoes cleavage fracture [17].

In very brittle materials, cleavage fracture can move ahead from one grain to another on the cleavage planes. Because of the fact that cleavage fracture occurs in a plane that is transgranular, that type of fracture has a crystalline appearance [17].

Also the shapes of the grains do not change in cleavage fracture and the appearance of the surface is generally flat. Because of that flat surface, fracture surface reflects the light and the surface seems brilliant [17].

At some conditions, in polycrystalline materials, the grain boundaries are weaker than the fracture planes. In this case, fracture does not occur transgranular (from inside the grain boundaries), but intergranular (through the grain boundaries) [17].

As the temperature increases, the fracture type of the metallic materials tends to change to intergranular fracture from transgranular fracture. This type of fracture that is occurred by the cause of the change in the temperature is named transgranular or intergranular creep fracture [17,18].

2.6.4 Stress Intensity Factor And Fracture Toughness

Griffith develops the first equation that is found to calculate the stress, to which the brittle material that has a crack can endure.

And the equation is given below:

$$\sigma = \left[\frac{2\gamma E}{\Pi c} \right]^{1/2} \quad [2.21]$$

σ = Fracture stress (MPa)

γ = Fracture surface energy (J/m²)

E = Elastic modulus (MPa)

c = Half crack length (m)

In this equation, instead of Griffith's surface energy value, γ ; G is generally used. So, this equation can be re-written as below:

$$\sigma = \left[\frac{EG_c}{\Pi c} \right]^{1/2} \quad [2.22]$$

G = Stress energy release (kJm⁻²)

G_c = Critical value of stress energy release (kJm⁻²)

Here, $G_c = 2\gamma$ and it shows the total work that is required for fracture to happen. Fracture takes place when $G = G_c$ condition is obtained. Irwin and his friends developed a parameter of stress intensity factor, K , from the calculations that are done at the crack point. K is a function of the stress applied, crack shape and the geometric factor. So, the Griffith equation can be written as below [17].

$$\sigma(\Pi c)^{1/2} = (EG_c)^{1/2} \quad [2.23]$$

The term $\sigma(\Pi c)^{1/2}$, can be defined as the force that is required for the crack propagation. For that reason, it can be named as stress intensity factor. It means that, it can be showed as $K = \sigma(\Pi c)^{1/2}$ [17].

When K has a critical value of K_c ($\text{MNm}^{-3/2}$), the fracture occurs. In this condition, $K_c = (EG_c)^{1/2}$ can be written. And from that equation, K_c can be defined as the fracture toughness [17]. To find out the fracture toughness (K_c) property of the material, stress intensity factor (K) is calculated. In the condition that $K = K_c$, crack grows and fracture occurs [17,16]. G_c and K_c values for different materials are given in Table 2.9.

This means that crack will propagate, and failure will occur at much lower applied stresses than the ones that are theoretically required. It is to the propagation of these cracks that fracture mechanics addresses itself [16]. Stress intensity factor (K), is a parameter that depends on the condition of stress and crack geometry and it is not related with the properties of the material; while K_c , is a parameter, which is related with the material properties [17]. Those equations that are listed above are true for the infinitely wide plates [16]. For the samples that are in certain dimensions, different equations that are developed by experimental or theoretical ways are used [17].

In other words, stress intensity factor can be defined for more complicated geometries by various mathematical techniques. The form of the stress intensity factor also depends on the type of loading applied to the crack [16]. As shown in Fig.2.11, K_I refers to an applied tensile stress perpendicular to the crack face, K_{II} to a shear force applied along the crack face in the direction of crack motion, and K_{III} to a shear force along the crack face perpendicular to its direction of motion [16].

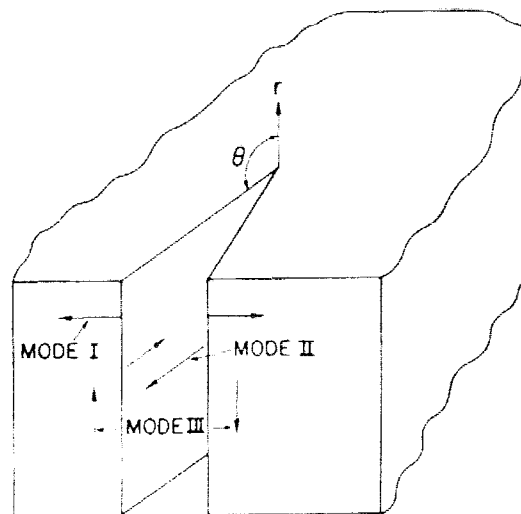


Fig.2.11 Three modes of loading for a crack in a plate [16].

Table 2.9 G_c and K_{Ic} values for different materials [17]

MATERIALS	G_c (kJm ⁻²)	K_{Ic} (MNm ^{-3/2})
Pure Ductile Materials (Cu, Ni, Ag, Al)	100-1000	100-350
High Strength Steels	15-118	50-154
Low Carbon Steels	100	140
Titanium Alloys	26-144	55-115
Fiberglass	40-100	42-60
Al Alloys (High and Low Strength)	8-30	23-45
Medium Carbon Steels	13	51
Polypropylene	8	3
Nylon	2-4	3
Cast Iron	0,2-3	6-20
Epoxy	0,1-0,3	0,3-0,5
Silicon Carbide (SiC)	0,05	3
Alumina (Al ₂ O ₃)	0,02	3-5
Soda Glass	0,01	0,7-0,8
Electrical Porcelain	0,01	1
Ice	0,003	0,2

2.7. Crack Mechanics

Design practice based on fracture mechanics generally assumed the pre-existence of cracks or crack-like defects or the early initiation of the cracks, in structural components, and that the lives of these structural components are determined by subcritical crack growth [19].

These assumptions have been well justified by service experience. Primary emphasis in recent years, therefore, has been placed on studies of subcritical crack growth [19].

Subcritical crack growth can be broadly grouped in to four categories according to the type of loading and the external chemical environment [19].

1. Sustained load crack growth inert environment (vacuum, inert gases, etc.).
2. Fatigue crack growth in environment.
3. Sustained load crack growth in aggressive environment, or stress corrosion cracking.
4. Fatigue crack growth in aggressive environment, or corrosion fatigue [19].

The first two of these are purely mechanical in nature while the later two entail mechanical and environmental interactions. All four categories of crack growth are affected by temperature, reflecting the temperature dependence of the kinetics of chemical and deformation processes that control crack growth. Because thermal and chemical environment are invariably present during service these factors have received and are being given a great deal of attention. [19]

Many variables can influence the subcritical crack growth behavior of materials or structural components. Some of the significant variables are as follows: [19]

Mechanical Variables

- For sustained load crack growth: (σ , K , state of stress, residual stress and prior loading)
- For fatigue crack growth: ($\sigma_{\max}$, $K_{\max}$, cyclic stress or stress intensity range $\Delta\sigma$ – ΔK , stress ratio R^* , cyclic load frequency f , state of stress, residual stress etc.)

Geometrical Variables

- Crack size, and relation to component dimensions.
- Crack geometry.
- Component geometry adjoining crack.
- Stress concentrations associated with design.

Metallurgical Variables

- Alloy composition
- Distribution of alloying elements and impurities.
- Microstructure and crystal structure.
- Heat treatment.
- Mechanical working.
- Preferred orientation of grains and grain boundaries.
- Mechanical properties. (strength, fracture toughness, etc.)

Environmental Variables

- Temperature, T .
- Types of environments. (gaseous, liquid, liquid metal, etc.)
- pH.
- Viscosity of environment, η .
- Coatings, inhibitors.
- Electrical potential, Φ .

[19]

2.7.1. Crack Initiation

Evaluation of the indentation cracking properties of brittle materials requires knowledge of the underlying fracture mechanics. The starting point for the requisite formulation is the characterization of the elastic-plastic stress field, with particular focus on the residual component of this field. Unfortunately, this formulation can be a formidable task, even for the idealization of a perfectly homogeneous, continuous solid. The difficulties especially pronounced in the modeling of crack initiation, for there one is concerned with the complex details of the contact near field [20].

Above some threshold in the loading, cracks initiate from the deformation zone, where strong stress concentrations exist. The threshold is found to be rate dependent, with a tendency to an increasingly delayed, post-indentation pop-in at lower peak loads. The presence of water strongly diminishes the delay times [21].

Once initiated, the cracks grow spontaneously into their well-defined radial/median and lateral configurations, to a size determined primarily by the material toughness. Again, these cracks continue to extend with time in water-containing environments. The role of residual stresses in driving these fracture processes is a vital element of the mechanics description [21].

The specific cracks, which form, and the sequence in which they form, is strongly influenced by the material parameter E/H . In this regard, the use of soda-lime glass as a “prototypical brittle material” in this description of indentation fracture behavior is suspect, because its E/H value is toward the low end of the range for brittle materials. Soda-lime glass is, in fact, experimentally observed to crack in ways, which are very different from the majority of brittle materials, in both morphology and sequence [22].

2.7.2. Crack Propagation

If it is considered a given crack, which may be introduced during fabrication, e.g. a welding crack or initiated by the alternating loads during operation of the component, it can be distinguished between different steps in further crack extension. The steps in crack propagation can be viewed at Fig.2.12 below [23].

First the crack may extend further in depth and length as a fatigue crack [Fig.2.12b]. If the crack size has sufficiently enlarged and a sufficiently large external load is applied, the crack penetrates the component and gives rise to a leak in case component is pressurized [Fig.2.12c] [23].

This event is called local failure or local instability, if it involves some fast unstable crack extension. After wall penetration the crack may get arrested and further increase by fatigue until unstable crack extension and complete (global) failure of the component occur [Fig.2.12d] [23].

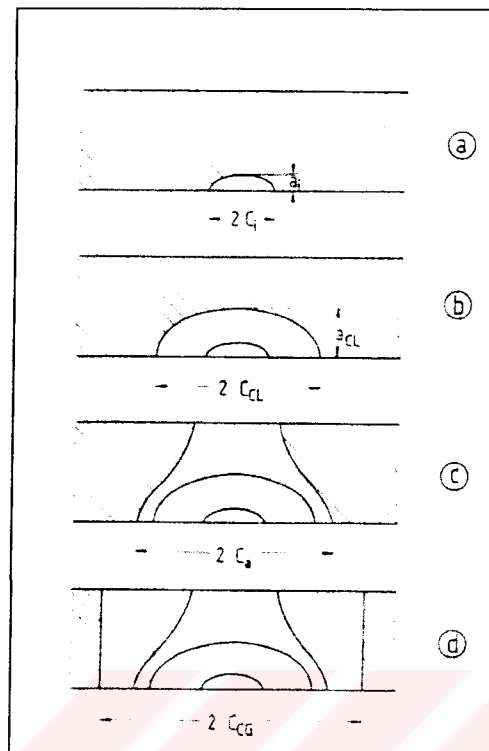


Fig.2.12 Different steps in crack extension: a) initial crack, b) fatigue crack extension, c) wall penetration, d) fatigue extension until global instability [23]

It is also possible that the crack does not become arrested after wall penetration and in this case global failure follows immediately local failure. The illustration of the different fracture modes under increasing load is given below in Fig.2.13 [23].

For the wall penetration (local instability) under rising load, different behaviors are possible, dependant on the toughness of the material, the loading conditions, and the size and shape of the crack and the component [23].

- a) For brittle materials such as glasses, ceramics or ferritic steels at low temperatures the crack extends in an unstable mode after reaching a critical load. The load-displacement curve is linear up to the critical load.
- b) The crack extends in a stable load, leading to a non-linear load-displacement curve and then suddenly extends through the wall and possibly to the whole component. This behavior can be observed for ferritic steels in the ductile-brittle

transition region, where stable crack extension takes place in a ductile, dimple mode and unstable crack extension in a brittle, cleavage mode.

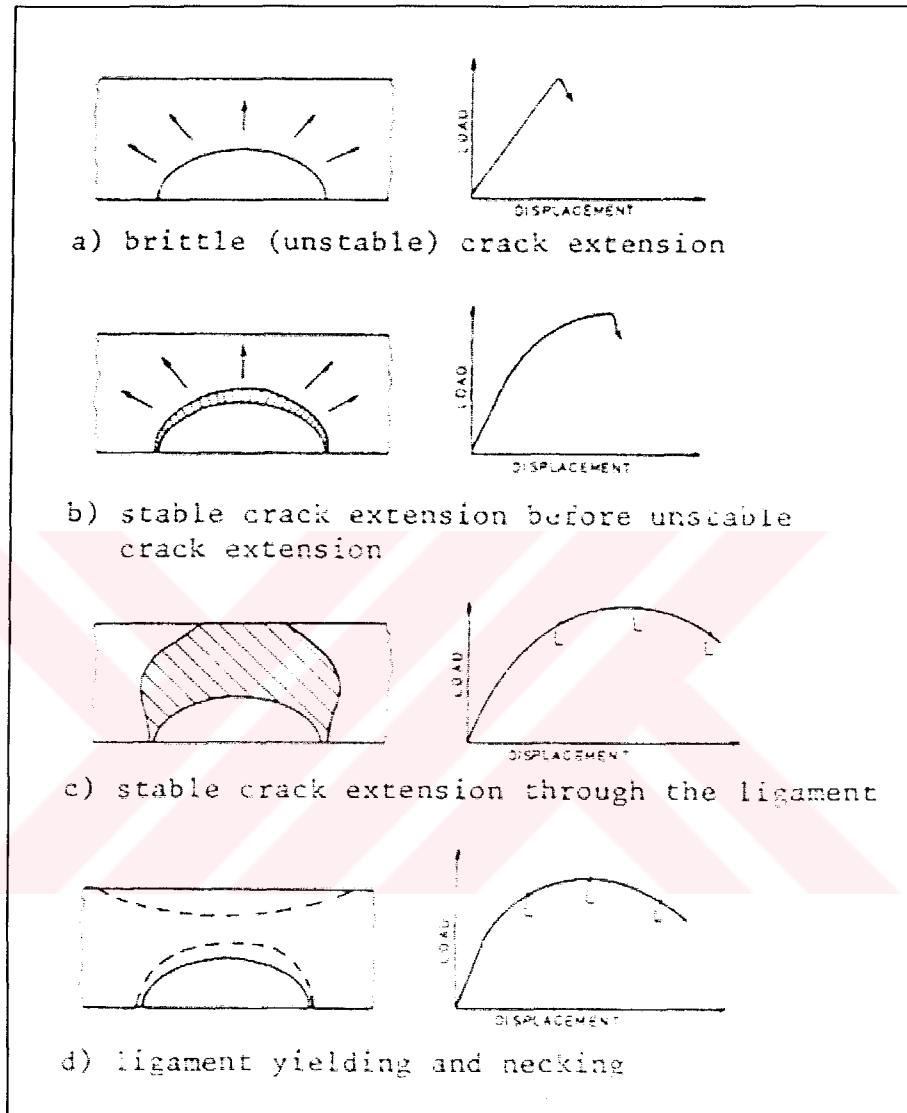


Fig.2.13 Different fracture modes under increasing load [23]

- c) The crack extends through the wall in a stable mode. In a displacement-controlled deformation, the load for wall penetration [L in Fig.2.13] may occur before, at or beyond the maximum load.
- d) For tough materials necking similar to that in a tensile specimen may occur after plastic deformation of the ligament. Again, depending on the strain

hardening capacity of the material, wall penetration may occur before, at or beyond maximum load [23].

The relationship between stress intensity and crack velocity is given in Fig. 2.14 [21].

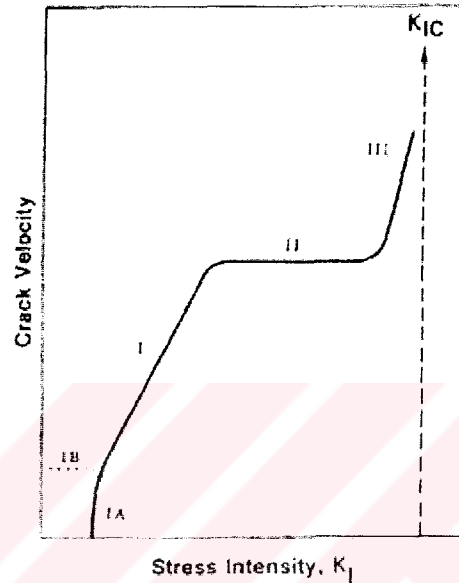


Fig.2.14 A plot of Log (Velocity) versus K_I [21].

Before considering the details of crack growth mechanisms, it should first be examined a schematic of the various possible segments that can contribute to a crack velocity (V) versus stress intensity factor (K_I) diagram. Each segment of this curve can be ascribed to different rate controlling mechanism, as follows [21]:

REGION I

This is the crack growth region of primary interest, since the time to fracture of glass structures, which undergo delayed failure, is controlled by flaws, which spend most of their growth period in this region [21].

REGION I-A

It is not clear that the mechanism of crack growth in the steeper regime of the $V-K_I$ diagram is radically different than that in Region I. Under some conditions, e.g. soda-lime-silica glass in H_2O , this regime ends in a stress corrosion limit [21].

REGION I- B

The crack shape is maintained because of the tendency of the small applied stress to preferentially remove corrosion products at the crack tip, so that this solution occurs there more rapidly [21].

REGION II

This regime appears when crack growth takes place. In an environment in which the minor constituent controls the crack tip reaction. Although, the Region II velocity is shown in Fig.2.13 to be completely stress independent, slopes in the range of 2 to 6 have been measured experimentally. Because diffusion can also take place in from the sides of a fracture mechanics specimen as well as from behind the crack tip, all parts of the crack front may not be in the same region [21].

REGION III

Crack growth in Region III has been least understood. The curves are quite steep i.e. 5-10 times the slope in Region I [21].

Depending on the chemical environment in which the data is obtained, crack velocity - K_I curves for glasses can consist of a number of segments of differing slope. Each segment represents a different controlling crack growth mechanism. These mechanisms can be summarized as [21]:

- I. Stressed enhanced chemical reaction between Si-O bonds and the active ingredient in the environment
- I-A. Same as I, except that changes in crack tip structure are taking place
- I-B. SiO_2 dissolution rate

- II. Diffusion rate of the active ingredient to the crack tip
- III. Electrostatic reactions between polar molecules and the rupturing Si-O bond.

2.7.3. Factors Effecting Surface Crack Length

A number of factors can prevent the actual measurement of the radial surface crack lengths or render the measured values invalid [24].

The first factor to be considered is the surface stress state before indentation, which maybe inadvertently neglected when applying the Vickers indentation test. The apparent surface crack length is a reflection of both the fracture toughness of the material and any pre-existing surface stresses, be they compressive or tensile [24].

A compressive surface stress will decrease the surface crack length relative to the equilibrium length in the absence of surface stresses; a tensile stress will do the reverse. Surface stresses may be induced in a number of ways, such as mechanical damage, thermal tempering, ion exchange, and ion bombardment. For example, mechanical damage due to surface grinding, a common processing step for ceramics produces a compressive surface stress [24].

Second, initiation and propagation subsurface lateral cracks, sideways away from the base of the indentation plastic zone and roughly parallel to the specimen surface just before and on unloading of the indenter; can also affect the surface crack length. Lateral cracks continue to extend after complete unloading under the action of the irreversible residual crack mouth opening matrix stress field, arcing towards the specimen surface. Thus, they often intersect the surface resulting in the removal of the surface material from within one or more of the regions bounded by the surface cracks, obliterating any trace of the said surface cracks along most of their length. The extend of lateral cracking is greater in harder materials, and the incidence of consequent gross chipping or spalling usually increases with increasing indenter load [24].

A third factor, is the occurrence of environmentally assisted time dependant post-indentation slow crack growth in susceptible materials such as silicate glasses , which is initiated by the residual stress field operating during and after unloading. All three types of indentation crack, i.e. radial surface, median, and lateral, can experience slow crack growth [24].

The last factor to be considered is the effect of microstructure in indentation crack morphology. When annealed soda-lime silicate glass is indented, the radial surface cracks emanating from the corners of a Vickers indent are equal in length and the indentation itself is equiaxial along the diagonals as a result of the isotropic structure of the glass. However, in brittle polycrystalline materials, the microstructure affects the indentation cracks in a number of ways, such as crack termination at porosity and/or grain boundaries normal to the crack path and crack deflection along grain boundaries [24].

2.7.4. Failure Paths of a Cracked Body

All possible failure paths that a cracked body can follow can be schematically represented as in Fig.2.15 [23].

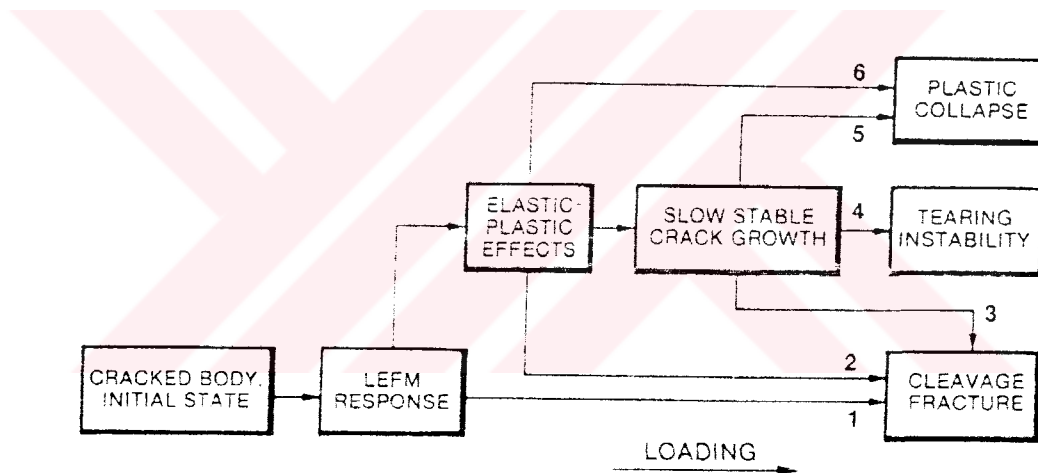


Fig.2.15 The different failure paths which a cracked body can follow [23]

Loading increases from the left to the right, and is scaled in such a way that the end point in the three different failure modes are placed on the same vertical line at the right hand side [23].

LEFM: Linear Elastic Fracture Mechanics

The fracture behavior of the brittle materials can be described with the fractographic results by LEFM quantitatively using some basic fracture mechanics formula for different defect types [25].

3. EXPERIMENTAL PART

3.1. The Properties of the Glass Samples

Four groups of commercial glass samples were used in the experimental studies. First three groups of these samples are uncolored and have different thicknesses. The nominal compositions of these samples are given in Table 3.1.

Table 3.1 The nominal compositions of the uncolored glass samples.

%SiO ₂	%Al ₂ O ₃	%Fe ₂ O ₃	%CaO	%MgO	%Na ₂ O
71-72	1,00-1,10	0,095-0,100	8,15-8,20	4,20-4,25	13,50-14,00

The fourth group of the glass samples which is colored has the nominal composition given in Table 3.2.

Table 3.2 The nominal composition of the colored glass samples.

%SiO ₂	%Al ₂ O ₃	%Fe ₂ O ₃	%CaO	%MgO	%Na ₂ O	Co (ppm)	Se (ppm)
71-72	1,20-1,30	0,325-0,335	8,35-8,40	4,15-4,20	13,50-14,00	42-44	23-25

These four groups of the glass samples have different thicknesses, which the values are;

1st group, uncolored: 0,214 cm

2nd group, uncolored: 0,386 cm

3rd group, uncolored: 0,794 cm

4th group, colored: 0,643 cm

3.2. Mechanical Tests

Five test methods were used to determine the mechanical properties of the glass samples. These tests are, "Ball on the Ring", "Three-point Bending of the Beam", "Vickers Indentation", "Knoop Indentation" and "Ultra Microhardness".

3.2.1. Ball on the Ring Test

This test is realized by using Adamel Lhomargy /MTS Model DY 31 equipment. During this test, a steel ball which has a radius of 3,017cm applies a load to the center of the upper surface of a glass sample placed on a support ring.

The various methods of loading are illustrated in Fig.3.1. All produce tensile stresses at the edge of the disc on its lower surface. In concentric loading method [Fig 3.1b], the stress is constant within the circular area bounded by the loading ring. It is important that the glass should be flat so that it makes a uniform contact with the support ring and the loading ring, if one is used. For this reason, the method is only suitable for testing material such as ground and polished plate glass or float glass. Even for these materials, it is advisable to use gaskets between the support and loading rings and the glass to help obtain uniform loading [26, 19].

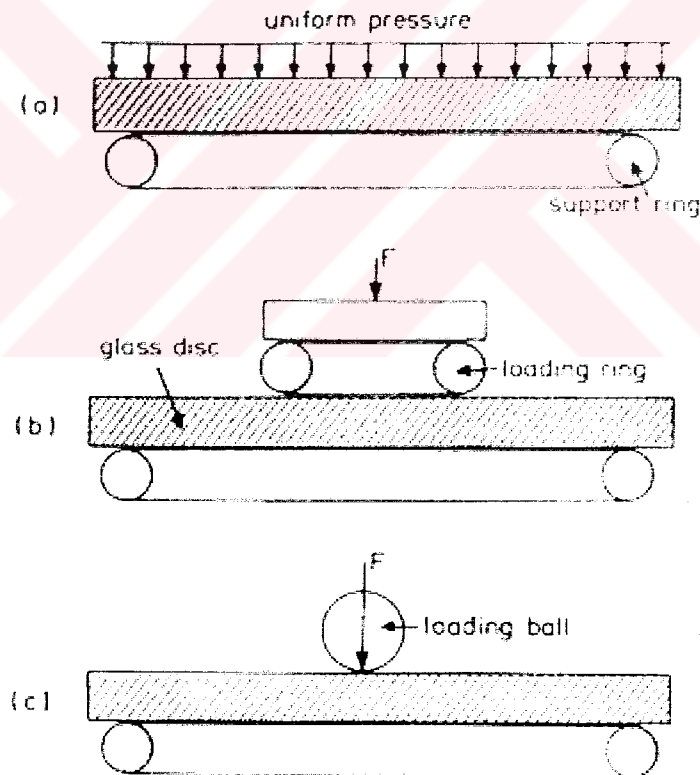


Fig 3.1 Loading in Ball on the ring test a) Uniform pressure loading b) Concentric ring loading c) Central loading [26]

The experiments are realized by choosing central loading during the ball on the ring test as shown in Fig 3.1c.

The glass specimens of 1st and 2nd group were prepared at the dimensions of 5 cm x 5 cm and tested at a cross-head speed of 1mm/min. Only 1st and 2nd group of the glass specimens which have the thickness of 0,214 cm and 0,386 cm could be used in this test due to limitation of the specimen thickness of the test equipment.

In the test procedure, the steel ball is pressed against the glass by a force, which is gradually increased until a fracture is seen to form around the circular area produced as the ball and glass deform [26].

The parameters of this test can be listed as; load, crosshead speed, thickness of glass specimen and the amount of the surface failures on the glass specimen.

By using the deflection and the maximum load values that are obtained as the results of this test, it is possible to calculate elastic modulus and maximum strength from the following equation [27].

$$\sigma = \left[\left(\frac{3P}{4\pi t^2} \right) \times \left(2(1+\mu) \times \ln \left(\frac{r_1}{r_2} \right) + \frac{(1-\mu) \times (r_1^2 - r_2^2)}{r^2} \right) \times 10^{-6} \right] \quad [3.1]$$

Here;

σ = Maximum strength (MPa)

P= Load (N)

t= Plate thickness (m)

μ = Poisson's ratio

r_1 = Radius of the supporting ring (m)

r_2 = Radius of the loading ring (m)

r= Radius of the disc (m)

Elastic modulus can be calculated from the deflection Eq. [3.2] given below.

$$y = P.L^3 / 48. I. E \quad [3.2]$$

Here,

y = Deflection (m)

L= Fulcrum span length (m)

E= Elastic modulus (N/m²)

I= Area moment of inertia of the beam cross section (m⁴)

The Eq. [3.2] can be rewritten as the Eq. [3.3], to obtain elastic modulus [26].

$$E = P.L^3 / 48. y I \quad [3.3]$$

Area moment of inertia of the beam cross section can be obtained from the equation [3.4] which is given as [26],

$$I = wt^3/12 \quad [3.4]$$

In this equation,

w= width of the strip (m)

t= thickness of the strip (m)

3.2.2. Three- Point Bending of the Beam

It is difficult to measure the strength of rods by the application of axial tension. Unless great care is taken in mounting the specimen in the grips of the tensile testing machine, unknown bending forces will be added to the measured tensile forces [26].

Also, fractures frequently occur near the grips either because of local stress concentrations or because the grips have caused further damage to the glass surface. For these reasons, the strength of rod specimens is usually measured by three-point bending method. The mechanism of this test method is given in Fig 3.2 [26].

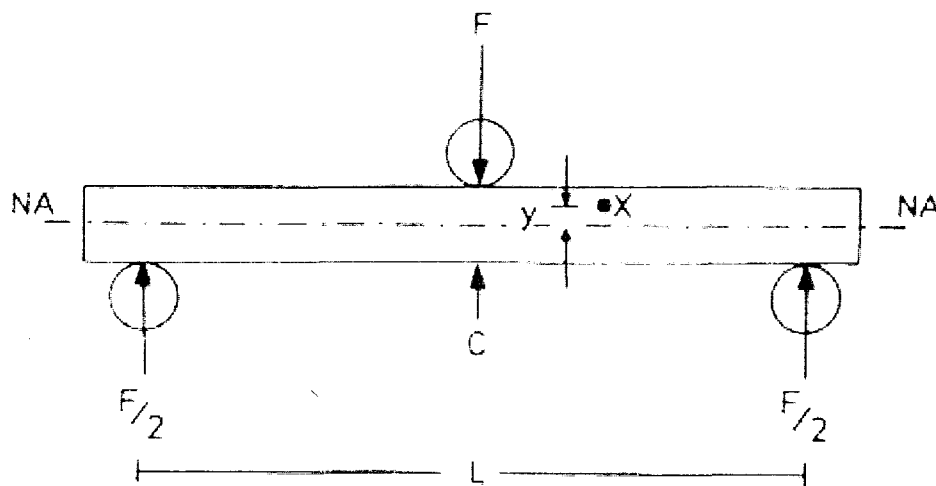


Fig 3.2 Three-point bending test [26]

This test is also achieved by using Adamel Lhomargy /MTS Model DY 31 equipment that has a maximum load of 2000N. To realize this test method, 1st and 2nd group of the glass specimens that have the dimensions of 5 cm x 10 cm were prepared (Only 1st and 2nd group of the glass specimens which have the thickness of 0,214 cm and 0,386 cm could be used in this test due to limitation of the specimen thickness of the test equipment). Glass specimens were tested at a crosshead speed of 1mm/min.

As understood from Fig 3.2, L is the span length and NA is the neutral axis. The bending forces produce stresses acting parallel to the rod axis which are tensile below the horizontal plane NA and compressive above it. The magnitude of the axial stress at a point such as X is given by a beam theory as given in Eq. [3.5] [26].

$$\sigma = My/I \quad [3.5]$$

Where, y is the vertical distance of X from plane NA, which can be defined as deflection, M is the bending moment at X due to the applied forces. For three point bending, the maximum tensile stress is at C immediately below the central knife-edge. At C, the bending moment can be written as in Eq. [3.6] [26].

$$M = PL/4 \quad [3.6]$$

For the float glass, the value of I (area moment of inertia) can be calculated from Eq. [3.4].

The maximum tensile stress occurs on the lower surface of the strip. The value of y in Eq. [3.5] is therefore $t/2$. Thus, finally, the maximum tensile stress (σ) can be rewritten as Eq. [3.7]. In this equation, w is width, t is thickness, P is load and L is fulcrum span length [26].

$$\sigma = 1,5 \frac{PL}{wt^2} \quad [3.7]$$

By using Eq. [3.3] and Eq. [3.4], it is also possible to calculate the elastic modulus from the three-point bending of the beam test results.

3.2.3. Vickers Indentation

To be able to realize this test method, Wilson Tukon Hardness Tester Model LL (Wilson Mechanical Instrument Division) microhardness equipment that has a maximum load of 9.8N, was used. The glass specimens that have the dimensions of 1.5 cm x 2.0 cm were prepared from four groups of the glass samples. Fig 3.3 shows the mechanism of this test method.

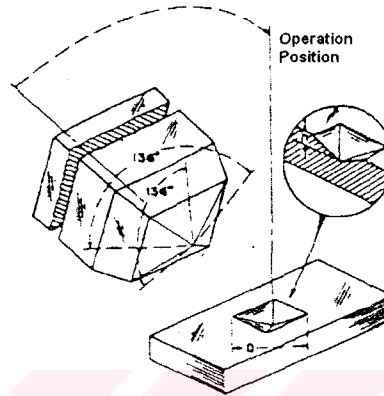


Fig 3.3 Vickers Indentation [28]

While performing the test, the load must be applied smoothly without impact. After removal of the load, both impression diagonals are measured, and the average value is used to calculate Vickers Hardness (HV), from the Eq. [3.8] [28].

$$HV = \frac{2P \sin(\alpha/2)}{a_v^2} = \frac{1.8544P}{a_v^2} \quad [3.8]$$

Where,

a_v = half length of the mean diagonal of the indent (mm)

P = load, (kgf)

α = face angle of the indenter (136°)

In nearly all cases, HV is determined by referring to tables of HV for each possible load and diagonal measurement [28].

Hardness of a material is inversely proportional with the mean diagonal of the indenter (pyramidal or spherical according to the test method) and this relation can be understood by viewing the following Eq. [3.9] [29];

$$H = \frac{P}{\alpha_o \cdot a^2} \quad [3.9]$$

Where,

H= Hardness of the material

P= Load

α_o = Indenter constant (for Vickers indenter, $\alpha_o = 2$)

a = Half length of the mean diagonal of the indenter.

The general view of the diagonal mark lengths (2a) and the crack lengths (2c) can be seen in Fig.3.4 [30].

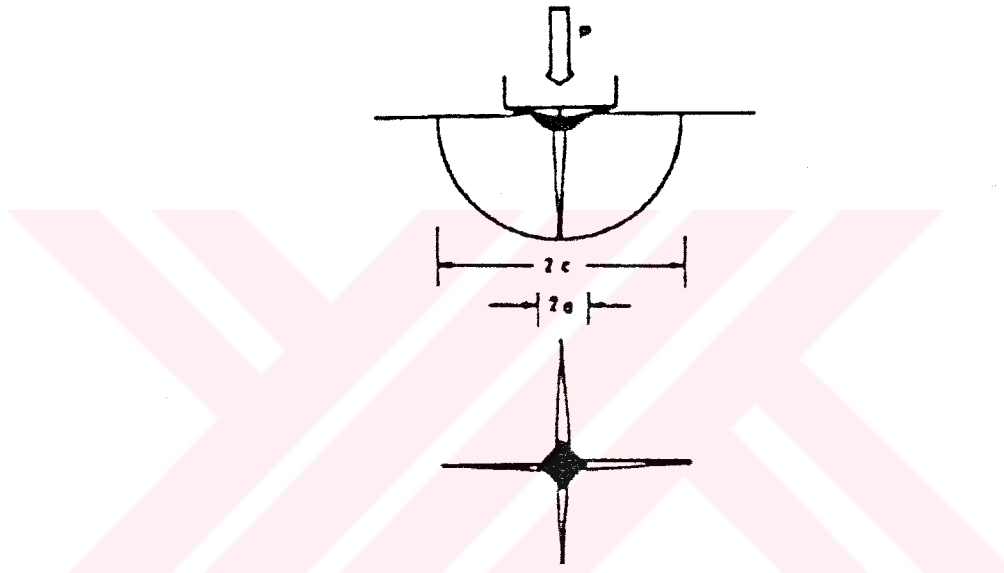


Fig.3.4 Diagonal mark (2a) and crack length (2c) at Vickers indentation [30]

It is possible to reach the fracture toughness (K_{Ic}) of the material by Vickers indentation test method, with the crack size values that are obtained from this test. This relation is given in Eq. [3.10] [30].

$$K_{Ic} = P / \beta_o \cdot c^{3/2} \quad [3.10]$$

In the equation, P is load (N), β_o is a constant, c is the half crack size (m). For a Vickers crack that has developed in a required size, ($c \gg a$), Anstis et al. [31] defined a stress intensity factor, K_{Ic} as in the following Eq. [3.11] [30].

$$K_{Ic} = X_r (P / \beta_o \cdot c_o^{3/2}) \quad [3.11]$$

In Eq. [3.11], X_r is a constant and given as the following Eq. [3.12] [30].

$$X_r = S (E/H)^{1/2} \quad [3.12]$$

Here, E/H is the ratio of elastic modulus and hardness and S , is a constant for Vickers cracks, which is not dependent to the material properties. ($S = 0,016 \pm 0,004$) [30].

Eq. [3.10] and Eq. [3.12] are the fundamental equations of the fracture mechanics. If the radial cracks are considered stable, in such a case, when $K_r = K_c$ equality is written by considering $c = c_o$, the final equation is obtained as Eq. [3.13] [30];

$$K_c = X_r (P / \beta_o \cdot c^{3/2}) = S (E/H)^{1/2} P / \beta_o \cdot c_o^{3/2} \quad [3.13]$$

If Eq. [3.10] and Eq. [3.13] are compared, it is possible to understand that β_o is a constant which is related to the stress/strain ratio that is against the stable crack initiation forces, which occur in a material that has tested by indentation technique.

3.2.4. Knoop Indentation

Wilson Tukon Hardness Tester Model LL (Wilson Mechanical Instrument Division) microhardness equipment that has a maximum load of 9.8N, was used to realize this test. The four groups of the glass specimens that have the dimensions of 1.5 cm x 2.0 cm were prepared. The mechanism of the test is shown in Fig 3.5.

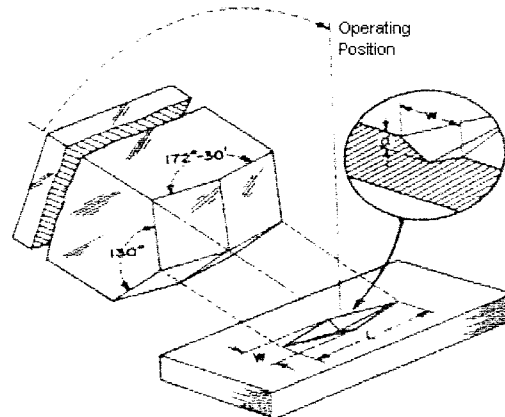


Fig.3.5 Knoop Indentation [28]

Knoop indentation hardness test is a method using a calibrated machine to force a pointed, rhombic-base, pyramidal diamond indenter having longitudinal angle of

172° 30' 00" and transverse angle of 130° 00' 00", under a predetermined load, into the surface of the material and to measure the long diagonal of the resulting impression after removal of the load [32].

The difference between the diagonal marks in Vickers indentation test and Knoop indentation test is illustrated in Fig.3.6 [33].

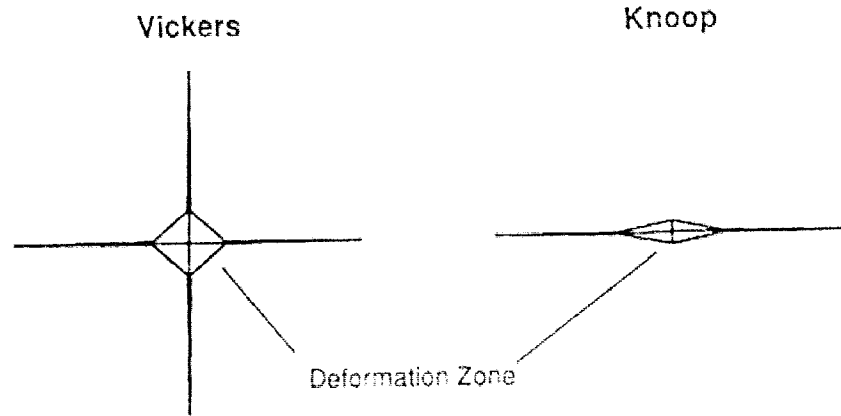


Fig.3.6 Vickers and Knoop diagonal marks

From this test method, Knoop microhardness and elastic modulus can be determined. The theoretical background on determining microhardness and elastic modulus of a material using the Knoop indentation testing is given by Marshall et al. [34] and Leigh et al. [35]. The microhardness is expressed by Eq. [3.14] [36];

$$\text{KHN} = 14229 \frac{P}{a_K^2} \quad [3.14]$$

In this equation, KHN is the Knoop Hardness Number and has unit of kg/mm², P is indenter load (given in g.f); and a_K is the long diagonal of the Knoop indentation (given in μm) [36]. Knoop Hardness Number (KHN) can be obtained by using the tables of KHN corresponding to the long diagonal of the Knoop indentation for each possible load without the calculation of KHN from Eq.[3.14].

The short diagonal of the Knoop indentation (b_K), is also measured to estimate the elastic modulus of the materials examined [37].

For the ideal case when the aspect ratio between the long (a_K) and the short (b_K) diagonal is 7.114, the elastic modulus can be calculated using the relationship described by Blau [38] as given in Eq. [3.15] [37].

$$\frac{b_K}{a_K} = \frac{1}{7.114} - \left(\frac{\alpha \cdot KHN}{E} \right) \quad [3.15]$$

Here, α is a constant (approximately 0,45), KHN and Elastic Modulus, E, are in GPa [37].

3.2.5. Ultra Microhardness Test

The experiments are realized by using Fischerscope HP100 Microhardness equipment which has the load range of 0.04 –100 gf and the penetration depth rate slower than 3 $\mu\text{m}/\text{sn}$. All four groups of the specimens were tested in this test.

The technical advantages of this equipment can be listed as the large range of hardness detection, the monitor system that enables the determination of the diagonal of the indenter and the possibility to obtain elastic and plastic properties and elastic modulus of the material. Fig. 3.7 shows the components of the ultra microhardness test equipment.

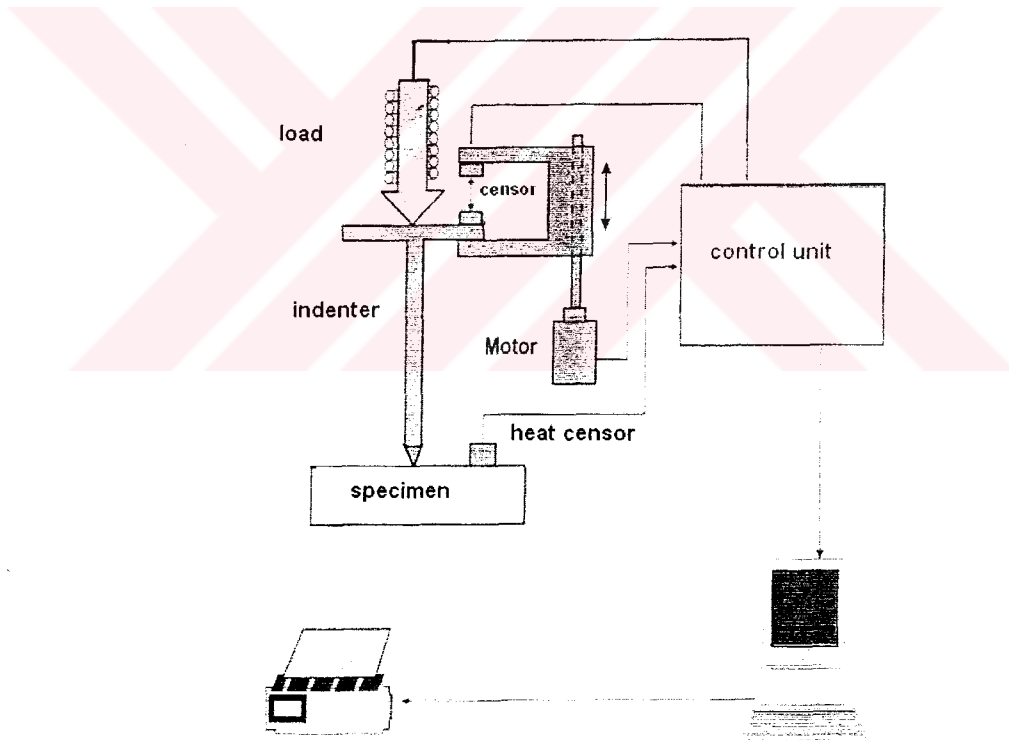


Fig. 3.7 The components of the Ultra Microhardness equipment [39]

In Fig. 3.8, the principle of this test method is illustrated. In this illustration, h_p shows indentation depth that is calculated in the plastic area and h_e shows indentation depth that is calculated in the elastic area. Measurement of the indentation depth was achieved with a capacitance displacement gauge of 2 nm accuracy. [39]

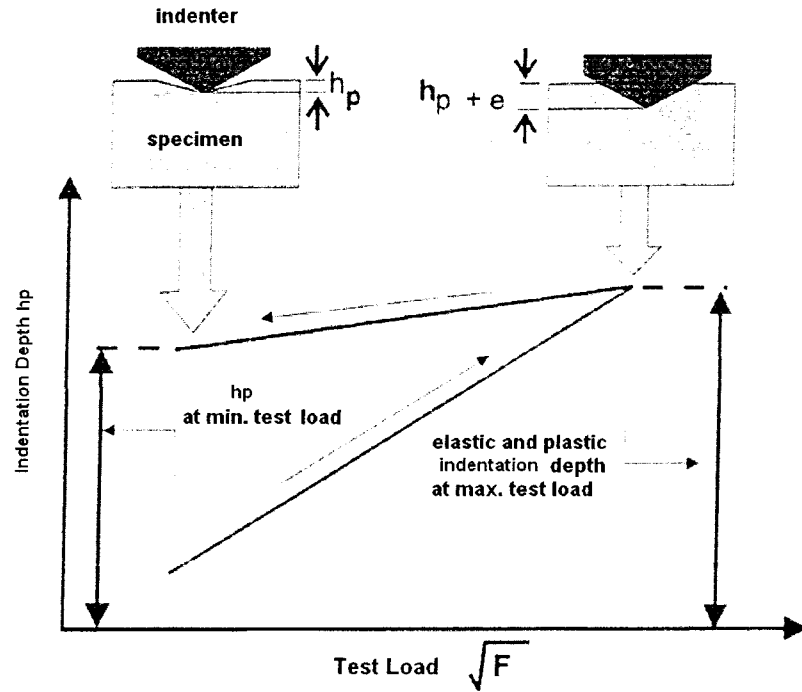


Fig. 3.8 The principle of Ultra Microhardness tester [39]

During the test, the load is increased in steps until the nominal test load is reached. The number of steps (≤ 60) for loading and the time between them is selected before the test. While unloading the same number of steps is used. Step by step indentation is given in Fig. 3.9 [39].

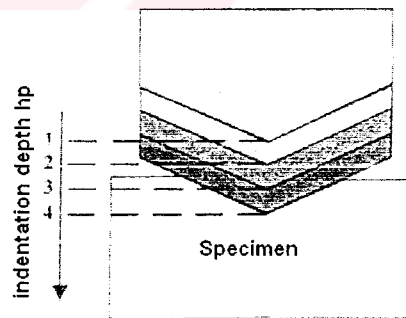


Fig. 3.9 Step by step indentation in Ultra Microhardness test [39]

Except the given microhardness value which has obtained from the equipment as a result of the experiments in this work and the theoretical relationship (see Eq.[3.8]) between the Vickers Hardness HV in GPa, the load in N and the diagonal in μm according to the ASTM standard E384, also; the following equations can be used to obtain microhardness.

Assuming ideal geometry, the ratio to the diagonal to the depth is 7 for the Vickers indenter. Doerner and Nix have already established that the depth to use is the plastic depth (h_p) and not the remanent depth (h_r). h_p is the intercept of the tangent to the initial linear portion of the unloading curve with the x axis as shown in Fig. 3.10. Hence, by substituting $7h_p$ for a_v in Eq.[3.8]; Eq.[3.16] is obtained [40].

$$HV_1 = 37.84 \times (P/h_p^2) \quad [3.16]$$

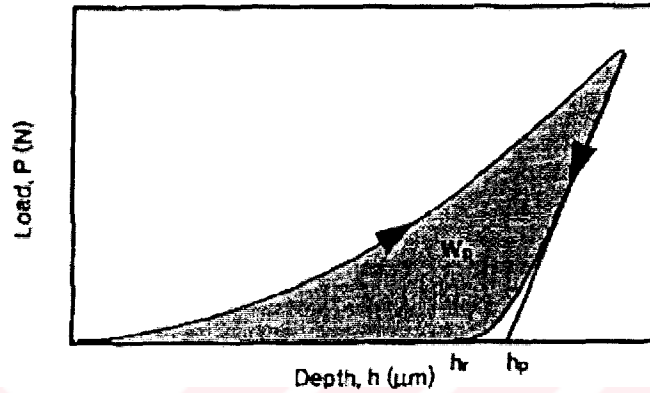


Fig.3.10 A typical load – depth plot in an ultra microhardness test [40]

Another method for calculating the Vickers Hardness from load-depth plot has been recently suggested by Berriche and Holt [40]. The argument in this case is that hardness is, by definition, a material's resistance to plastic deformation and consequently it should be related to the ratio of the plastic energy W_p , dissipated to the volume v of the indentation produced. Determination of W_p is not possible with the conventional microhardness equipment, but by Ultra Microhardness equipment as it is used in this work, it can be found. W_p can be calculated from the load-depth plots by numerical integration of the loading part and the unloading part, and then subtracting the latter from the former [40].

A first approximation to calculating the hardness from W_p is to set the mean pressure over the indentation P_M equal to the plastic work (shaded area in the Fig.3.10) over the value of indentation, which can be calculated from h_p since the geometry of the indenter is known. Since for the Vickers indenter $HV/P_M = 0.9272$ and $v = 24.5 (h_p)^3/3$ then the Eq.[3.17] is obtained for HV_2 in GPa, W_p in μJ and h_p in μm [40].

$$HV_2 = 113.51 \times (W_p / h_p^3) \quad [3.17]$$

3.3 Test Results

3.3.1. Ball on the Ring Test

From the equipment, the values of $P_{\max}$ (N), (maximum load at which the rupture takes place) and deflection, γ (mm), are determined. In Table 3.3; the values for the 1st and 2nd group of specimens are given.

Table 3.3 Ball on the ring test results for the 1st and 2nd group of specimens.

Group of specimens	1 st group (t= 2,14 mm)		2 nd group (t= 3,86 mm)	
Exp.No	$P_{\max}$ (N)	γ (mm)	$P_{\max}$ (N)	γ (mm)
1	843,4	0,63	1887,3	0,72
2	756,7	0,48	1885,4	0,70
3	539,1	0,41	1902,1	0,75
4	471,9	0,36	1316,7	0,52
5	669,6	0,47	1664,7	0,69
6	435,8	0,30	1318,9	0,54
7	654	0,43	1183,8	0,51
8	305	0,16	1548,4	0,57
9	305,9	0,23	1888,8	0,73
Average	553,489	0,386	1621,789	0,637

According to the values that are given at Table 3.3; the relationship between deflection γ (mm), and $P_{\max}$ for the 1st group of specimens is given in Fig.3.11.

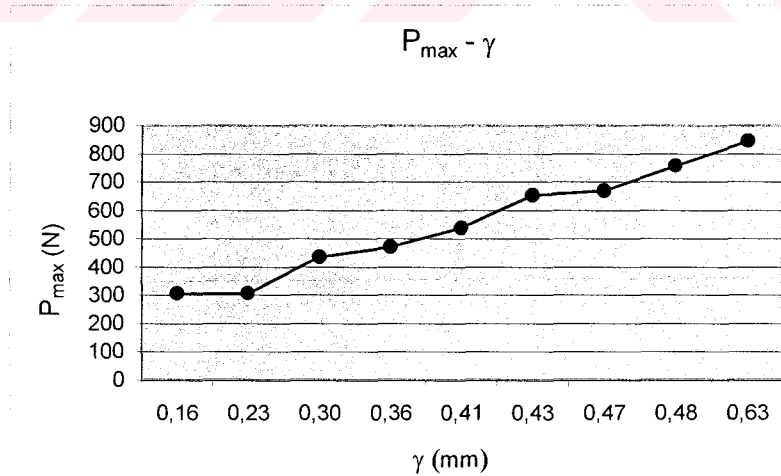


Fig.3.11 $P_{\max} - \gamma$ diagram for the 1st group of specimens

Also Fig.3.12, which shows the relationship between γ (mm) and $P_{\max}$ (N) for the 2nd group of specimens, can be illustrated from the values given in Table 3.3.

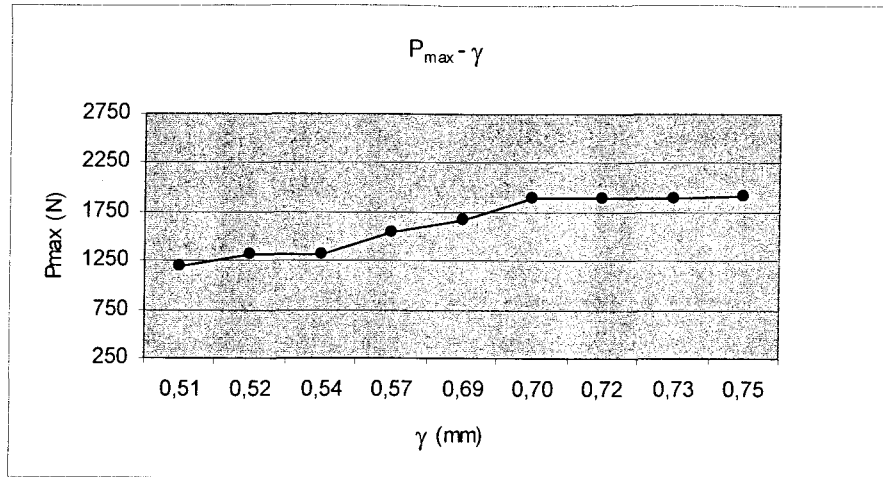


Fig.3.12 $P_{max} - \gamma$ diagram for the 2nd group of specimens

From Fig.3.11 and Fig.3.12, it is seen that deflection increases with increasing load. This argument satisfies the literature about this subject [26].

σ_{max} (maximum strength) can be calculated by using Eq. [3.1] from the values given at Table 3.3. In Eq. [3.1]; the radius of the supporting ring, (r_1), is 0,021 m, the radius of the loading ring, (r_2), is 0,0095 m and the radius of the disc, (r), is 0,0301 m. Also; to be able to calculate elastic modulus, Eq. [3.3] is used.

The area moment of inertia of the cross section beam, I (m^4), in Eq. [3.3] is calculated from Eq. [3.4] and found 40,835 mm^4 for the 1st group. I (m^4) is found 239,635 mm^4 for the 2nd group of specimens. In Eq. [3.3] the fulcrum span length, L , is 79 mm. The results of these calculations for the 1st group and 2nd group of specimens are given at Table 3.4.

Table 3.4 Ball on the ring values calculated for the 1st and 2nd group of specimens.

Group of specimens	1 st group (t= 2,14 mm)		2 nd group (t= 3,86 mm)	
Exp.No	$\sigma_{max} \times 10^{-3}$ (GPa)	E (GPa)	$\sigma_{max} \times 10^{-3}$ (GPa)	E (GPa)
1	99,888	336,746	68,703	112,356
2	89,620	396,545	68,634	115,450
3	63,848	330,747	69,242	108,708
4	55,890	329,729	47,931	108,536
5	79,304	358,367	60,600	103,413
6	51,614	365,406	48,011	104,691
7	77,457	382,577	43,093	99,494
8	36,123	479,501	56,366	116,439
9	36,229	334,550	68,757	110,905
Average	65,553	368,241	59,037	107,202

3.3.2. Three Point Bending of the Beam

As a result of the three point bending of the beam, the values of $P_{\max}$ (N) (maximum load at which the rupture takes place) and deflection, γ (mm), were determined from the test equipment. In Table 3.5 below; these values for the 1st and 2nd group of specimens are given.

Table 3.5 Three point bending of the beam test results for the 1st and 2nd group

Group of specimens	1 st group (t= 2,14 mm)		2 nd group (t= 3,86 mm)	
Exp.No	$P_{\max}$ (N)	γ (mm)	$P_{\max}$ (N)	γ (mm)
1	219,6	0,15	510,1	0,26
2	223,0	0,18	511,3	0,29
3	224,8	0,18	525,2	0,30
4	225,5	0,19	535,1	0,32
5	229,2	0,21	541,9	0,33
6	232,5	0,25	569,2	0,34
7	238,6	0,26	579,5	0,35
8	241,7	0,29	594,7	0,35
9	295,8	0,32	604,7	0,36
10	299,6	0,35	634,7	0,37
11	300,4	0,37	647,5	0,38
Average	248,245	0,25	568,5	0,331

In Fig. 3.13; the relationship between γ (mm) and $P_{\max}$ (N) is shown due to the values in Table 3.5 for the 1st group of specimens.

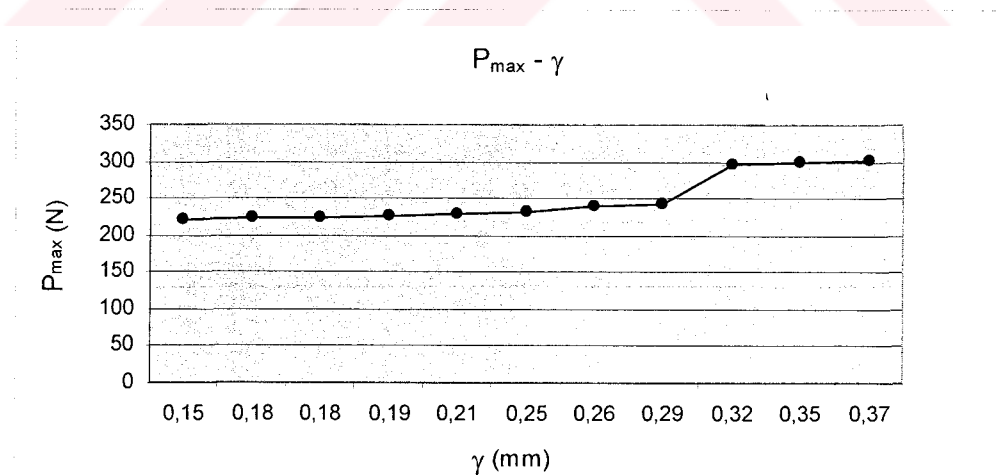


Fig. 3.13 $P_{\max}$ - γ diagram for the 1st group of specimens

For the 2nd group of specimens; Fig.3.14 is given below to be able to illustrate the relationship between γ and $P_{\max}$.

The relationship between γ and $P_{\max}$ is not linear as seen in Fig.3.13 for the 1st group of specimens. However, this relationship is linear for the 2nd group of specimens (see Fig.3.14) as expected.

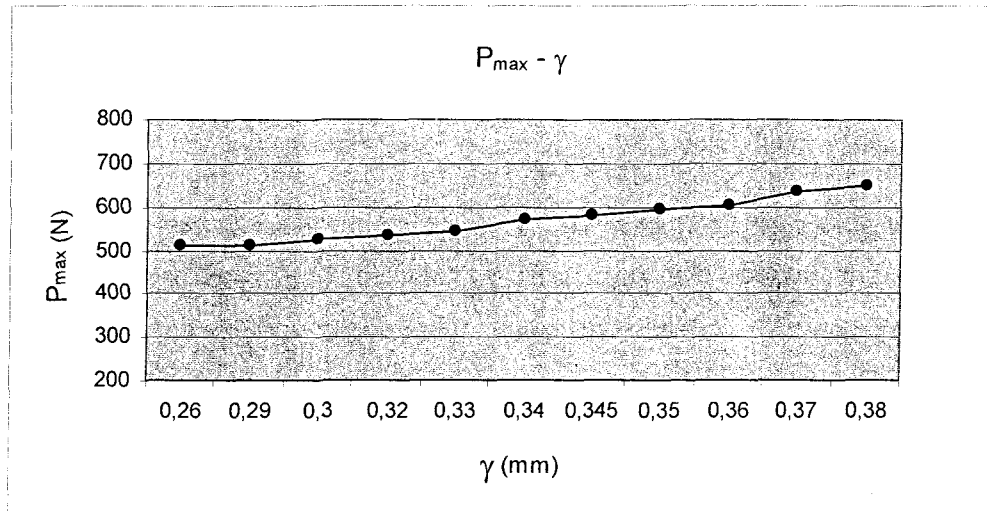


Fig. 3.14 $P_{\max}$ - γ diagram for the 2nd group of specimens

The maximum bending strength, ($\sigma_{\max}$), was calculated from the values given in Table 3.5 and by using the Eq. [3.7]. To calculate elastic modulus, Eq. [3.3] is used. The area moment of inertia of the cross section beam, I (m^4), in Eq. [3.3] is calculated from the Eq. [3.4]. Similar to the ball on the ring test, I (m^4) found $40,835 \text{ mm}^4$ for the 1st group and $239,635 \text{ mm}^4$ for the 2nd group of specimens. In Eq. [3.4] the fulcrum span length, L , is taken 79 mm. The values that are calculated for the 1st group and 2nd group of specimens are given in Table 3.6.

Table 3.6 Three point bending of the beam values calculated for the 1st and 2nd group.

Group of specimens	1 st group (t= 2,14 mm)		2 nd group (t= 3,86 mm)	
Exp.No	$\sigma_{\max} \times 10^{-3}$ (GPa)	E (GPa)	$\sigma_{\max} \times 10^{-3}$ (GPa)	E (GPa)
1	113,646	368,257	81,139	84,095
2	115,405	311,632	81,330	75,573
3	116,337	314,148	83,541	75,040
4	116,699	298,540	85,116	71,676
5	118,614	274,540	86,197	70,387
6	120,322	233,934	90,540	71,759
7	123,478	230,838	92,178	71,999
8	125,083	209,647	94,596	72,832
9	153,080	232,519	96,186	71,999
10	155,047	215,320	100,958	73,529
11	155,461	204,225	102,994	73,037
Average	128,470	263,054	90,434	73,811

3.3.3 Vickers Indentation

While realizing this test different loads (4,9 N, 6,86 N and 9,8 N) were applied to the three groups of the glass specimens for 1 minute, by the diamond Vickers indenter of the microhardness equipment. From the experiments of the 4th group of the specimens that are colored, the diagonal indentation marks and cracks could not be observed.

The lengths of the two diagonal marks of the indent as well as the two radial crack lengths were measured by the help of the divisions at the ocular of the microhardness equipment at a magnification of 400x.

The average sizes of the diagonals (2a), and of the cracks (2c), were then determined. The Vickers hardness (HV) values that are corresponding to the average sizes of the diagonal marks are found from the hardness table.

The picture, which shows the diagonal mark and the crack length that is seen in Vickers test for the 1st group at 6,86 N of load; is given in Fig.3.15. This picture is captured with an optical microscope at a magnification of 320x.

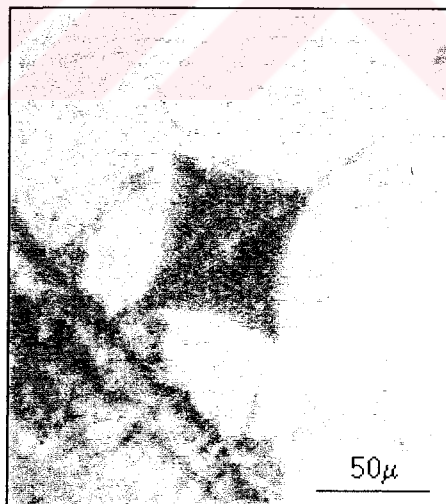


Fig.3.15 Diagonal mark and crack for the 1st group of specimens

The values of 2a, 2c and HV that are obtained at loads (P), of 4,9 N 6,86 N and 9,8 N for the 1st group of specimens which have thickness of 2,14 mm are given in Table 3.7.

Table 3.7 Vickers indentation test results for the 1st group of specimens.

P = 4,90 N	Exp.No.	2c (μm)	2a (μm)	HV (kg/mm ²)
	1	90	36,5	696
	2	91	36,5	696
	3	95	36,5	696
	4	92	37	677
	5	93,5	37,5	659,5
	6	109	38	642
	7	100	38,5	625,5
	Average	95,79	37,21	670,29
	St.Dev	6,695	0,809	28,726
P = 6,86 N	Exp.No.	2c (μm)	2a (μm)	HV (kg/mm ²)
	1	138,25	46,75	595
	2	136,75	47	588
	3	135,5	48	561,5
	4	123	50	519,4
	5	130	50	519,4
	6	135,5	50	519,4
	7	141	50	519,4
	Average	134,29	48,82	546,01
	St.Dev	5,994	1,519	34,726
P = 9,80 N	Exp.No.	2c (μm)	2a (μm)	HV (kg/mm ²)
	1	176,5	52,5	673
	2	172	54	636
	3	178	55	613
	4	172,5	55	613
	5	166,5	56,5	581
	6	170,5	56,5	581
	7	182,5	56,5	581
	Average	174,07	55,14	611,14
	St.Dev	5,311	1,520	34,585

According to the values that are given at Table 3.7; the change in Vickers Hardness, HV (kg/mm²), with the increasing load is shown in Fig.3.16.

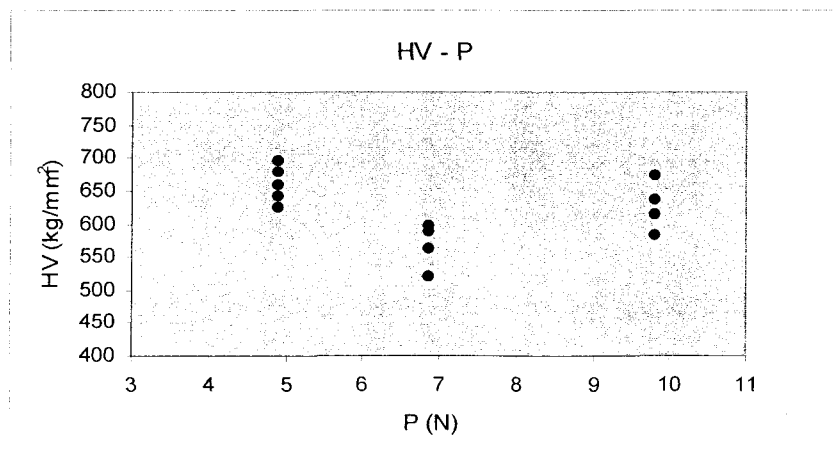


Fig.3.16 HV (kg/mm²) – P (N) diagram for the 1st group of specimens

$HV_{average}$, for the 1st group of specimens, is calculated as 609,15 kg/mm² from the HV values given at Table 3.7 for different loads. The change in 2a and 2c values according to load (P), for the 1st group of specimens is shown in Fig.3.17 below.

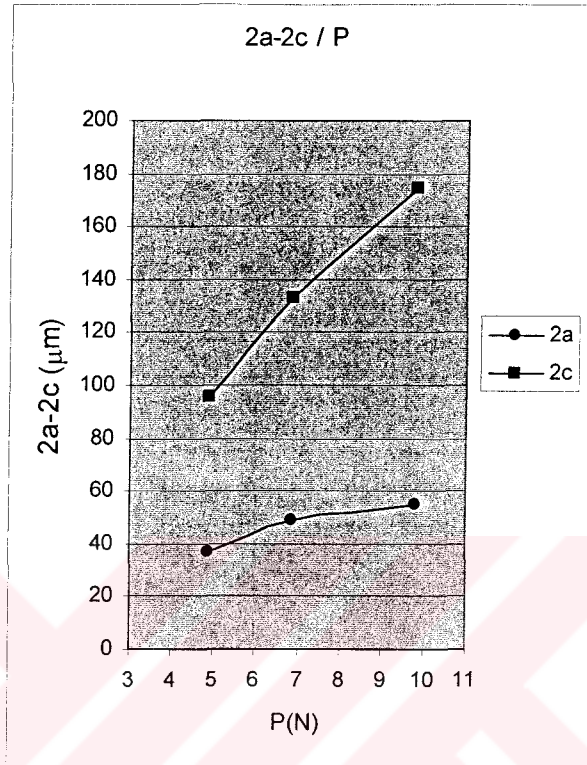


Fig.3.17 The change of average diagonal length (2a) and crack size (2c) with load for the 1st group of glass specimens.

From the values at Table 3.7 and by using the Eq. [3.13]; K_{Ic} (fracture toughness) can be calculated when elastic modulus (E), is taken 73,061 GPa according to the results of the Ultra Microhardness test for the 1st group of specimens.

Also K_{Ic} values for the Vickers indentation test, can be calculated when H/E ratio ($H/E = 0,044$) for the 1st group of the specimens in the Knoop indentation test is used in Eq. [3.13]. The results that are determined for the 1st group of the glass specimens are given in Table 3.8.

In Eq.[3.13], $P/c^{3/2}$ ratio is used to calculate K_{Ic} for the glass specimens. Therefore, it is important to see the change of $P/c^{3/2}$ ratio with load as given in Fig.3.18.

Table 3.8 Kc values calculated from the crack size for the 1st group of specimens.

P= 4,90 N	Exp.No.	c (μm)	Kc (MN/m ^{3/2}) (E= 73,061)	Kc (MN/m ^{3/2}) (H/E= 0,044)
	1	45	0,841	1,238
	2	45,5	0,828	1,218
	3	47,5	0,776	1,142
	4	46	0,826	1,198
	5	46,75	0,816	1,169
	6	54,5	0,657	0,929
	7	50	0,758	1,057
	Average	47,89	0,786	1,136
	St.Dev	3,35	0,064	0,109
P= 6,86 N	Exp.No.	c (μm)	Kc (MN/m ^{3/2}) (E= 73,061)	Kc (MN/m ^{3/2}) (H/E= 0,044)
	1	69,125	0,669	0,910
	2	68,375	0,684	0,925
	3	67,75	0,710	0,938
	4	61,5	0,854	1,085
	5	65	0,786	0,998
	6	67,75	0,738	0,938
	7	70,5	0,695	0,884
	Average	67,14	0,734	0,954
	St.Dev	2,997	0,065	0,070
P= 9,80 N	Exp.No.	c (μm)	Kc (MN/m ^{3/2}) (E= 73,061)	Kc (MN/m ^{3/2}) (H/E= 0,044)
	1	88,25	0,623	0,902
	2	86	0,666	0,937
	3	89	0,645	0,890
	4	86,25	0,676	0,933
	5	83,25	0,732	0,984
	6	85,25	0,706	0,950
	7	91,25	0,638	0,858
	Average	87,04	0,669	0,922
	St.Dev	2,655	0,039	0,042

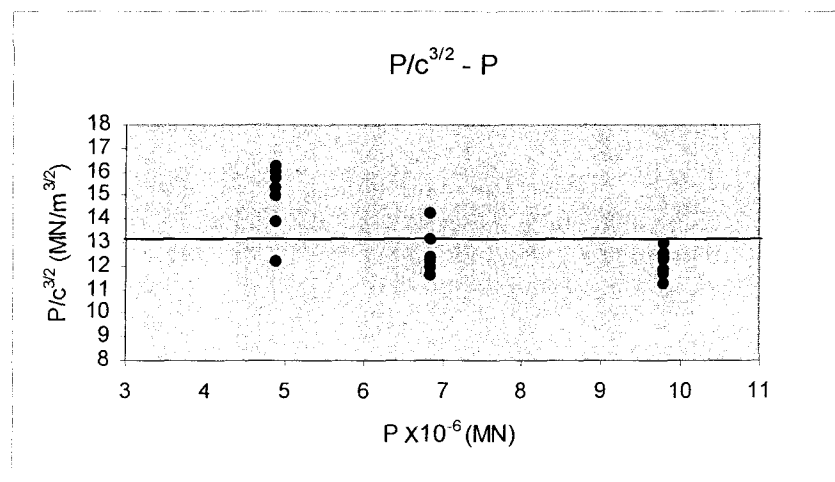


Fig.3.18 P/c^{3/2} (MN/m^{3/2}) – P (MN) diagram for the 1st group of specimens

According to the values that are given at Table 3.8; the change in fracture toughness, K_c ($\text{MN}/\text{m}^{3/2}$), with increasing load; can be seen in Fig.3.19 for the 1st group of specimens.

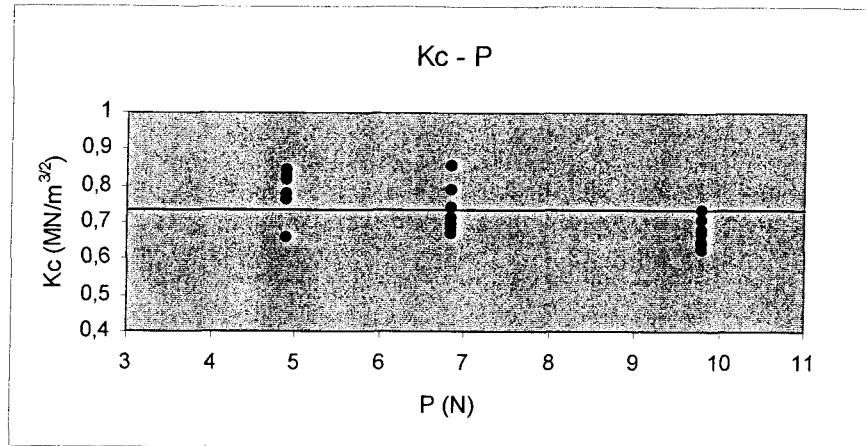
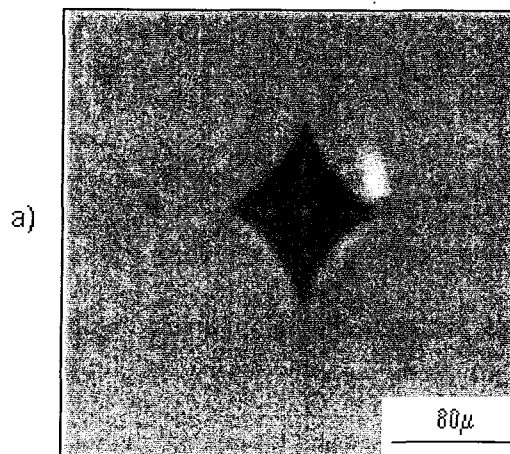


Fig.3.19 K_c ($\text{MN}/\text{m}^{3/2}$) – P (N) diagram for the 1st group of specimens

$K_{c\text{average}}$ is obtained as $0,730 \text{ MN}/\text{m}^{3/2}$ for the 1st group of specimens from the K_c values that have been calculated at different loads.

The diagonal mark and the crack of 2nd group of specimens are shown in Fig.3.20.a and Fig.3.20.b for the applied load of 4,90 N and 6,86 N respectively.

The picture at Fig.3.20.a is captured with an optical microscope using an enlargement of 200x and the picture at Fig.3.20.b is captured with an optical microscope using an enlargement of 320x.



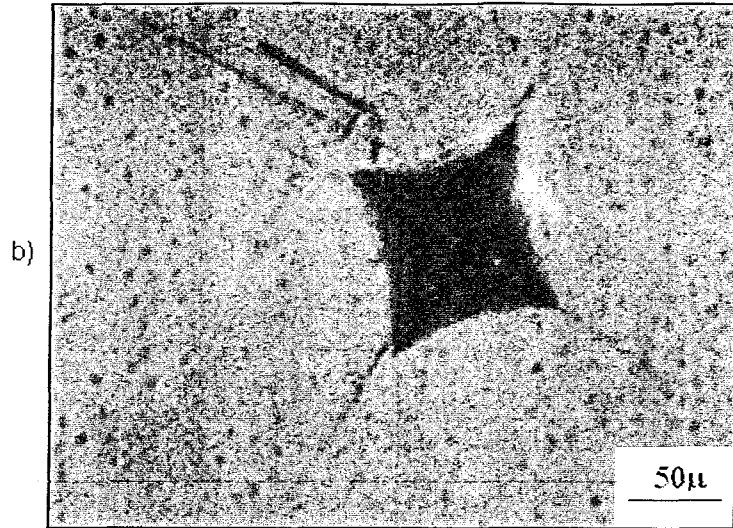


Fig.3.20 a. Diagonal mark and the crack for 2nd group at 4,90 N of load

b. Diagonal mark and the crack for 2nd group at 6,86 N of load

Table 3.9 shows the results at loads of 4,90 N, 6,86 N and 9,80 N for the 2nd group of specimens which have thickness of 3,86 mm.

According to the values that are given at Table 3.9; the change in Vickers Hardness, HV (kg/mm²), with increasing load is shown in Fig.3.21 below.

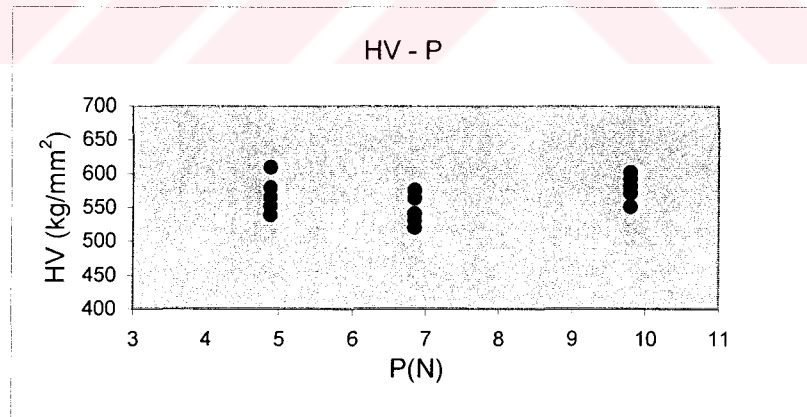


Fig.3.21 HV (kg/mm²) – P (N) diagram for the 2nd group of specimens

HV_{average}, for the 2nd group of specimens, is calculated as 564,257 kg/mm² from the HV values that are given at 4,9 N, 6,86 N and 9,8 N of loads.

Table 3.9 Vickers indentation test results for the 2nd group of specimens.

P = 4,90 N	Exp.No.	2c (μm)	2a (μm)	HV (kg/mm ²)
	1	87,5	39	609,5
	2	95	39	609,5
	3	100,5	39	609,5
	4	90	40	579,5
	5	99	40,5	565
	6	89	41	551,5
	7	86	41,5	538,5
	Average	92,43	40	580,43
	St.Dev	5,75	1,04	29,91
P = 6,86 N	Exp.No.	2c (μm)	2a (μm)	HV (kg/mm ²)
	1	129	47,5	575,4
	2	126,5	48	563,5
	3	125	49	540,4
	4	134,5	49	540,4
	5	127,5	49,5	529,9
	6	124,5	50	519,4
	7	126,5	50	519,4
	Average	127,64	49	541,2
	St.Dev	3,38	0,96	21,39
P = 9,80 N	Exp.No.	2c (μm)	2a (μm)	HV (kg/mm ²)
	1	157	55,5	602
	2	166,5	56	591
	3	166	56,5	581
	4	168,5	57	571
	5	155,5	58	551
	6	164	58	551
	7	170	58	551
	Average	163,93	57	571,14
	St.Dev	5,59	1,04	21,06

The change in 2a and 2c values according to load for the 2nd group is shown in Fig.3.22.

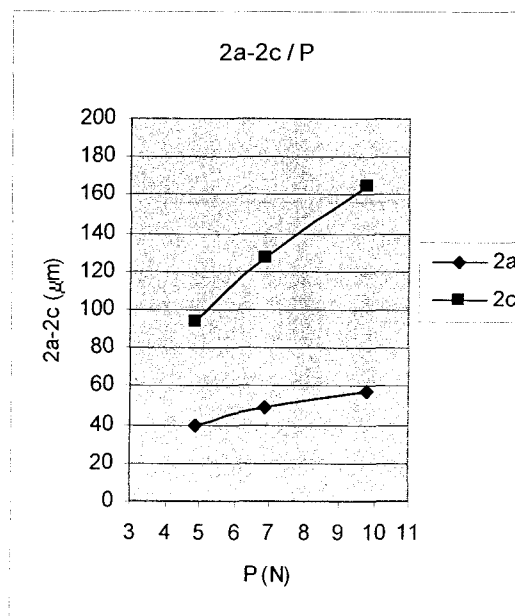


Fig.3.22 The relationship between 2a - 2c and load for the 2nd group of specimens.

The fracture toughness (K_{Ic}) values were calculated from the values given at Table 3.9. with Eq. [3.13]. At this calculation, the elastic modulus (E), of the glass samples is taken as 73,031GPa which is obtained from the results of the Ultra Microhardness test. The calculated K_{Ic} values are given at Table 3.10 for the 2nd group of glass specimens.

Also K_{Ic} values for the Vickers indentation test, can be calculated when H/E ratio ($H/E= 0,064$) for the 2nd group of the specimens in the Knoop indentation test is used in Eq. [3.13]. The results that are determined for the 2nd group of the glass specimens are given in Table 3.10.

Table 3.10 K_{Ic} values calculated from the crack size for the 2nd group of specimens.

	Exp.No.	c (μ m)	K_{Ic} (MN/m ^{3/2}) ($E= 73,031$)	K_{Ic} (MN/m ^{3/2}) ($H/E= 0,064$)
P = 4,90 N	1	43,75	0,938	1,071
	2	47,5	0,829	0,947
	3	50,25	0,762	0,870
	4	45	0,922	1,027
	5	49,5	0,809	0,890
	6	44,5	0,961	1,044
	7	43	1,024	1,099
	Average	46,21	0,892	0,992
	St.Dev	2,87	0,09	0,090
P = 6,86 N	1	64,5	0,755	0,838
	2	63,25	0,786	0,863
	3	62,5	0,817	0,878
	4	67,25	0,732	0,787
	5	63,75	0,801	0,852
	6	62,25	0,838	0,883
	7	63,25	0,818	0,863
	Average	63,82	0,792	0,852
	St.Dev	1,69	0,038	0,033
P = 9,80 N	1	78,5	0,785	0,891
	2	83,25	0,726	0,816
	3	83	0,735	0,820
	4	84,25	0,725	0,801
	5	77,75	0,833	0,904
	6	82	0,769	0,835
	7	85	0,728	0,791
	Average	81,96	0,757	0,837
	St.Dev	2,80	0,041	0,044

For the 2nd group of specimens, it is possible to view the schematic diagram of the relationship between $P/c^{3/2}$ ratio and increasing load as given in Fig.3.23.

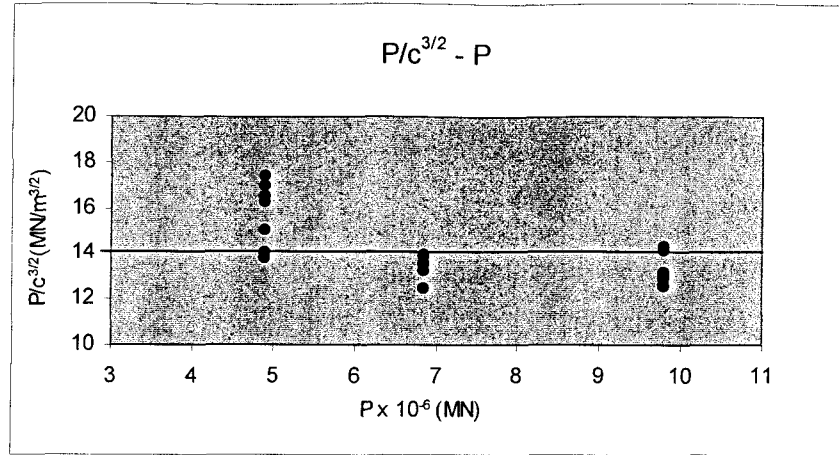


Fig.3.23 $P/c^{3/2}$ (MN/m^{3/2}) – P (MN) diagram for the 2nd group of specimens

According to the values that are given at Table 3.10; the change in fracture toughness, K_c (MN/m^{3/2}), with increasing load is shown in Fig.3.24 for the 2nd group of specimens.

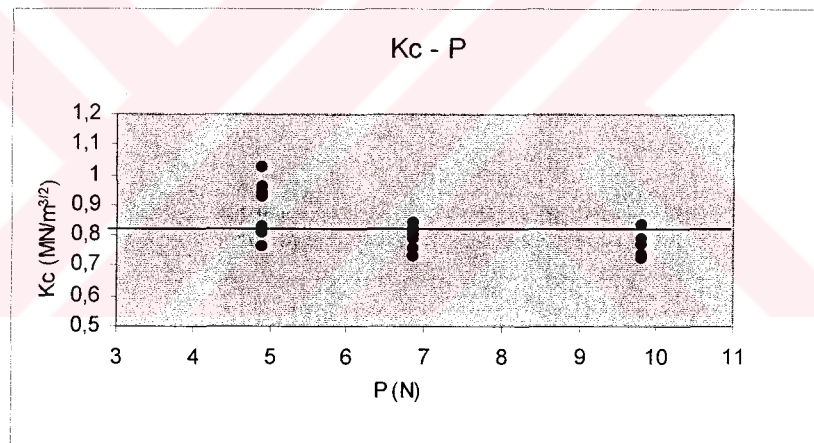


Fig.3.24 K_c (MN/m^{3/2}) – P (N) diagram for the 2nd group of specimens

$K_{c_{average}}$ is obtained 0,814 MN/m^{3/2} for the 2nd group of specimens from the K_c values that have been calculated at 4,9N, 6,86N and 9,8N of loads.

Fig.3.25 shows the diagonal mark and the crack for 3rd group of specimens at 6,86 N of load. The picture is captured with an optical microscope using an enlargement of 320x.

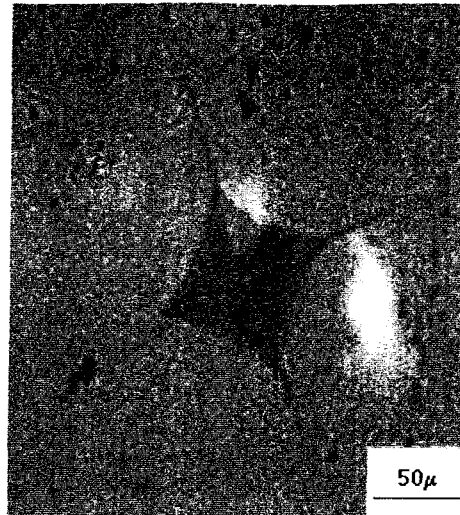


Fig.3.25 Diagonal mark and the crack for 3rd group at 6,86N of load

The Vickers indentation test results for the 3rd group of specimens ($t = 7,94$ mm) at different loads are given in Table 3.11 below.

Table 3.11 Vickers indentation test results for the 3rd group of specimens.

P = 4,90 N	Exp.No.	2c (μm)	2a (μm)	HV (kg/mm ²)
	1	82	38,5	625,5
	2	83,5	38,5	625,5
	3	83	39,5	594
	4	89,5	39,5	594
	5	80,5	40	579,5
	6	84	40,5	565
	7	85	40,5	565
	Average	83,93	39,57	592,64
	St.Dev	2,849	0,838	25,377
P = 6,86 N	Exp.No.	2c (μm)	2a (μm)	HV (kg/mm ²)
	1	94,5	47,5	575,4
	2	97,5	48	563,5
	3	90,5	49	540,4
	4	95,5	49	540,4
	5	97	49	540,4
	6	97,5	50	519,4
	7	98,5	50	519,4
	Average	95,86	48,93	542,70
	St.Dev	2,719	0,932	20,831
P = 9,80 N	Exp.No.	2c (μm)	2a (μm)	HV (kg/mm ²)
	1	127,5	56	591
	2	128,5	56	591
	3	126	56,5	581
	4	125	58	551
	5	126,5	58	551
	6	128,5	59	533
	7	129,5	59	533
	Average	127,36	57,50	561,57
	St.Dev	1,600	1,323	25,709

According to the values that are given at Table 3.11; the change in Vickers Hardness, HV (kg/mm^2), with increasing load is shown in Fig.3.26 below for the 3rd group of specimens.

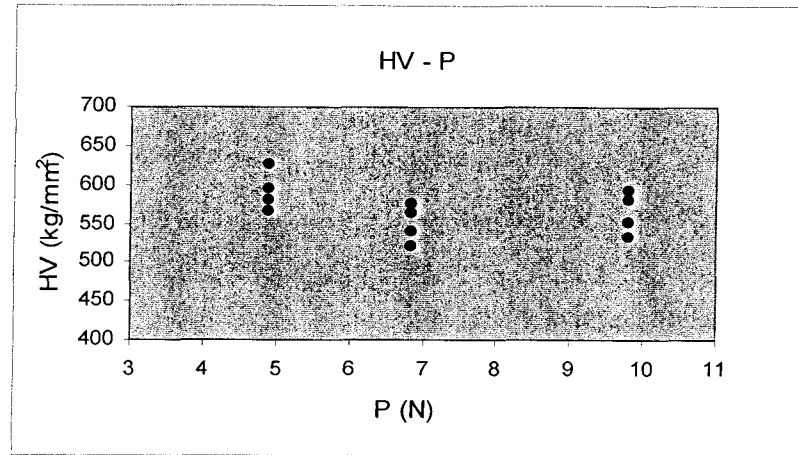


Fig.3.26 HV (kg/mm^2) – P (N) diagram for the 3rd group of specimens

HV_{average} , for the 3rd group of specimens, is calculated as $565,64 \text{ kg/mm}^2$ from the HV values that are given at 4,9 N, 6,86 N and 9,8 N of loads.

The change in 2a and 2c values according to load (P), for the 3rd group is illustrated in Fig.3.27 below.

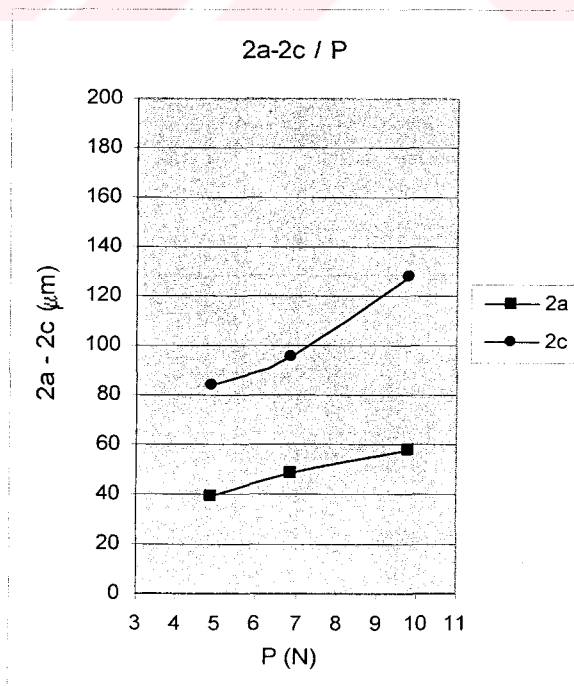


Fig. 3.27 The relationship between 2a - 2c and load for the 3rd group of specimens

The fracture toughness (K_{IC}) values were calculated from the values given at Table 3.11. with Eq. [3.13]. At this calculation, the elastic modulus (E), of the glass samples is taken as 72,658 GPa which is obtained from the results of the Ultra Microhardness test. The calculated K_{IC} values are given at Table 3.12 for the 3rd group of glass specimens.

Also K_{IC} values for the Vickers indentation test, can be calculated when H/E ratio ($H/E = 0,070$) for the 3rd group of the specimens in the Knoop indentation test is used in Eq. [3.13]. The results that are determined for the 3rd group of the glass specimens are given in Table 3.12.

Table 3.12 K_{IC} values calculated from the crack size for the 3rd group of specimens.

	Exp.No.	c (μm)	K_{IC} ($MN/m^{3/2}$) ($E = 72,658$)	K_{IC} ($MN/m^{3/2}$) ($H/E = 0,070$)
P = 4,90 N	1	41	1,018	1,129
	2	41,75	0,991	1,098
	3	41,5	1,026	1,108
	4	44,75	0,916	0,990
	5	40,25	1,087	1,160
	6	42	1,033	1,089
	7	42,5	1,015	1,070
	Average	41,96	1,01	1,092
	St.Dev	1,42	0,05	0,054
P = 6,86 N	1	47,25	1,201	1,277
	2	48,75	1,158	1,219
	3	45,25	1,322	1,363
	4	47,75	1,220	1,257
	5	48,5	1,192	1,228
	6	48,75	1,206	1,219
	7	49,25	1,188	1,200
	Average	47,93	1,21	1,252
	St.Dev	1,36	0,05	0,055
P = 9,80 N	1	63,75	1,080	1,164
	2	64,25	1,068	1,151
	3	63	1,109	1,185
	4	62,5	1,152	1,199
	5	63,25	1,132	1,178
	6	64,25	1,124	1,151
	7	64,75	1,111	1,137
	Average	63,68	1,11	1,167
	St.Dev	0,80	0,03	0,022

For the 3rd group of specimens, it is possible to view the schematic diagram of the relationship between $P/c^{3/2}$ ratio and increasing load as given in Fig.3.28.

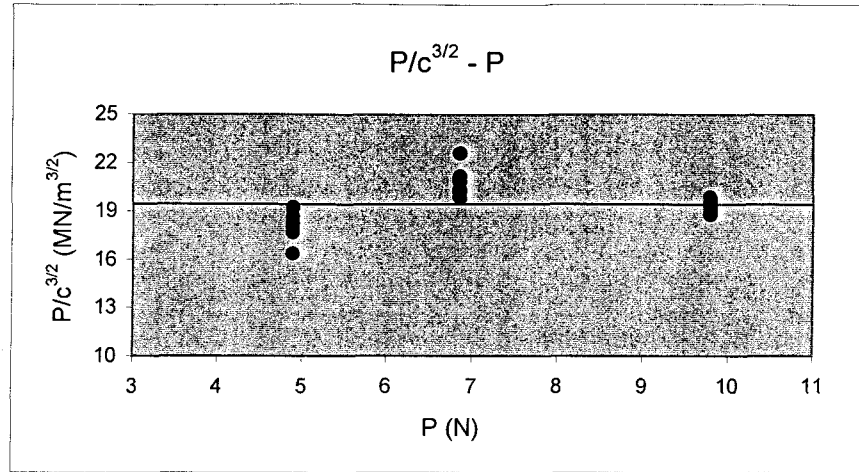


Fig.3.28 $P/c^{3/2}$ (MN/m^{3/2}) – P (MN) diagram for the 3rd group of specimens

According to the values that are given at Table 3.12; the change in fracture toughness, K_c (MN/m^{3/2}), with increasing load is shown in Fig.3.29 for the 3rd group of specimens.

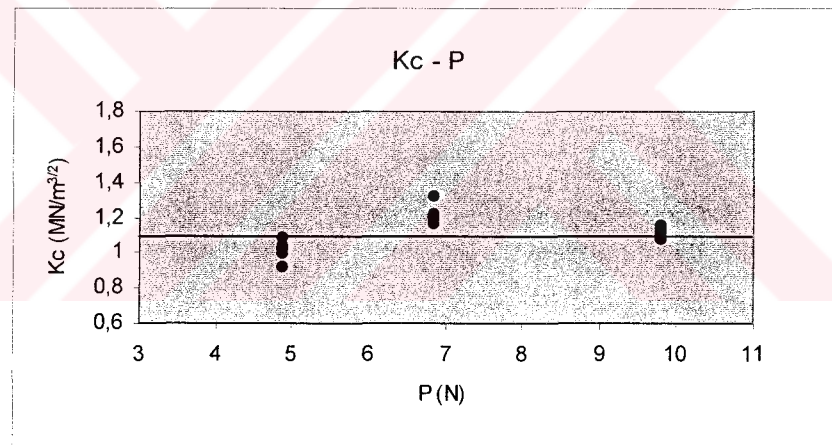


Fig.3.29 K_c (MN/m^{3/2}) – P (N) diagram for the 3rd group of specimens

$K_{c_{average}}$ is obtained as 1,112 MN/m^{3/2} for the 3rd group of specimens from the K_c values that have been calculated at 4,9N, 6,86N and 9,8N of loads.

3.3.4. Knoop Indentation

As in Vickers indentation test, 4,9 N, 6,86 N and 9,8 N of loads were applied to the four groups of the specimens. The lengths of the short and the long diagonal marks of the indent were measured by the help of the divisions at the ocular of the microhardness equipment at a magnification of 400x.

The picture, which shows the diagonal indentation mark and the crack length that is seen in Knoop indentation for the 1st group at 6,86 N of load; is given in Fig.3.30. This picture is captured with an optical microscope using an enlargement of 200x.

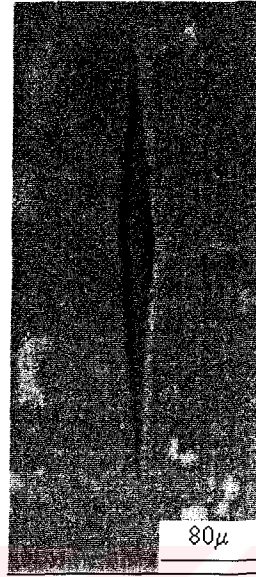


Fig.3.30 Diagonal mark for 1st group at 6,86N of load

The Knoop hardness values (KHN), were calculated by using Eq.[3.14], the elastic modulus values were determined by using Eq.[3.15]. In order to use Eq.[3.15], $H/E \geq 0,03$ condition must be obtained for brittle materials [34]. In this study, test results that are performed on four groups of specimens satisfy this condition, as shown in Table 3.13.

Fig.3.31 shows the change in Knoop Hardness Number (KHN), with increasing load (P), for the 1st group of specimens.

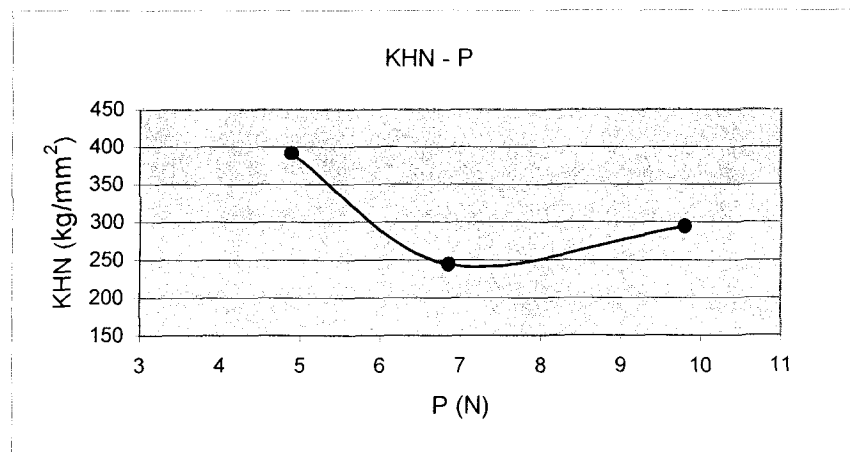


Fig.3.31 Knoop Hardness Number (KHN) – Load (P) diagram for the 1st group

Table 3.13 Knoop indentation test results for four groups of specimens.

	P (N)	a(μ m)	b(μ m)	H (kg/mm ²)	E (GPa)	H/E
1 st group	4,9	135	16	390,370	81,776	0,048
	6,86	202	25	244,101	67,649	0,036
	9,8	220	26	293,988	60,635	0,048
2 nd group	4,9	125	14	455,328	73,178	0,062
	6,86	152	17	431,107	68,897	0,063
	9,8	182	20	429,568	64,200	0,067
3 rd group	4,9	121	14	485,930	89,996	0,054
	6,86	150	16	442,680	59,762	0,074
	9,8	175	18	464,620	56,291	0,083
4 th group	4,9	128	15	434,235	85,657	0,051
	6,86	161	17	384,256	50,252	0,076
	9,8	190	21	394,155	60,179	0,065

Also the variation of the elastic modulus by the increasing load can be illustrated as in Fig.3.32 below for the 1st group of specimens.

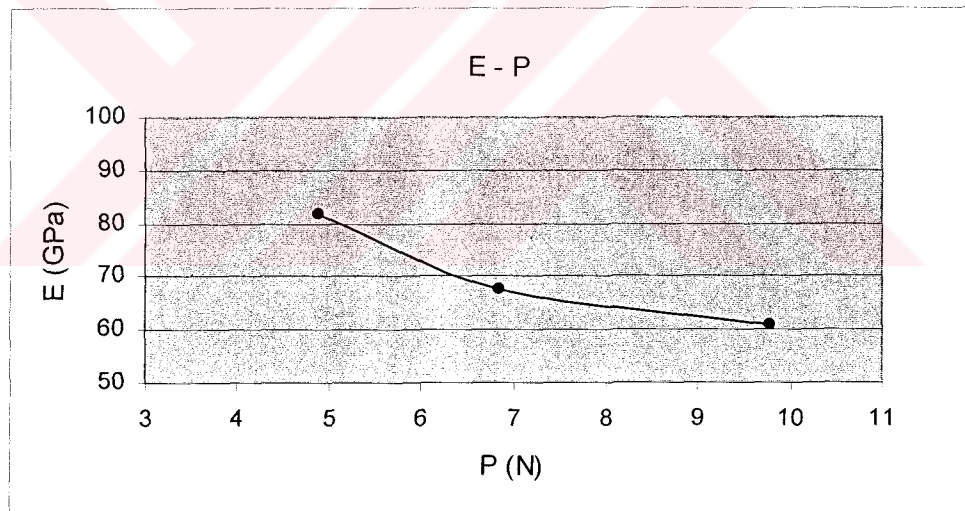


Fig.3.32 Elastic modulus (E) – Load (P) diagram for the 1st group

According to the values at Table 3.13 KHN – P diagram can be illustrated, for the 2nd group of specimens, as given in Fig.3.33.

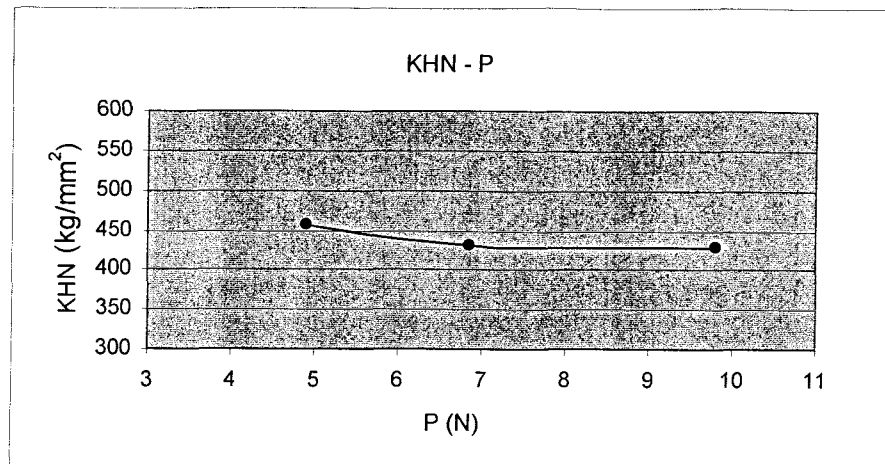


Fig.3.33 Knoop Hardness Number (KHN) – Load (P) diagram for the 2nd group

The picture, which shows the diagonal mark and the crack length is seen in Knoop indentation test at a load of 4,9 N, for the 2nd group of the glass specimens that have thickness of 3,84 mm; is given in Fig.3.34.

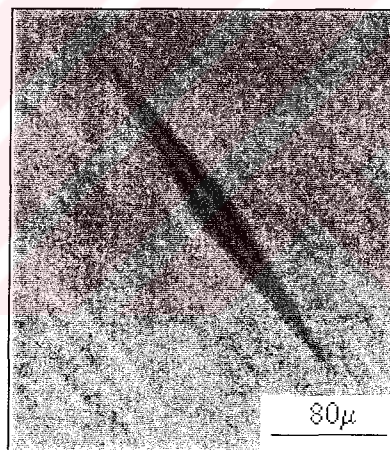


Fig.3.34 Diagonal mark for the 2nd group at 4,9N of load

The relationship between elastic modulus (E) and load (P) is given in Fig.3.35 for the 2nd group of glass specimens.

In Fig.3.36, it is given the diagonal mark and the crack length in Knoop indentation test for the 3rd group of glass specimens at 9,8 N of load. Fig.3.36 is captured with an optical microscope using an enlargement of 200x.

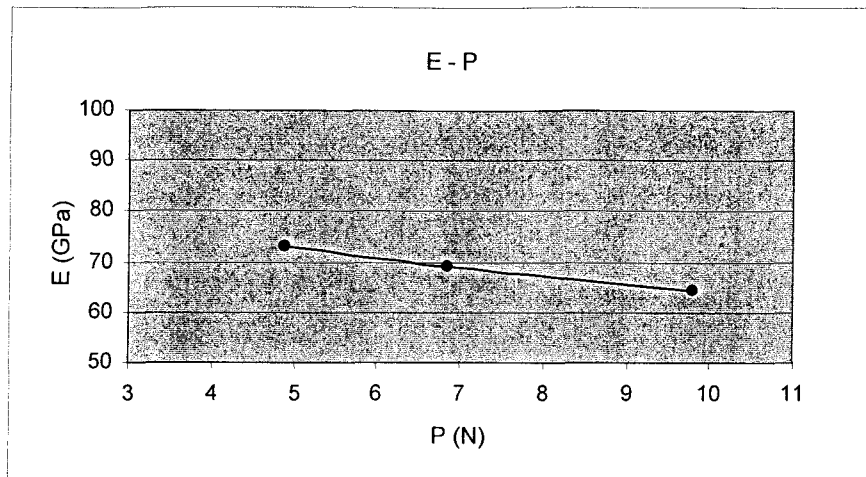


Fig.3.35 Elastic modulus (E) – Load (P) diagram for the 2nd group

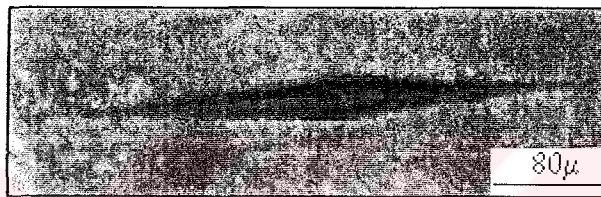


Fig.3.36 Diagonal mark for 3rd group at 9,8N of load

Fig.3.37 below, which is illustrated from the values at Table 3.13; shows the change in Knoop hardness with increasing load.

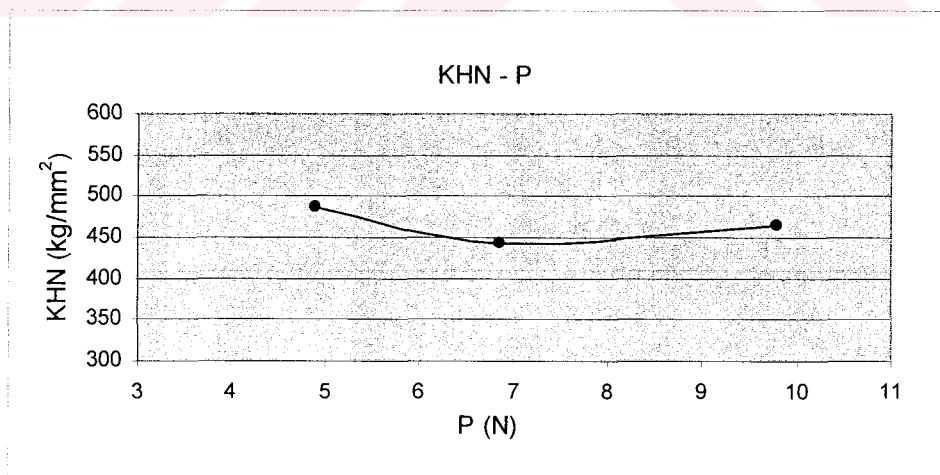


Fig.3.37 KHN – Load diagram for the 3rd group

According to the values at Table 3.13 E – P diagram can be illustrated, for the 3rd group of specimens, as given in Fig.3.38.

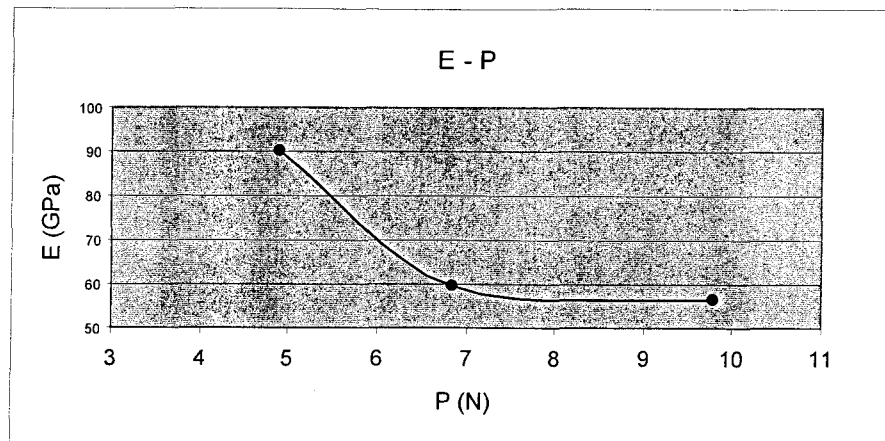


Fig.3.38 Elastic modulus (E) – Load (P) diagram for the 3rd group

The picture, which shows the diagonal mark and the crack length that is seen in Knoop indentation for the 4th group at 6,86 N of load; is given below Fig.3.39. This picture is captured with an optical microscope using an enlargement of 200x.

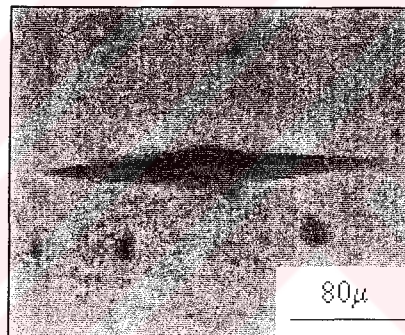


Fig.3.39 Diagonal mark for 4th group at 6,86N of load

Fig.3.40 shows the change in Knoop hardness with the increasing load for the 4th group of specimens.

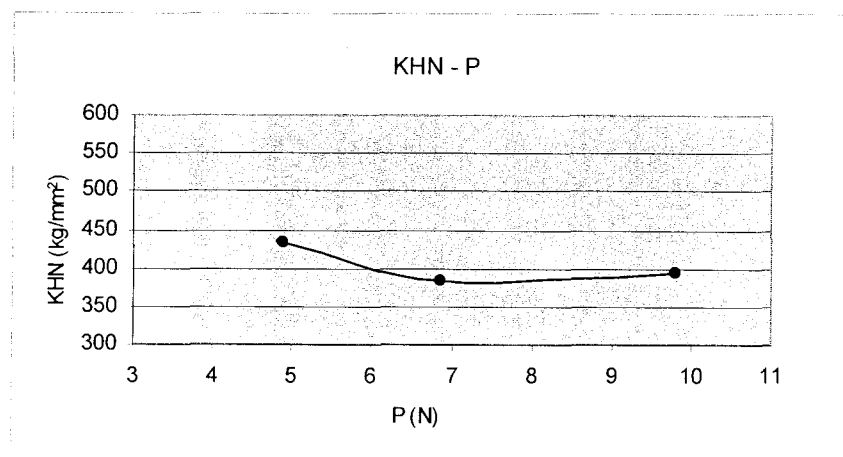


Fig.3.40 KHN – Load diagram for the 4th group

Elastic modulus (E), versus load (P) diagram for the 4th group of specimens is given in Fig.3.41 below.

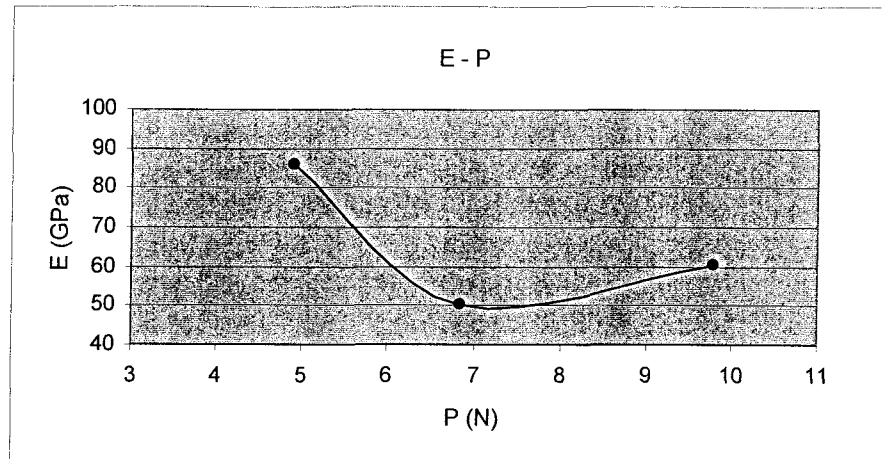


Fig.3.41 Elastic Modulus – Load diagram for the 4th group

3.2.5. Ultra Microhardness Test

To realize this test, 1st, 2nd, 3rd and 4th group of glass specimens that have the dimensions of 1.5 cm x 2.0 cm were prepared. The load range for this test has selected as, 50 mN, 100 mN, 250 mN, 500 mN, 750 mN, 1000 mN for each group of glass specimens. In this work, number of steps used for loading was 60 and the time between consecutive steps was 1s.

The diagonal mark that is seen in ultra microhardness test for the 1st group at 750 mN of load; is shown in Fig.3.42. This picture is captured with an optical microscope using an enlargement of 320x.

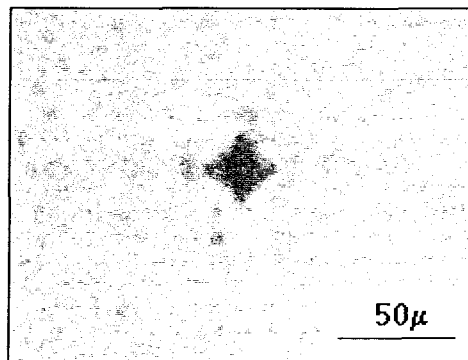


Fig.3.42 Diagonal mark for 1st group at 750 mN

Fig.3.43 also shows the diagonal mark at a load of 1000 mN for the 2nd group of the glass specimens. This picture is also captured with an optical microscope using an enlargement of 320x.

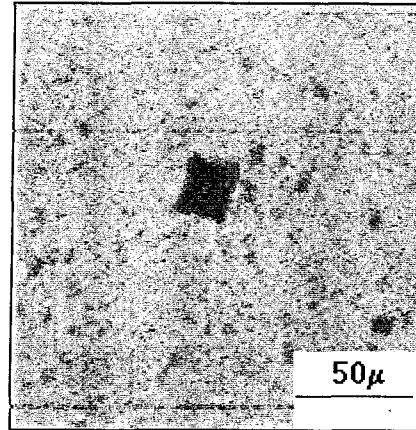


Fig.3.43 Diagonal mark for 2nd group at 1000 mN

The results of Ultra microhardness test; as, the mean values of W_e (elastic energy), W_p (plastic energy), W_t (total energy), H_p (hardness at plastic area), $E/(1-\mu^2)$ (the ratio to calculate elastic modulus in which the Poisson's ratio, μ , is taken 0,25 for the glass specimens) and h_p' (plastic indentation depth) are given in Table 3.14 for the 1st group of specimens at each load mentioned above.

Table 3.14 Results of ultra microhardness test for the 1st group.

Pmax (mN)	Wt (nj)	We (nj)	Wp (nj)	$E/(1-\mu^2)$ (Gpa)	H_p (N/mm ²)	h_p' (μm)	E (Gpa)
50	12,08	7,02	5,07	76,56	8143	0,482	71,775
100	34,19	19,57	14,62	77,08	8046	0,686	72,263
250	133,77	76,83	56,94	77,94	8136	1,078	73,069
500	372,69	215,93	156,77	79,72	8477	1,494	74,738
750	692,73	397,34	295,39	79,14	8415	1,836	74,194
1000	1084,83	623,13	461,69	77,15	8356	2,127	72,328

From the mean values of E (GPa) at each load for the 1st group, the average elastic modulus value which can be used for 1st group is calculated 73,061 GPa.

The values at Table 3.14 are used to illustrate Fig.3.44 which shows the relationship between load and h_p' for the 1st group of specimens.

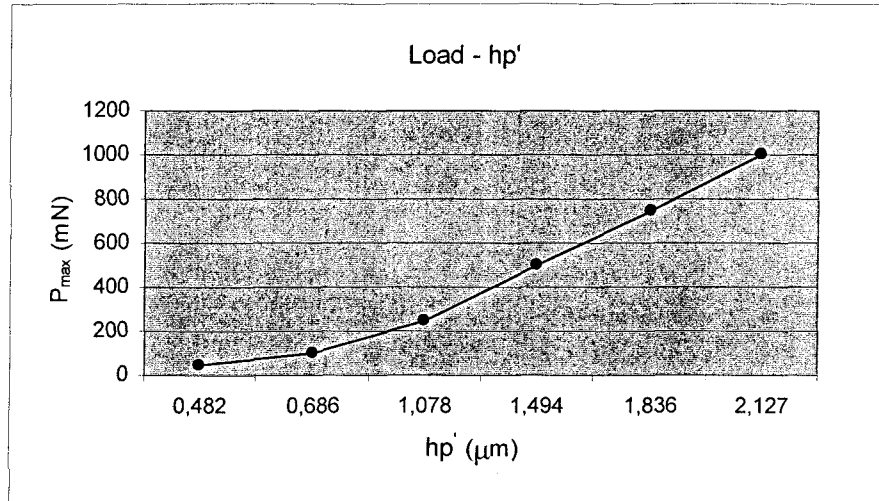


Fig.3.44 Load – indentation depth diagram for the 1st group

Fig.3.45 shows the variation of H_p according to h_p' for the 1st group. This figure is illustrated by using the data at Table 3.14.

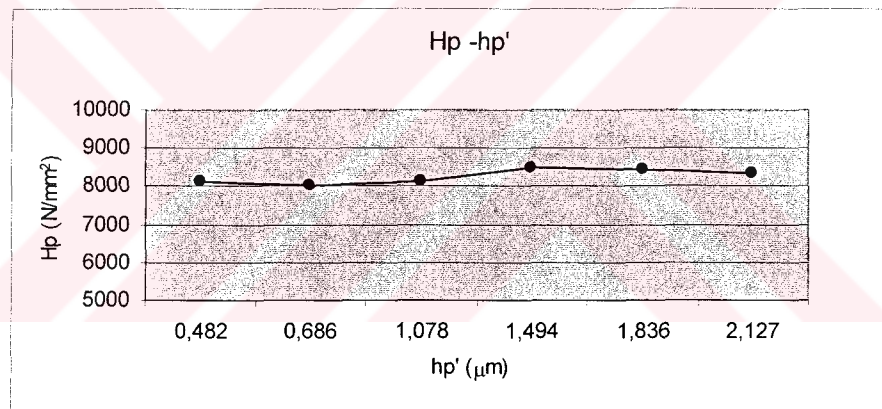


Fig.3.45 H_p – h_p' diagram for the 1st group of specimens

By using Eq.[3.16] and Eq.[3.17], HV_1 and HV_2 values for the 1st group were calculated. The values obtained are given at Table 3.15.

Table 3.15 HV_1 and HV_2 values for the 1st group of specimens.

Pmax (mN)	hp (μm)	HV ₁ (GPa)	HV ₂ (GPa)
50	0,482	8,144	5,139
100	0,686	8,041	5,141
250	1,078	8,141	5,159
500	1,494	8,477	5,336
750	1,836	8,419	5,418
1000	2,127	8,364	5,446

The variation of HV_1 and HV_2 values according to hp' are given for the 1st group in Fig.3.46.

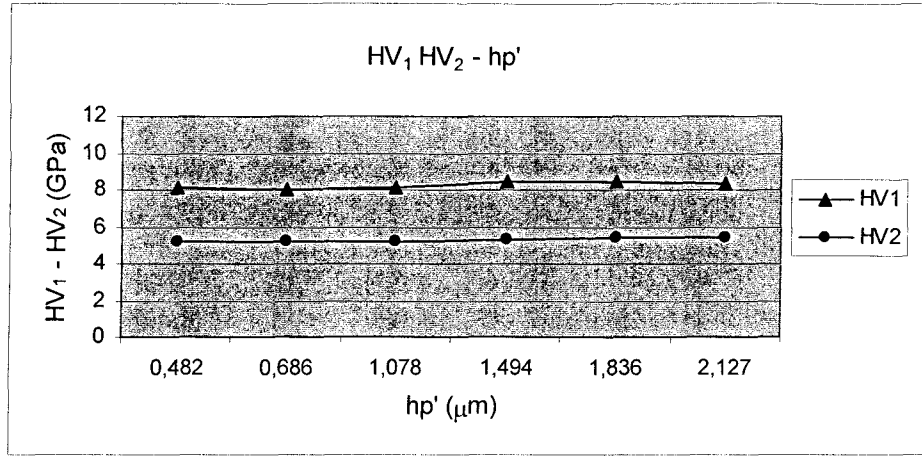


Fig.3.46 HV_1 HV_2 - hp' diagram for the 1st group of specimens

Table 3.16 shows the values that are obtained from the equipment by the experiments that are done for 2nd group of specimens at each load mentioned above. To calculate E (GPa), the Poisson's ratio, μ , is taken 0,25 for the glass specimens. From the mean values of E (GPa) at each load for the 2nd group, the average elastic modulus value which can be used for 2nd group is calculated 73,031 GPa.

Table 3.16 Results of ultra microhardness test for the 2nd group.

Pmax (mN)	Wt (nj)	We (nj)	Wp (nj)	$E/(1-\mu^2)$ (Gpa)	Hp (N/mm ²)	hp' (μm)	E (Gpa)
50	12,22	6,87	5,35	75,72	7808	0,492	70,988
100	34,33	19,31	15,02	76,96	7800	0,696	72,150
250	135,24	75,17	60,07	77,87	7939	1,092	73,003
500	377,14	214,63	162,51	79,22	8301	1,509	74,269
750	694	393,66	300,34	79,3	8336	1,844	74,344
1000	1077,9	610,77	467,13	78,33	8273	2,137	73,434

The values at Table 3.16 are used to illustrate Fig.3.47 which shows the relationship between load and hp' for the 2nd group of specimens.

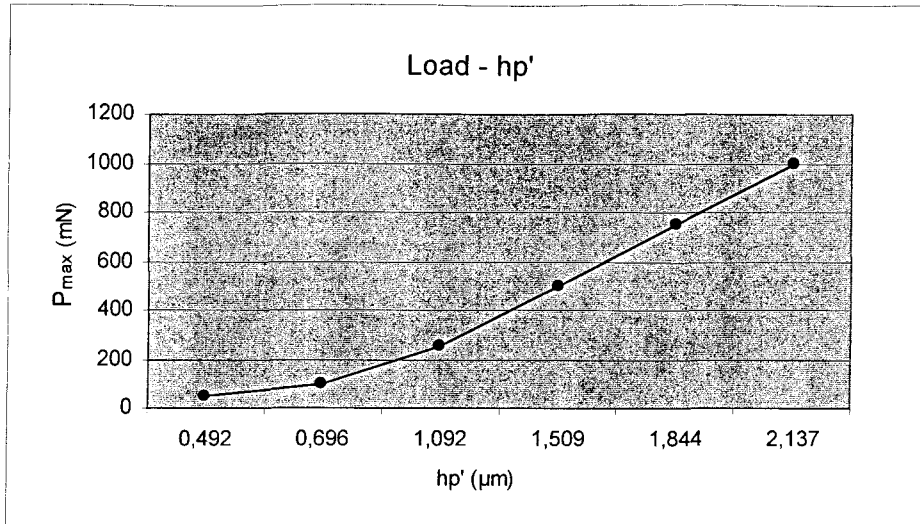


Fig.3.47 Load – indentation depth diagram for the 2nd group

Fig.3.48 shows the variation of H_p according to h_p' for the 2nd group. This figure is illustrated by using the data at Table 3.16.

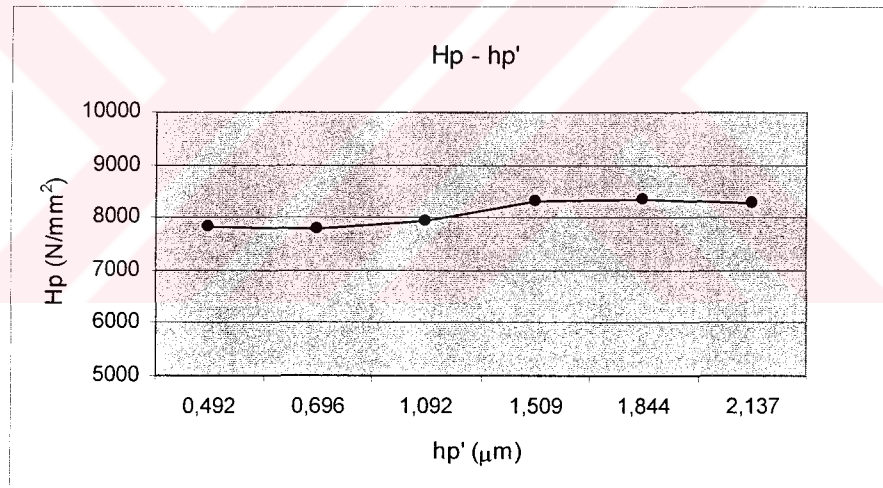


Fig.3.48 H_p – h_p' diagram for the 2nd group of specimens

By using Eq.[3.16] and Eq.[3.17], HV_1 and HV_2 values for the 2nd group were calculated. The values obtained are given at Table 3.17.

Table 3.17 HV₁ and HV₂ values for the 2nd group of specimens.

Pmax (mN)	hp (μm)	HV ₁ (GPa)	HV ₂ (GPa)
50	0,492	7,816	5,099
100	0,696	7,811	5,056
250	1,092	7,933	5,236
500	1,509	8,308	5,368
750	1,844	8,346	5,437
1000	2,137	8,285	5,433

The variation of HV₁ and HV₂ values according to hp' are given for the 2nd group of specimens in Fig.3.49.

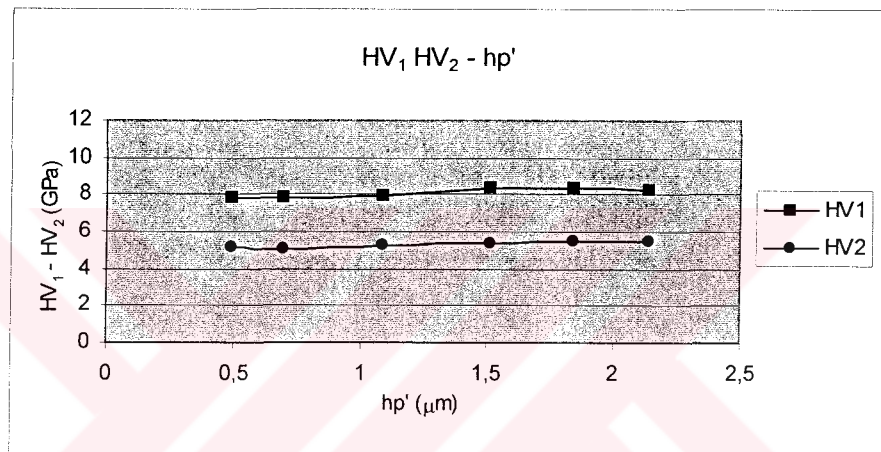


Fig.3.49 HV₁ HV₂ - hp' diagram for the 2nd group of specimens

Table 3.18 shows the values that are obtained from the equipment by the experiments that are done for 3rd group of specimens at each load mentioned above. To calculate E (GPa) the Poisson's ratio, μ , is taken 0.25 for the glass specimens.

Table 3.18 Results of ultra microhardness test for the 3rd group.

Pmax (mN)	Wt (nj)	We (nj)	Wp (nj)	$E/(1-\mu^2)$ (Gpa)	Hp (N/mm ²)	hp' (μm)	E (Gpa)
50	12,32	6,93	5,39	74,97	7690,00	0,50	70,284
100	34,6	19,51	15,09	77,13	7943,00	0,69	72,309
250	134,97	75,75	59,22	78,89	8077,00	1,08	73,959
500	384,59	216,34	168,25	76,95	7973,00	1,54	72,141
750	697,92	398,07	299,85	78,65	8219,00	1,86	73,734
1000	1075,2	608,55	466,65	78,42	8166,00	2,15	73,519

From the mean values of E (GPa) at each load for the 3rd group, the average elastic modulus value which can be used for 3rd group is calculated 72,658 GPa.

The values at Table 3.18 are used to illustrate Fig.3.50 which shows the relationship between load and h_p' for the 3rd group of specimens.

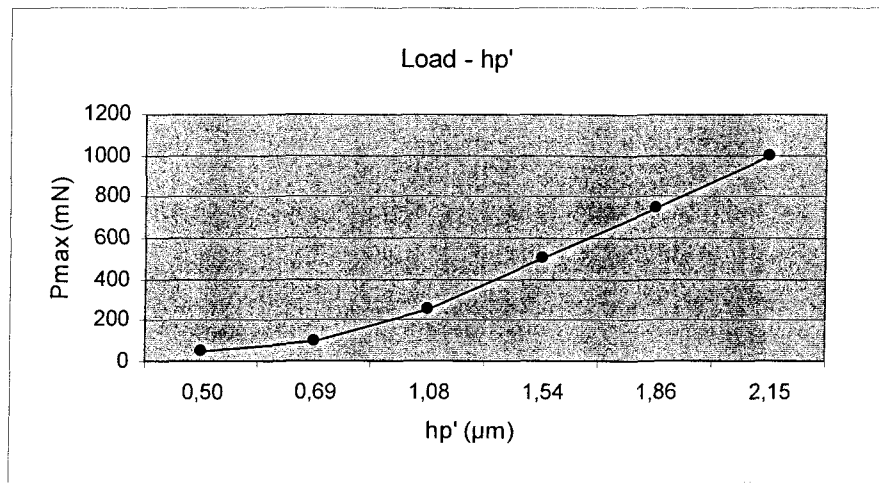


Fig.3.50 Load – indentation depth diagram for the 3rd group

Fig.3.51 shows the variation of H_p according to h_p' for the 3rd group. This figure is illustrated by using the data at Table 3.18.

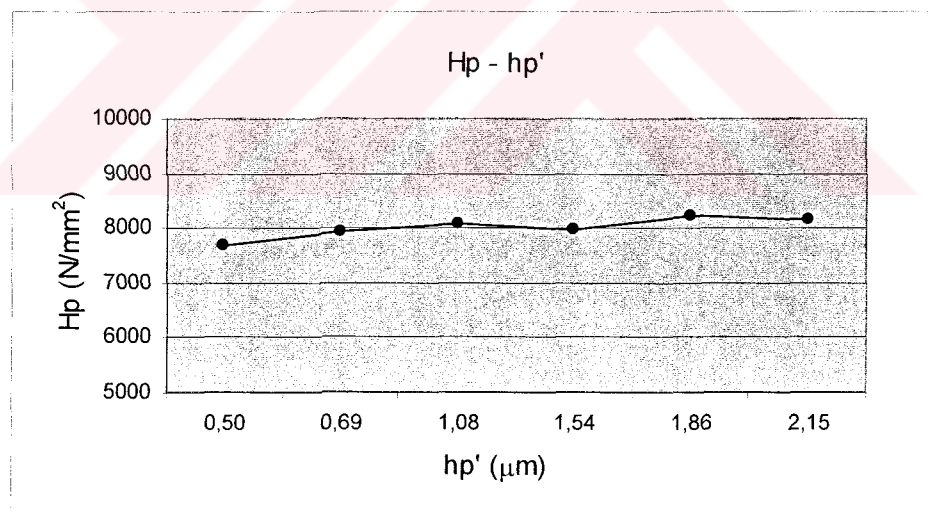


Fig.3.51 H_p – h_p' diagram for the 3rd group of specimens

By using Eq.[3.16] and Eq.[3.17], HV_1 and HV_2 values for the 3rd group were calculated. The values obtained are given at Table 3.19.

Table 3.19 HV₁ and HV₂ values for the 3rd group of specimens.

Pmax (mN)	hp' (μm)	HV ₁ (GPa)	HV ₂ (GPa)
50	0,50	7,691	5,014
100	0,69	7,948	5,214
250	1,08	8,080	5,307
500	1,54	7,978	5,229
750	1,86	8,230	5,315
1000	2,15	8,178	5,322

The variation of HV₁ and HV₂ values according to hp' are given for the 3rd group of specimens in Fig.3.52.

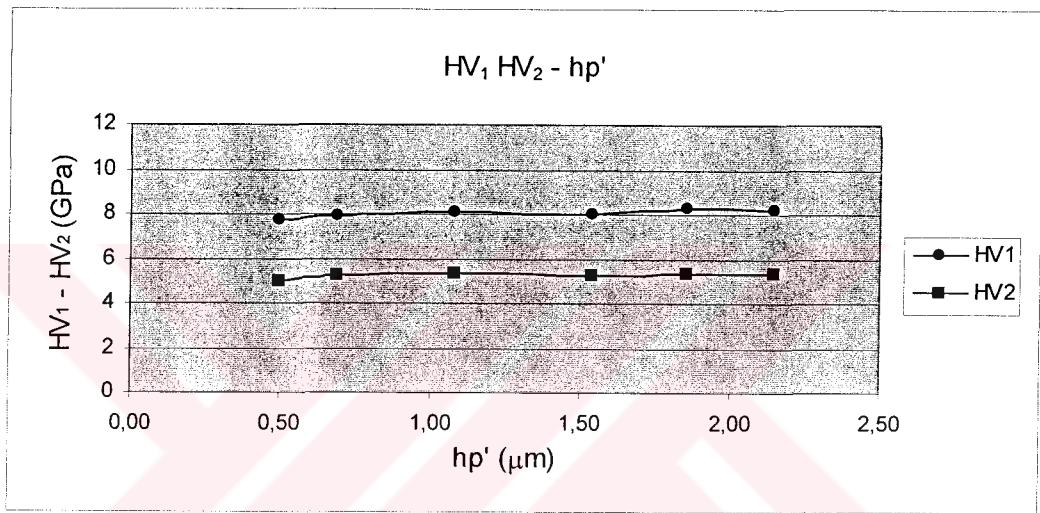


Fig.3.52 HV₁ HV₂ - hp' diagram for the 3rd group of specimens

Table 3.20 shows the values that are obtained from the equipment by the experiments that are done for 4th group of specimens at each load mentioned above. To calculate E (GPa) the Poisson's ratio, μ , is taken 0.25 for the glass specimens.

Table 3.20 Results of ultra microhardness test for the 4th group.

Pmax (mN)	Wt (nj)	We (nj)	Wp (nj)	E/(1- μ^2) (Gpa)	Hp (N/mm ²)	hp' (μm)	E (Gpa)
50	11,63	6,86	4,78	35,16	7655	1,023	32,963
100	34,15	19,45	14,7	78,62	8249	1,036	73,706
250	135,85	75,59	60,26	76,93	7696	1,109	72,122
500	378,15	213,78	164,33	79,72	8281	1,511	74,738
750	698,54	394,85	303,69	79,03	8151	1,865	74,091
1000	1069,47	606,37	463,1	74,99	7459	2,251	70,303

From the mean values of E (GPa) at each load for the 4th group, the average elastic modulus value which can be used for 4th group is calculated 66,320 GPa. The

values at Table 3.20 are used to illustrate Fig.3.53 which shows the relationship between load and h_p' for the 4th group of specimens.

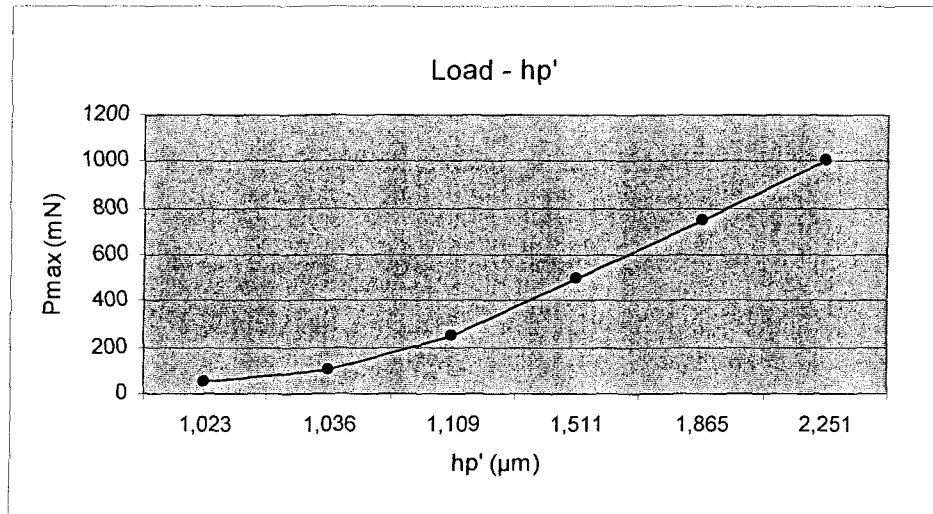


Fig.3.53 Load – indentation depth diagram for the 4th group

Fig.3.54 shows the variation of H_p according to h_p' for the 4th group. This figure is illustrated by using the data at Table 3.20.

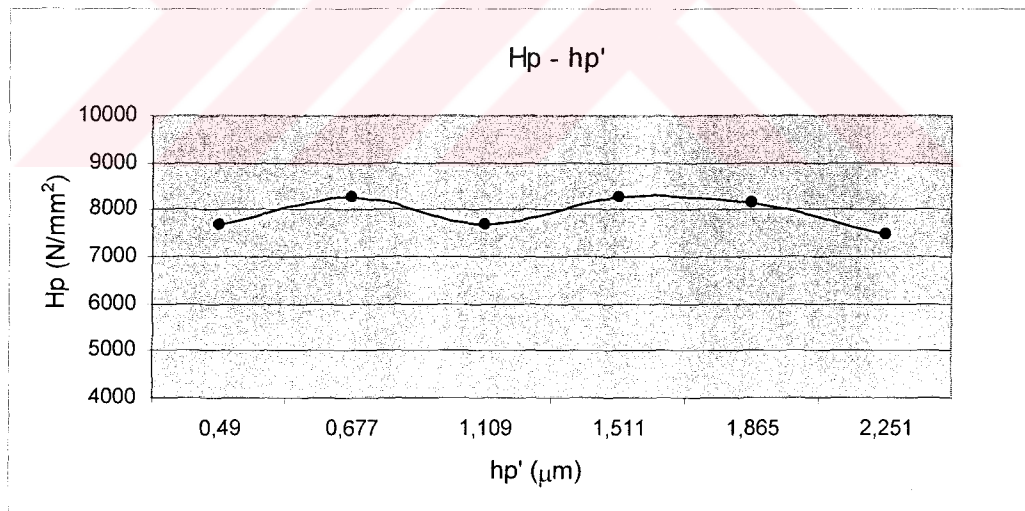


Fig.3.54 H_p – h_p' diagram for the 4th group of specimens

By using Eq.[3.16] and Eq.[3.17], HV_1 and HV_2 values for the 4th group were calculated. The values obtained are given at Table 3.21.

Table 3.21 HV₁ and HV₂ values for the 4th group of specimens.

Pmax (mN)	hp (μm)	HV ₁ (GPa)	HV ₂ (GPa)
50	1,023	1,808	0,507
100	1,036	3,526	1,501
250	1,109	7,692	5,015
500	1,511	8,287	5,407
750	1,865	8,159	5,314
1000	2,251	7,468	4,609

The variation of HV₁ and HV₂ values according to hp' are given for the 4th group of specimens in Fig.3.55.

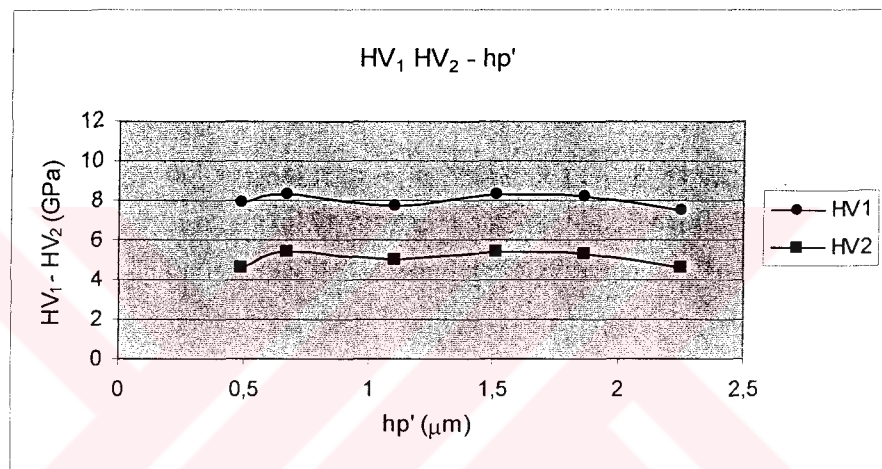


Fig.3.55 HV₁ HV₂ - hp' diagram for the 4th group of specimens

For the four groups of specimens Fig.3.56 shows the change in Hp (N/mm²) with increasing load, P (mN).

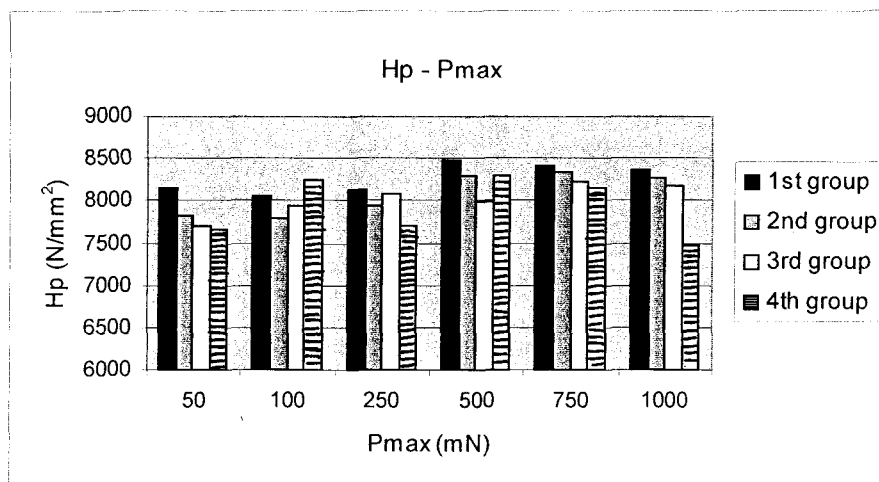


Fig.3.56 Hardness – Load diagram for the ultra microhardness test

4. DISCUSSION

In this study, to investigate the general mechanical properties of the glass samples, such as elastic modulus (E), hardness (H), fracture toughness (K_c) and maximum fracture strength ($\sigma_{\max}$) various tests have been done.

The average elastic modulus values of each group of specimens that are obtained from ball on the ring test, three point bending of the beam, Knoop indentation and ultra microhardness test; are given Table 4.1.

In Table 4.1; the ball on the ring and the three point bending test results are given just for the 1st group (t=2,14 mm) and the 2nd group (t=3,86 mm) of the glass specimens; due to the limitation of the specimen thickness of the test equipment as already mentioned at Chapter 3.2.1 in this study.

Table 4.1 Average elastic modulus values for the glass specimens.

	AVERAGE ELASTIC MODULUS VALUES			
	Ball on the ring test	Three point bending	Knoop indentation	Ultra microhardness
1 st Group	368,241 GPa	263,054 GPa	70,020 GPa	73,061 GPa
2 nd Group	107,201 GPa	73,811 GPa	68,758 GPa	73,031 GPa
3 rd Group	—	—	68,683 GPa	72,658 GPa
4 th Group	—	—	65,363 GPa	66,320 GPa

The schematic illustrations of the measured elastic modulus in Knoop indentation test according to increasing load are shown in Fig.3.32, Fig.3.35, Fig.3.38 and Fig.3.41. From these figures it is seen that as the indentation load increases the elastic modulus value is decreased.

Because with increasing load, the elastic recovery of the short diagonal becomes relatively lower than the long diagonal i.e. the ratio of the short diagonal (b_K) to the long diagonal (a_K) increases (see Table 3.13). This result is verifying the studies in literature [36].

From Table 4.1; it is seen that the results of the Knoop indentation and the ultra microhardness tests are satisfying the approximate elastic modulus values ($E=68 - 72$ GPa) for the glass material that are given in the literature [31, 34, 41, 42, 43, 44] while in the ball on the ring and the three point of the beam test methods, it is not possible to obtain a satisfying value for the elastic modulus. It has also seen that; Eq.[3.3] which is used to obtain elastic modulus from these test methods is more suitable for the test equipment that uses a loading cylinder instead of loading ball. Because by using cylindrical load, the loading is performed more uniform and it leads more veritable results for the elastic modulus.

These test methods are usually used to obtain the mechanical properties such as maximum bending strength, (σ_{max}), deflection, (y) and also to determine the variations of the deflection with increasing load (see Fig.3.11 and Fig.3.12).

In the ball on the ring and the three point bending test methods, σ_{max} values decreases with increasing thickness according to the group (see Table 3.6). This relationship is expected according to the inverse proportion in Eq.[3.1] and Eq.[3.7]. Literary arguments also support this relationship [26].

The hardness values given in Table 4.2 are obtained from Vickers Indentation, Knoop indentation and the ultra microhardness test. The results of the ultra microhardness and Knoop indentation tests are obtained for all four groups of specimens. From the experiments of the 4th group of the specimens that are colored in Vickers indentation test; the diagonal indentation marks and the cracks could not be observed as mentioned in Chapter 3.3.3.

Knoop indentations are much shallower than Vickers indentations produced with the same load. This estimation matches the theoretical prediction [33].

Table 4.2 shows that the results of the Knoop indentation and the Vickers indentation tests are satisfying the approximate hardness values ($H=550 \text{ kg/mm}^2$) for the glass material that are given in the literature [31, 34, 41].

In Knoop indentation test the lowest hardness (H , kg/mm^2) values are determined while the highest hardness values are obtained from ultra microhardness test. (see Table 4.2) The reason for that result can be defined as the indentation load range of the ultra microhardness test, which is 10^6 times lower than the other test methods (see Fig.3.56).

Table 4.2 Average hardness values for the three group of specimens.

	AVERAGE HARDNESS VALUES		
	Knoop indentation	Vickers indentation	Ultra microhardness
1 st Group	309,486 kg/mm^2	609,15 kg/mm^2	826,217 kg/mm^2
2 nd Group	438,668 kg/mm^2	564,257 kg/mm^2	807,617 kg/mm^2
3 rd Group	464,410 kg/mm^2	565,64 kg/mm^2	801,133 kg/mm^2
4 th Group	404,215 kg/mm^2	—	791,517 kg/mm^2

In ultra microhardness test, HV_1 and HV_2 values (which are calculated from plastic energy, W_p , see Chapter 3.2.5) are found independent from plastic indentation depth, h_p . This result can be understood also from Fig.3.46, Fig.3.49, Fig.3.52 and Fig.3.55 and it satisfies the literary investigations [40].

Fracture toughness (K_{IC}) is determined from the Vickers indentation test method in this study. The test results of this study which satisfy the literary investigations [24, 31, 45]; predict that $P/c_0^{3/2}$ ratio in Eq. [3.13] for Vickers cracks is constant over the range of investigated indentation loads (4,9N, 6,86N and 9,8N).

In other words, the indentation parameter $P/c_0^{3/2}$ is effectively invariant with respect to indentation load for the glass specimens.

Knowing that $P/c_0^{3/2}$ ratio is constant in these test results; proves that K_c calculations that are done in this study for the glass specimens are veritable. This argument also satisfies the literary investigations [29].

Both K_c values of Vickers indentation test (the one that is obtained according to the H/E ratio in Knoop indentation and the other one that is obtained according to the elastic modulus (E) values in ultra microhardness test) are shown in Fig. 4.1 below.

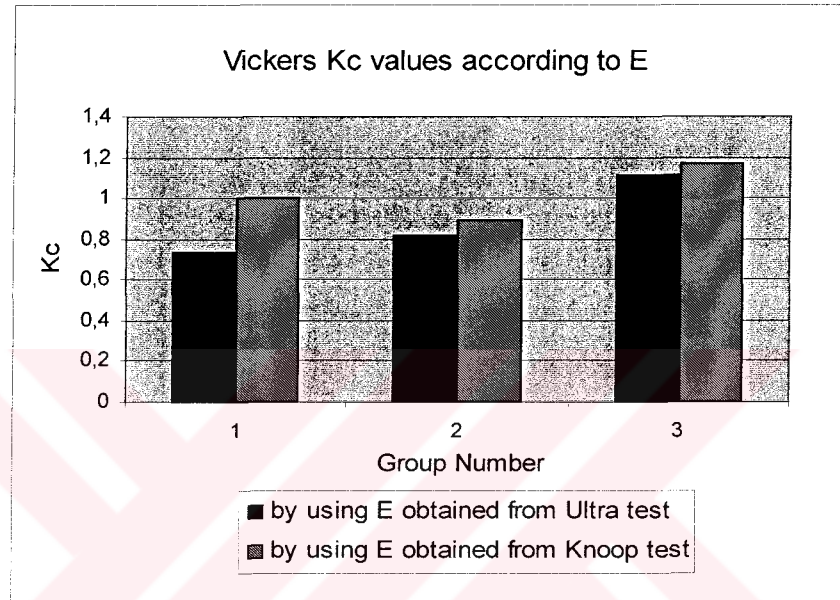


Fig. 4.1 K_c values according to elastic modulus that is used.

K_c results of the Vickers indentation test are found approximately similar and they are satisfying the K_c values ($K_c = 0,7-0,8 \text{ MN/m}^{3/2}$) for the soda-lime glass that are given in the literature [31, 43, 46] (see also Table 3.8, Table 3.10 and Table 3.12).

5. CONCLUSION

In order to determine the mechanical properties of soda-lime glasses; four groups of glass specimens which have different thicknesses (1st group $t= 0,214$ cm, 2nd group $t= 0,386$ cm, 3rd group $t= 0,794$ cm, 4th group $t=0,643$ cm) are tested by various methods. The general results of this study can be listed as below.

- To obtain elastic modulus for the glass specimens, Knoop indentation and Ultra microhardness tests are found the most suitable ones.
- Hardness values are determined veritably from Vickers indentation and Knoop indentation test results for the glass specimens.
- Hardness values (HV_1 and HV_2) that are calculated from plastic energy (W_p); are found independent from plastic indentation depth (h_p).
- Maximum fracture stress, σ_{max} , values that are calculated from the ball on the ring and three point bending of the beam test method have shown thickness depended variation.
- For the Vickers cracks, $P/c^{3/2}$ ratio found constant over the range of investigated indentation loads. This result also supports that Vickers indentation test is suitable for investigating K_c values for the glass specimens. Both K_c values of Vickers indentation test (the one that is obtained according to the H/E ratio in Knoop indentation and the other one that is obtained according to the elastic modulus (E) values in ultra microhardness test) are found approximately similar and they match the predicted values for the literature [31, 43, 46]. This result shows K_c calculation for the glass specimens in Vickers indentation by using the both ways; is veritable.

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CIRRICULUM VITAE

Elsen Ayşe Erorta was born in Eskişehir in 1978. After graduating from Eskişehir Anatolian High School in 1995, she started her studies at Metallurgical and Material Engineering Department in Istanbul Technical University. She graduated from Metallurgical and Material Engineering Department in 1999. In September 1999, she started her M.Sc. in the same the department where she is still continuing her studies.

