

Durability of structural adhesives in bridges



Master Project

DURABILITY OF STRUCTURAL ADHESIVES IN BRIDGES

Submitted by: Omar Moussa

Table of contents

| | |
|---|----|
| 1. Introduction..... | 3 |
| 2. Material of study..... | 5 |
| 2.1 Definitions..... | 5 |
| 2.2 Physical characterization..... | 5 |
| 2.2.1 Thermosetting resins..... | 5 |
| 2.2.2 Curing kinetics..... | 6 |
| 2.2.3 n th order and autocatalytic resins..... | 7 |
| 2.2.4 Glass transition temperature..... | 8 |
| 2.3 Mechanical characterization..... | 8 |
| 3. Literature review..... | 9 |
| 3.1 Bearings & expansion joints for bridges..... | 9 |
| 3.1 Skid resisting surfaces..... | 10 |
| 3.1 Wires and strands anchors..... | 11 |
| 3.1 Composite concrete-steel construction..... | 11 |
| 3.1 Segmental concrete construction..... | 13 |
| 3.6 Epoxy coated rebars..... | 15 |
| 4. Experimental Investigation..... | 17 |
| 4.1 Physical testing..... | 17 |
| 4.1.1 Dynamic tests..... | 20 |
| 4.1.1.1 Experimental procedure..... | 21 |
| 4.1.1.2 Tests results..... | 21 |
| 4.1.2 Isothermal tests..... | 24 |
| 4.1.2.1 Experimental procedure..... | 24 |
| 4.1.2.2 Tests and results..... | 24 |
| 4.1.2.3 Modelling..... | 34 |
| 4.1.3 Tg analysis..... | 40 |
| 4.1.3.1 Experimental procedure..... | 41 |
| 4.1.3.2 Tests results..... | 42 |
| 4.2 Mechanical Testing..... | 47 |
| 4.2.1 Tension tests..... | 48 |
| 4.2.1.1 Test specimens..... | 48 |
| 4.2.1.2 Machinery..... | 49 |
| 4.2.1.3 Experimental procedure..... | 50 |
| 4.2.1.4 Test Results..... | 50 |
| 4.2.2 Compression tests..... | 60 |
| 4.2.2.1 Test specimens..... | 60 |
| 4.2.2.2 Experimental procedure..... | 61 |
| 4.2.2.3 Test Results..... | 62 |
| 5. Application of adhesives in bridges..... | 65 |
| 5.1 Advantages of adhesives..... | 65 |
| 5.1.1 High strength material..... | 65 |
| 5.1.2 Workable material..... | 66 |
| 5.1.3 Easy maintenance..... | 66 |
| 5.2 Selection of adhesive..... | 66 |
| 5.3 Exposure conditions on a bridge..... | 67 |
| 5.4 Joints in bridges..... | 68 |
| 5.4.1 Girder-deck joint..... | 69 |
| 5.4.2 Parapet joint..... | 70 |
| 5.4.3 Guard rail joint..... | 71 |
| 5.4.4 Deck joints..... | 71 |
| 5.4.5 Expansion joint fixation..... | 72 |
| 5.4.6 Bearing joint..... | 72 |
| 6. Conclusion..... | 74 |
| References..... | 76 |

1. Introduction

Besides the 50s revolution of the use of adhesives in the new construction in the works of strengthening and repair of different structural elements, adhesives were extensively used in bridges for a long time. Different applications on bridges were carried out in the last few decades. The most common application of adhesives in bridge engineering was in the form of resin mortar for either bridge bearings or expansion joint nosings [1]. Recently more applications of structural, semi-structural and non structural joints could be executed using adhesives in bridges. In reason of its ease of execution and maintenance as well as its long-term durability, resins represent highly challenging materials in last few decades for the means of formulating bridge connections. Although adhesives are recently used on wide ranges in joints in bridge engineering, their complicated behaviour, particularly under low temperatures, could disallow an easier use of such materials in structures, notably in bridges.

As the following project targets to provide a better understanding of thermo-mechanical behaviour of resins, two different categories of testing were carried out, in order to investigate the most important and basic characteristics of resins as well as direct relations connecting different properties. The first series of tests was focusing on the physical characterization of resins aiming to investigate the influence of the degree of cure (conversion degree) on different characteristics as well as the behaviour of the material, From previous experiences on the behaviour of resins, it was expected that the more cured the material, the better properties it could present, however this investigation was held in LTC lab using a DSC machine. Different categories of tests were carried out during the physical characterization in order to establish a reliable relation between conversion degree/conversion rate and time. Another effective resin property that was considered during the physical characterization of resins is the glass transition temperature (T_g); T_g which represents the temperature at which the material loses part of its strength and/or stiffness, can also involve another concern which is the degradation of adhesives when exposed to high temperatures. The second series of testing involved in this project is mechanical

testing, which was held in Lab of structures. This series was aiming to investigate the mechanical properties of the resin, basically compressive, tensile and shear strengths of these materials. Finally this project was focusing on relating the physical properties including mainly the degree of cure as well as the glass transition temperature to the mechanical properties and their influence on the mechanical behaviour of adhesives.

2. Material of study:

2.1 Definitions:

Structural adhesives include anaerobics, epoxies, reactive acrylics, polyurethanes and special formulations of cyanoacrylates they are used to bond metals, glass, ceramics, concrete, plastics and composites [6]. As structural adhesives, epoxies are the most widely accepted and used; therefore primarily structural bonding with epoxy will be discussed in this project.

Epoxies typically contain several constituents, the most important being the resin. In a broad sense, the term epoxy refers to a chemical group consisting of an oxygen atom bonded with two carbon atoms already united in some way. Epoxy resins are a group of polymers with extremely different chemical, thermal and mechanical properties. The resins are obtained through refining of petroleum. The mixing of epoxy resin with a hardener results in an epoxy adhesive. The properties of epoxy plastics are highly dependant on the hardener used.

In this report EPOXY SIKADUR 30 is used for testing. This material consists of two components as aforementioned, the resin which is the basic material and the catalyst which is the material responsible for the hardening of this resin. EPOXY SIKADUR 30 is formulated with 3:1 resin to catalyst mixture. Another one distinguishable feature of this epoxy from other traditional epoxies is the presence of fillers which influence the behaviour of the material during physical characterization process.

2.2 Physical characterization

2.2.1 Thermosetting resins

Epoxy is considered as a thermosetting resin. Thermosetting resins are those which exist in an un-reacted or partially reacted state and which will undergo cross-linking (see *fig. 2.1*) after mixing the base components or heating to elevated temperatures. The properties of thermosetting materials are much dependant upon their chemical formulation or composition along with conditions, such as temperature and time, to which the resin is exposed during processing. Small changes in the formulation or processing conditions,

which can affect the curing of the resins, can significantly affect the properties of the end product [2-4].

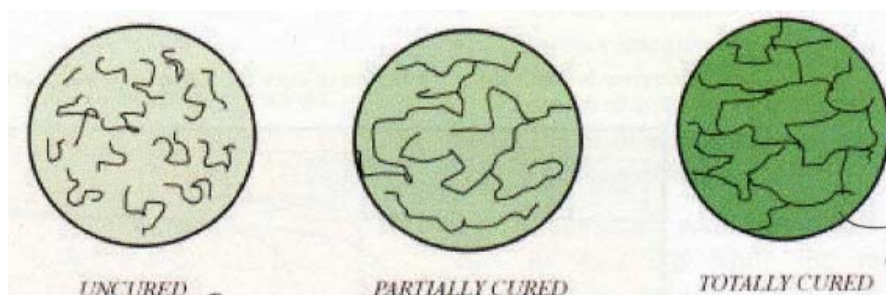


Fig.2.1 Representation of increase in cross link density of a thermosetting material^[4]

2.2.2 Curing kinetics

One important aspect of thermosetting resins, such as an epoxy, is the cure kinetics associated with the material. Kinetics refers to the modelling of the effect of temperature and time on the degree of cure of a thermosetting resin. The establishment of cure kinetics provides the engineer with valuable information that can be used to optimize processing conditions or to predict the shelf lifetime of resins. One of the easiest means of determining the cure kinetics of resin is the Differential Scanning Calorimetry (DSC) to be discussed later in chapter 4. Different approaches can be used to determine the cure kinetics of resins using DSC. The most reliable approach is the isothermal one as it provides the highest degree of accuracy of the cure kinetics of thermosetting material, such as epoxy. This is because the maintenance of isothermal conditions eliminates potential problems such as occurrence of thermal gradients [2-4].

Thermosetting resin undergoes an irreversible chemical reaction during curing. As the components in the resin system cure, heat is evolved by the resin, which is monitored by the DSC machine in use. *Fig 2.2* represent the change taking place by heating an uncured epoxy resin. The plot shows the heat flow as a function of the sample temperature. With further increase in the sample temperature, the resin eventually undergoes curing and this is observed as the large exothermic peak.

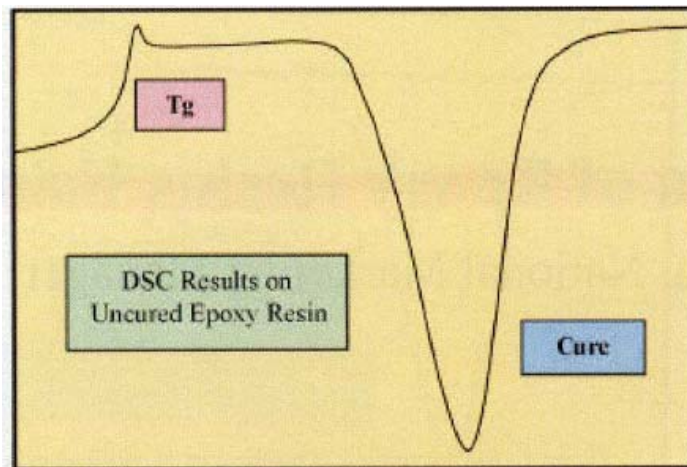


Fig.2.2 DSC results on an uncured epoxy resin^[4]

The onset of cure is the temperature at which the heat flow deviates from a linear response and the exothermic peak temperature reflects the maximum rate of curing of the resin. At the completion of curing or cross-linking, the DSC heat flow returns to a quasi-linear response. The area under the exothermic peak can be integrated to give the heat of cure.

2.2.3 *nth* order and autocatalytic resins

Many epoxy resins follow *n*th order kinetics. These resins need an external source to activate the curing reaction such as temperature. *N*th exhibits its maximum rate of cure right at the start of the experiment (time=0) as shown in *fig 2.3*. Autocatalytic resins, which work on the activation of the reaction itself, will be having its maximum heat evolution at 30% to 40% of the reaction as shown in *fig 2.4*. Logically autocatalytic resins take more time to reach the desired curing degree due to the lack of an activation source of the reaction [2,5].

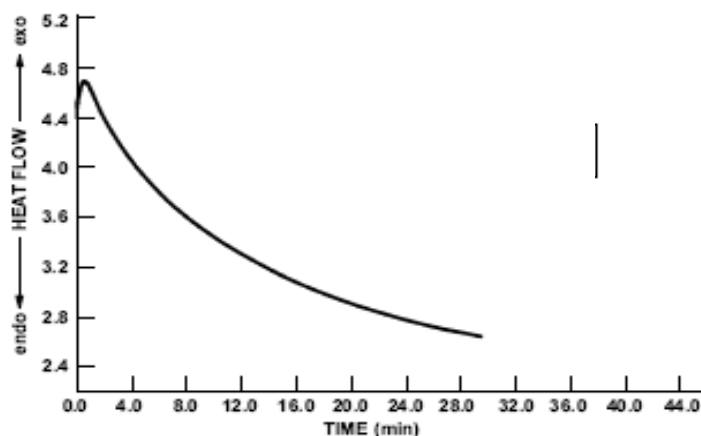


Fig.2.3 Behaviour of n^{th} order resin^[5]

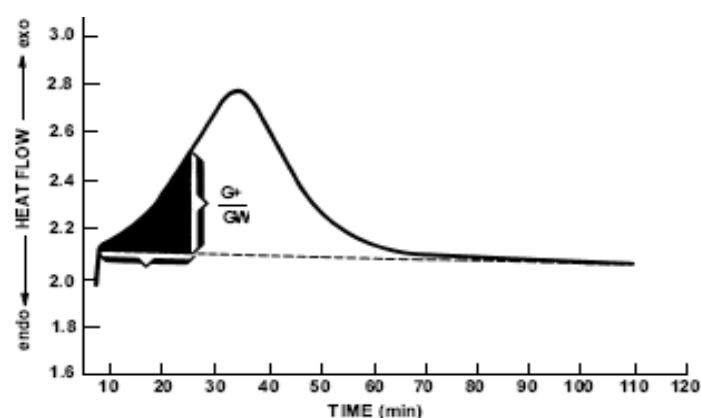


Fig.2.4 Behaviour of autocatalytic resins^[5]

2.2.4 Glass transition temperature

Glass transition temperature (T_g) represents the region in which the resin transforms from a hard, glassy solid to a viscous liquid. Glass transition temperature can be deduced as the intermediate point between the two inflection points preceding the curing process as shown in *fig 2.2*. After the material reaches the glass transition temperature, it starts losing part of its strength and stiffness. For such reason, a material with high T_g is expected to be used in bridge applications where material can be, in some joints, subjected to a high range of temperature variations.

2.3 Mechanical characterization

The determination of mechanical properties of adhesives is very important in order to get a better understanding for the strength and stiffness of the material. In the application of bridges, which represents the main topic of this project, a sufficient stiffness and strength

should be provided by the adhesive in order to sustain the loads to which it is subjected. Both compressive and tensile strengths are considered as basic properties that are indispensable for joints applications in bridges. This project focuses mainly on investigating these two material strengths.

3. Literature Review

In literature, it is found that different applications were carried out on the use of resins in bridges. In this chapter different uses of resins in structures and particularly in bridges will be discussed.

3.1 Bearings and expansion joints for bridges:

Bearings and expansion joints are the most commonly used applications of resin in bridges; they are widely used in Germany and the UK [1,21]. In bridge bearings, a resin mortar is used as a bedding compound on which to seat rubber or steel bearing pads. These pads used to transfer loads from superstructure to the piers and abutments and the stress they resist is largely compressive in nature.

Expansion joints in concrete bridges were traditionally formed by the use of steel edging angles anchored or bolted into the concrete deck either side of the expansion gap. Such joints have a limited life due to disintegration of the supporting concrete under the action of traffic impact and they are very difficult to repair or replace, therefore resin mortar nosings were installed as shown in *fig 2.1*. In the past, early nosings were based on relatively slow curing epoxy systems so heating and testing in cold weather was indispensable. Another problem is transverse cracking that appears in some nosings and it is found that the reason was the use of fast curing resins as it causes warping and curling in the expansion joint nosing as shown in *fig 2.2*. This occurs due to the differential contraction following the exothermic reaction, the bottom of the nosing being restrained by adhesion to the concrete deck. On cooling the nosing curls and lifts at the transverse joints or shrinkage cracks, and maybe accompanied by cracks extending down into the concrete deck [1]. So the final solution is to have a careful formulation of the resin. This includes the use of slower cure rate, the use of larger size aggregate to allow heat to dissipate or by flexibilising the epoxy to permit some stress relief during cure. Polyurethane resin mortars have also been used successfully for a limited number of applications. They are cheaper than epoxies and can cure at lower temperatures but have a tendency to swell due to water absorption and can tend to “foam” on the long-term.

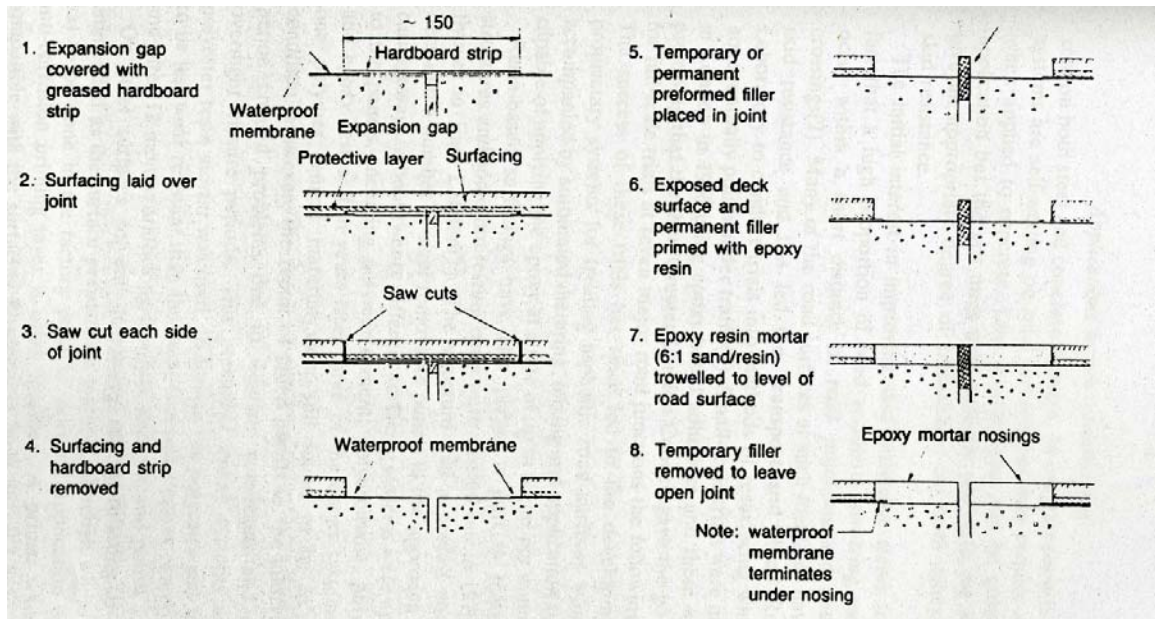


Fig.3.1 Installation of epoxy nosing^[1,2]

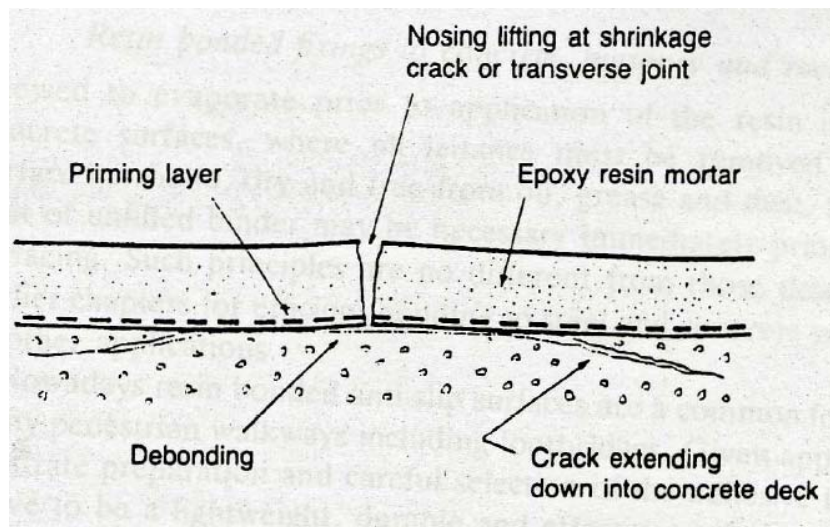


Fig.3.2 Curling of expansion joint nosing^[1,2]

3.2 Skid resistant surfacings:

One of major applications of adhesives involved the use of resins for abrasion resistant and non-slip surfaces to heavy duty floors and roads as well as in bridges. This was achieved using synthetic anti-skid grit [1]. The initial interest in improving skid resistance stems from the fact that a high proportion of road accidents involving

casualties occur within a distance of road junctions and pedestrian crossings, many of the road surfaces at such locations have poor skid resistance. Resin based surfacings at road junctions was a good solution. Recently resin bonded anti-slip surfaces are a common feature of many pedestrian walkways including footbridges. Given appropriate substrate preparation and careful selection of the adhesive they can prove to be a lightweight, durable and effective surfacing method.

3.3 Wire and strand anchors:

Steel wire and strands formed into cables are mainly used in the prestressing of concrete and in suspended or cable stayed structures, in both cases we splay the wires or strands at the end anchorages in order to spread the load being transferred to the support material. In cable-supported bridges the strand ends is splayed in a conical socket which is then filled with molten metal. When cable is tensioned the conically formed deflector is pulled into the socket and load is transferred in compression by wedge action. Sometimes the molten metal is replaced by a low viscosity 2-part resin, usually polyester for its speed of cure. Also an interfacial bond is necessary otherwise the strands would pull out before the wedging action could develop, usually the frictional force between the strands and the anchorage is sufficient to retain the cable end in the socket.

Pourable epoxy resin has also been used to bed deflector plates and anchorage plates in certain special applications in prestressed concrete. For instance in one box shaped arched bridge, some cracking was discovered in some parts of the concrete, a system of prestressing was found as a solution but it required anchorages capable of providing adequate strength to spread the load within the corners of the bottom of the box, hence the use of deflectors and anchor plates bedded in epoxy resin.

3.4 Composite steel-concrete construction:

One important application of epoxy resin adhesives in bridge construction is their use them to form the necessary shear connection between steel girders and the concrete deck slab in composite bridges, in place of conventional welded mechanical fasteners.

Three different ways are presented in which this shear connection can be achieved [1]:

- A) Post-bonding: adhesives might be used to bond precast concrete slab units directly to the steel surface. It has been successfully employed in Germany. On the same bridge, epoxy resins can be used in variety of forms and locations on the superstructure (*see fig. 2.3*). This included rubber bearings bedded in epoxy mortar and an epoxy adhesive coating between the main steel girders and the bearings [1,21]. Of most interest structurally, however, is the use of epoxy resin adhesive mortar between the precast concrete deck-panels and the main girders. The intention was to create a monolithic structure having the same degree of strength and composite action as might be expected with conventional joining methods. Another application is the use of the epoxy in the form of an epoxy adhesive surfacing on the precast concrete deck panels.

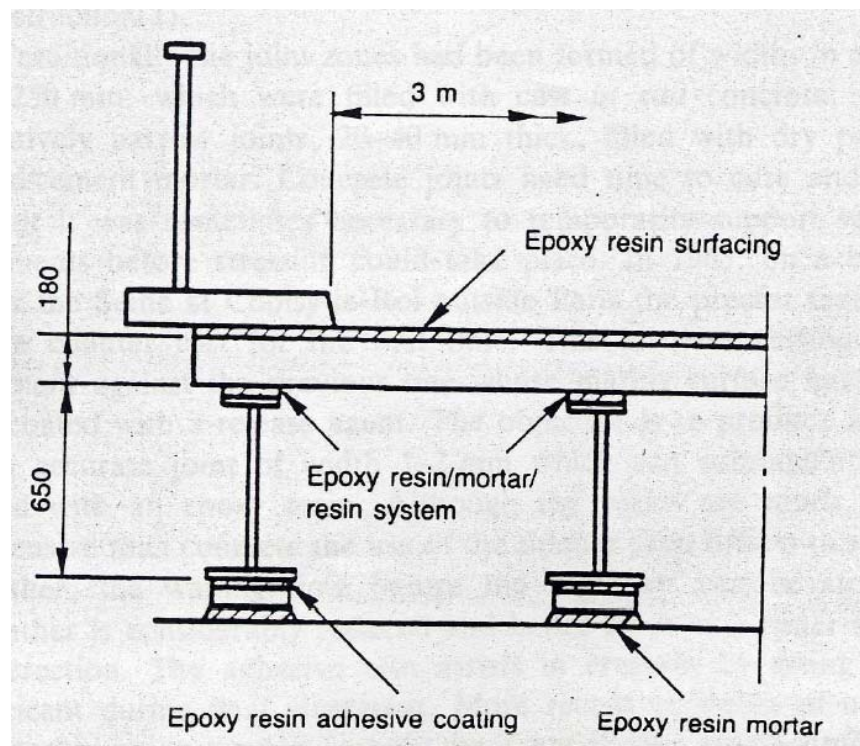


Fig. 3.3 German bonded bridge^[1]

- B) Grip layer: A layer of coarse aggregate may be bonded to the steel to form a rough layer onto which fresh concrete is subsequently poured (in slab panels for example).

Premature adhesive failures in this application so another bonding technique should be considered.

- C) Pre-bonding: Fresh concrete is poured directly onto a layer of uncured adhesive spread over the prepared steel surface. It has been used in the reinforcement of slab units by externally bonded plates (open sandwich slabs).

3.5 Segmental concrete construction:

Use of epoxy in the joints between units in segmental precast, prestressed bridge construction (*see fig 2.4*) is increased recently; long span bridges can be constructed by stressing precast concrete segments together to form a monolithic structure. The advantage of segmental structures is the speed of erection [1]. The zones between segments at which the joints exist are to be filled with epoxy instead of concrete as concrete joints need much time to cure so sometimes we need to support the segments before stressing could take place. Another advantage for the use of resin is the thin joint width (1-2 mm) compared to that of concrete (250 mm) or dry packed cement/sand mortar (20-40 mm) [1]. Also the adhesive assists in the erection as it acts as a lubricant (facilitate proper positioning) during final alignment which facilitates the erection process. In this case usually the adhesive is not designed as a structural element (supporting element) it's just designed as a gap filler to transmit compressive stresses which also serves to more evenly distribute these stresses. So it is not used to resist the vertical shear which develops between adjacent units since shear keys (horizontal reinforcement bars joining segments for shear resistance) are formed for this purpose.

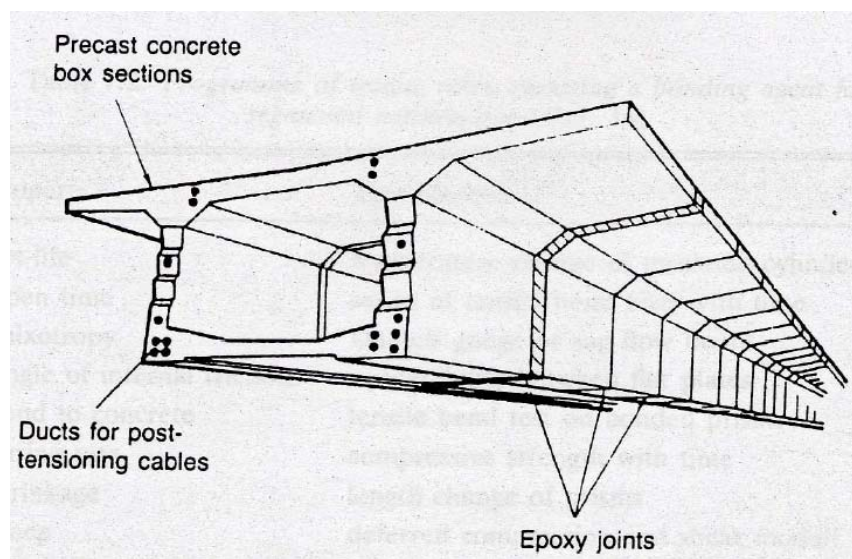


Fig 3.4 Segmental bridge construction^[1]

Site testing on adhesives was carried out on different bridges in order to check the long term durability with a temperature range at the time of the application (4°C- 38°C). Control of correct mixing and materials was achieved measuring hardness of small specimens after curing for 20 minutes in a small oven. Subsequently slant shear and compressive strength tests were performed.

Construction of M180 bridge near Scunthorpe is one good example, aliphatic amine cured epoxy was used during severe UK winter conditions. A series of flexural strength, deflection and creep were carried out on cubes bonded together forming a beam aiming to examine the curing behaviour and characteristics of adhesive in cold weather. A minimum compressive strength of 0.3 N/mm² is recommended during the curing period, according the tested joints results in *fig. 2.5* show that the lowest proposed reliable limit for full curing must be at least 3 days at temperature in excess of 5°C, below this temperature site heating must be employed [1].

Creep of epoxy resin system under sustained load has been always of some concern. However, with a thin glue line and at relatively low stress levels developed in segmental construction, compressive creep will not pose a problem with most type of resins and particularly epoxies.

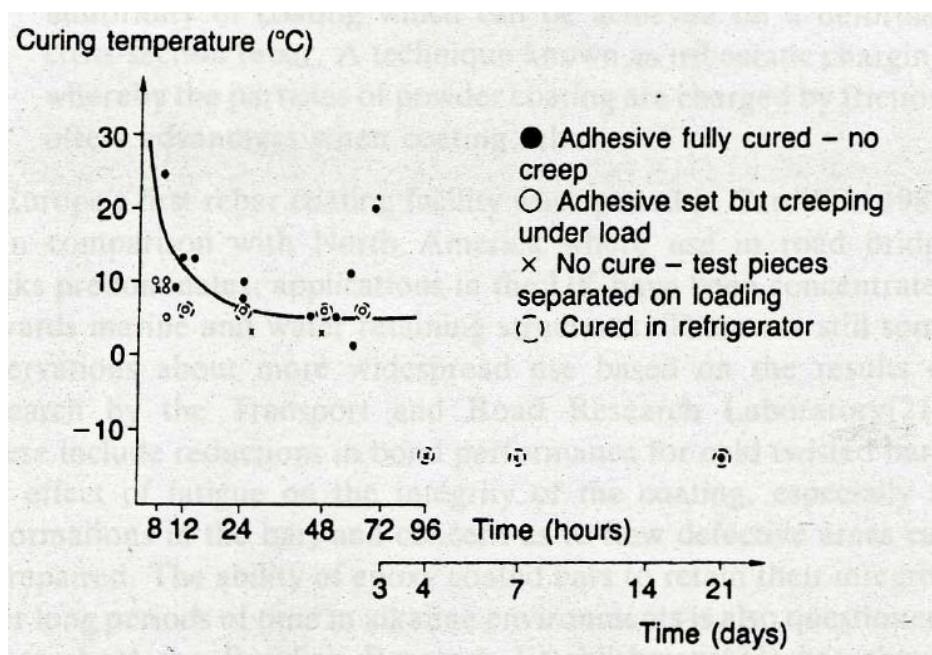


Fig. 3.5 Effect of low temperature on cure rate of an epoxy^[1]

3.6 Epoxy coated rebars:

Epoxy is used in the application of protecting roads, bridges and marine structures from the corrosion of steel reinforcement due to chloride ions attack, due to de-icing salts or the effect of sea spray. Electrical potential differences occur and currents flow from anode to cathode because of the variations in conditions along the length of reinforcement bar. Material dissolved at the anodes resulting in either general or local corrosion of the RFT bar. It starts as red rust which is expansive and finally cracking and spalling of concrete cover takes place. Localized corrosion is much more dangerous and causes more loss of the steel bar cross section. Finally researches in the USA in early 1970s were led to the use of organic coatings, particularly epoxy, could be used to protect steel RFT bars in the concrete of bridge decks and buildings from rapid corrosion. In the UK different techniques have been used in order to increase the steel reinforcement bars resistance against corrosion. These include galvanized reinforcement and the use of stainless steel. Epoxy coated bars was a later solution to be introduced with different coating thicknesses. In Europe special requirements were set in order to get this coating thickness accepted, a uniform thickness of the range of 150-250 microns [1].

It become clear now that adhesives can be a very profitable material in the applications of bridges, providing that an extreme care should be given to make the right choice considering different parameters affecting the performance of adhesives in joints such as curing degree and curing rate, mentioning also the mechanical properties which should be sufficient to sustain loads in case of structural and semi-structural joints and give a satisfactory performance in case of non-structural joints.

4. Experimental investigation

After showing several applications for the use of adhesives in bridges, more applications are proposed by this project extending the use of these materials in bridges in order to profit from the advantages of adhesives as much as possible. In order to investigate different properties of adhesives as well as their applicability in structures, notably in bridges, different methods and tests for physical and mechanical characterization of resin's properties were carried out. Practically these series of tests can help as well the engineer to make the right choice concerning the suitable type of resin to use depending on the position of joint, different loads acting on the joint, as well as the weathering and exposure conditions to which the joint is subjected. In the scope of this report physical characterization as well as part of the mechanical properties of EPOXY SIKADUR 30 resin were carried out, finally a relation between both them was produced in order to get the relation between the curing degree and temperature of the resin and their influence on the compressive, tensile, and shear strengths of the material. Other factors such as humidity, as well as different mechanical properties like resistance to peeling and impact should be included in order to be able to make the best choice of the resin and its dimensions, but in this project, the basic resin properties were considered, as extensive work is planned for further research.

4.1 Physical Testing:

Different physical tests are carried out aiming to get a direct relation between conversion degree/conversion rate and time or temperature under which this degree of conversion is measured. Physical characterization is executed in the LTC lab using Dynamic Scanning calorimetry (DSC) machine, in order to specify the needed material characteristics. DSC is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as both the specimen and the reference are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

There are two major types of DSC systems in common use; the first is the power compensation DSC shown in *fig 4.1* in which the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The

temperatures of the sample and that of the reference are made identical by varying the power input to the two furnaces, the energy required to do this is a measure of the enthalpy or heat capacity changes in sample relative to the reference [9].

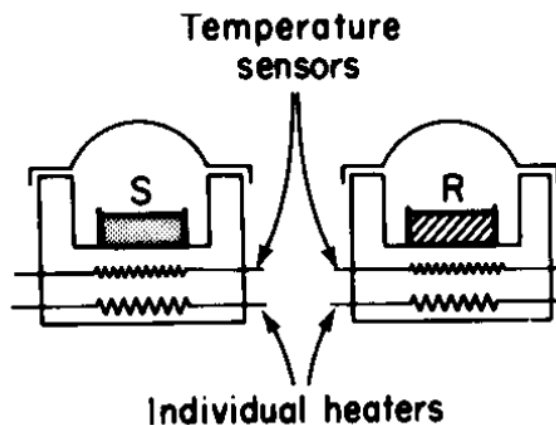


Fig 4.1 Power-compensation DSC.

The second system is the heat-flux DSC (*see fig 4.2*) where the sample and reference are connected by a low-resistance heat-flow path. The assembly is enclosed in a single furnace. Heat capacity changes in the sample cause a difference in its temperature relative to the reference; the resulting heat flow is small compared to that in other methods, such as the DTA (Differential Thermal Analysis) because the sample and reference are in good thermal contact. The heat-flux DSC system is the one employed during the physical properties investigation.

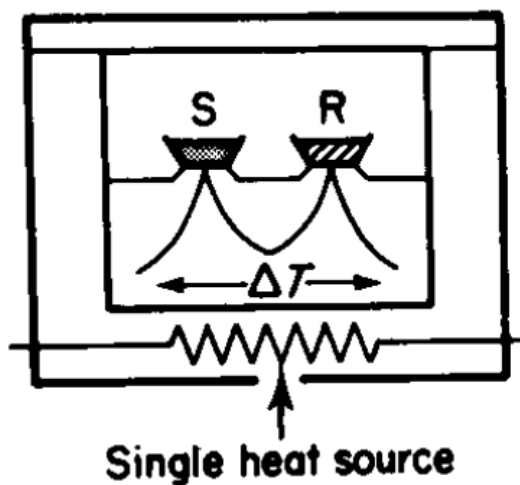


Fig 4.2 Heat-flux DSC.

One distinguishable advantage of the power compensation DSC that doesn't exist in heat-flux DSC is that this system allows a fast "lock in" on the isothermal target temperature due to fast response time of the power-compensation DSC. Therefore no data were lost during the use of this system. On the other hand in case of heat-flux, the initial data could be lost (not recorded) due to a slow response of the system, this is a unfavourable in case of testing a n^{th} order sample, as the highest peak is expected to be in the beginning of the test.

Different types of physical testing were carried out in order to get a better understanding on the curing behaviour of the material and its influence on its mechanical properties in the process of study particularly the stiffness and the strength.

The DSC machine used during physical characterization process of adhesives (*see fig. 4.3*) is of heat flux type as aforementioned where both the specimen and reference are placed in the same chamber, the DSC machine is connected to a bottle of liquid nitrogen through a cooling system that works on controlling the environmental condition inside the machine's chamber to reach lower temperature ranges. Reaching very low temperature ranges is critical for DSC scans, where usually a range between -50°C to 400°C is needed to investigate the total/residual heat released from the specimen. The software should be adjusted with the liquid nitrogen as the cooling system by loading a LNCS file imposing the liquid nitrogen as the cooling system in use. Also standby temperature of 70°C is adjusted inside the testing chamber in order to avoid any external influence on the specimens, especially that of humidity.

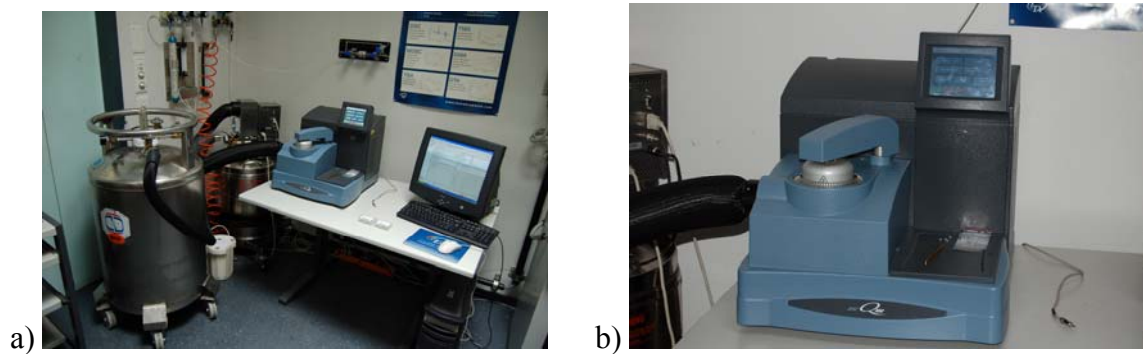


Fig 4.3 a) DSC set machine, b) DSC chamber.

Testing specimens are special capsules in which the material is enclosed, each capsule consists of two parts, a hermetic pan in which the material is placed and a hermetic lid which acts as a cover so that an air sealed specimens can be prepared. An empty capsule is of 57 mg, a material (Epoxy 30 with ratio 3:1) weighs between 10-15 mg is placed in the hermetic pan, and the capsule is closed tightly using a pressure jack that works manually (*see fig 4.4*).

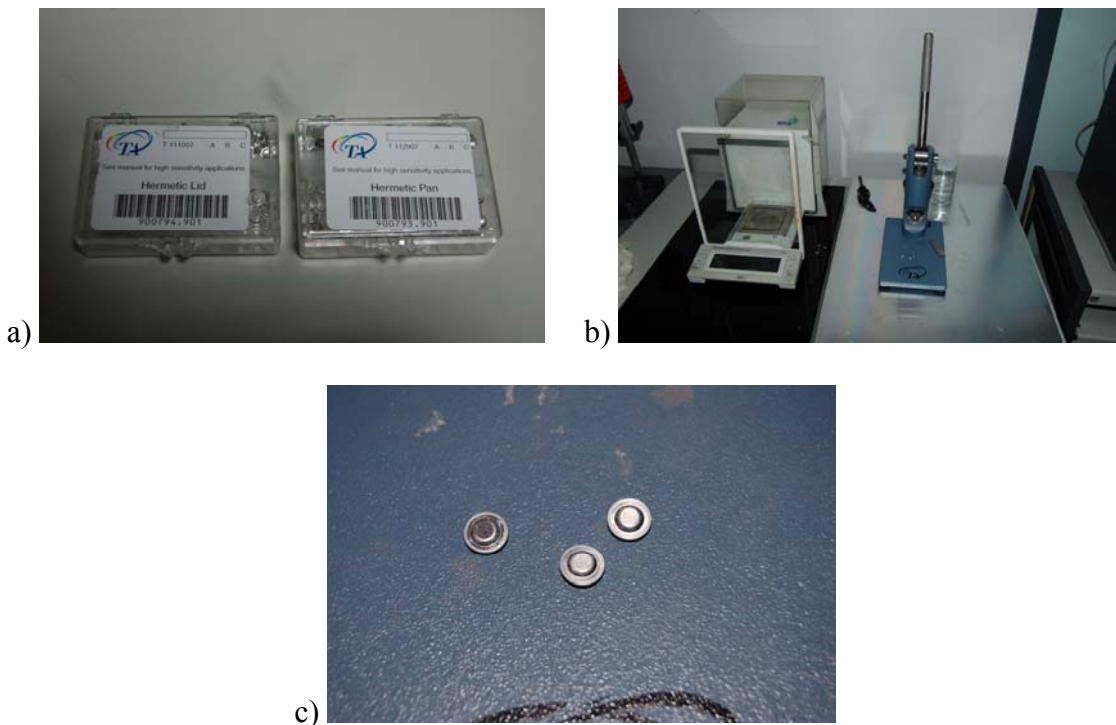


Fig 4.4 a) Used pan Type, b) specimens preparation equipments, c) Prepared specimen

4.1.1 DYNAMIC TESTS

Dynamic scan aims to get the maximum amount of heat released (j/g) from the material. Besides of giving a direct information on the material (maximum released heat flow), the results were used in constructing the conversion degree/rate Vs time relation as well as in the modelling (parameter estimation) in order to construct the same relations under any given temperature.

4.1.1.1 Experimental Procedure:

After preparing the epoxy 30 with a ratio 3:1, 10-15 mg of the material was enclosed in the capsule. The capsule was then placed in the DSC machine's chamber with a reference specimen (an empty capsule) placed beside it, in order to measure the heat transfer between the two capsules as aforementioned above. A temperature control program is set inside the chamber along with a specific rate of increase (between 5°C/min – 20°C/min). For a dynamic scan, the temperature inside is left to equilibrate at -50°C for one minute (to get a uniform temperature inside the chamber) then the temperature starts to increase with the given rate till 300°C.

4.1.1.2 Tests & Results:

- a) Investigating the effect of the period the fabrication till testing: 4 specimens are fabricated on the same day, then one was tested directly after fabrication while the other three were stored in freezer then tested after 1,2 and 5 days from fabrication date. The dynamic scan was carried out with a constant rate of increase of 15°C/min for the four specimens.

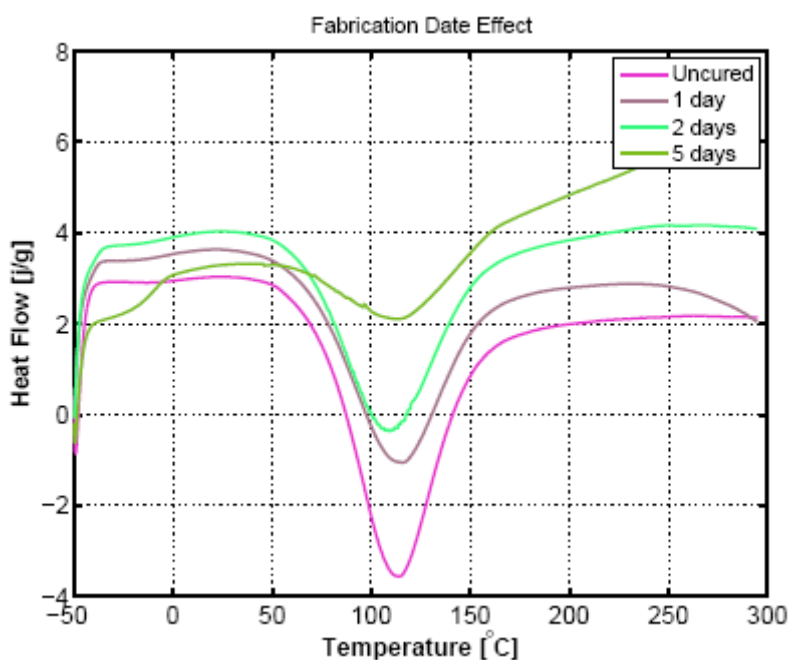


Fig. 4.5 Investigating the time factor effect under the same rate of cure.

It can be shown in fig.4.5 that as the period between the fabrication and the testing of the material is getting longer, the more cured the material becomes even if it is stored in the freezer for a while; still the reaction is taking place. Therefore it's highly recommended to test the specimen directly after the fabrication in order to avoid any initial curing of the material; this conclusion can be also demonstrated by the noticeable up-shift of the exothermic peak, while the points of onset and end of curing rest almost the same. Concluding that the area over the curve is being reduced indicates that a fewer heat was released from the specimen due to initial curing of the material.

- b) Investigating the total heat released by the material, during the interlocking of molecules (curing of material) using different heating rates (ramps). Four different heating rates were investigated during a dynamic scan in order to cite the influence of the rate of heat on the heat flow results.

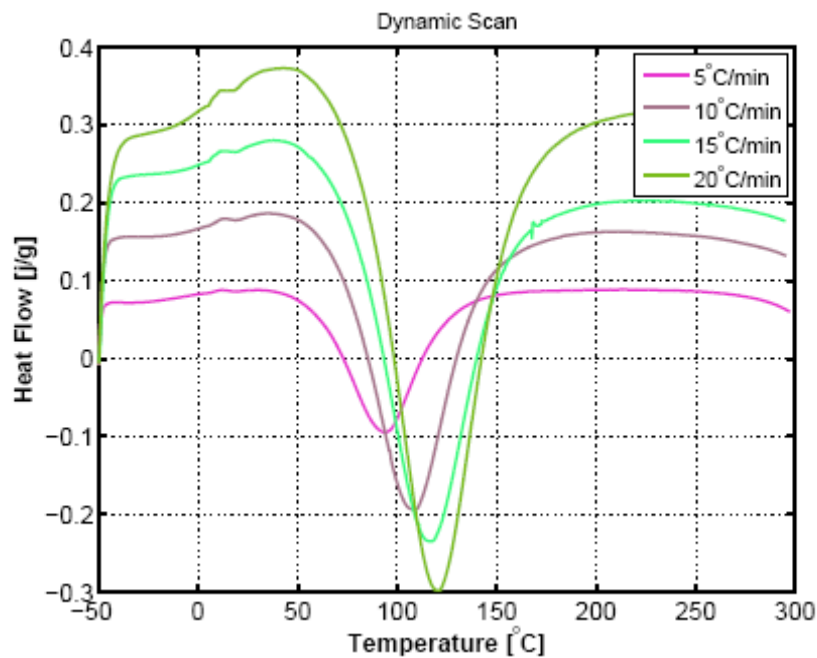


Fig.4.6 Investigating maximum amount of heat released under different heating rates.

Considering the previous recommendation of testing the specimen directly after fabrication, it can be noticed that the total heat released from the material according to the previous tests shown in fig.4.6 is around 108.054 j/g, this total heat was

deduced by the calculation of the area (see fig 4.7) over the exothermic part (peak between onset and end of curing) of the dynamic scan (an average area of 1.8009 over curve); this value is the average of the last three tests excluding the first test (5°C/min) as it gives a lower value (so maybe the material was partially cured before carrying out this test).

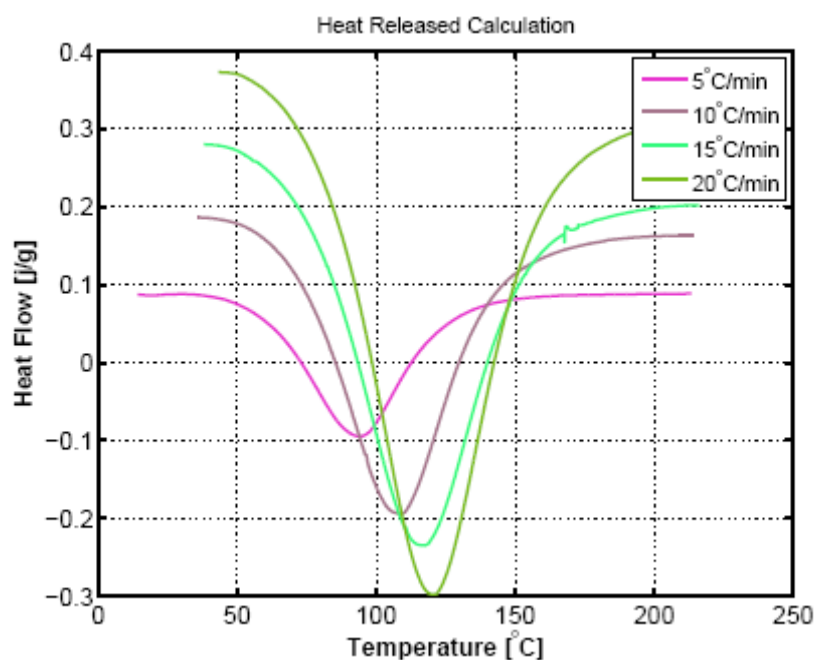


Fig. 4.7 The area over the curve corresponding to the amount of heat released along with the exothermic peak.

| Rate of cure (°C/min) | Area | Total Heat released (j/g) | Exothermic peak (°C) | Tg (°C) |
|-------------------------|---------|---------------------------|----------------------|---------|
| 5 | 1.6223 | 97.338 | 93.92 | 6.49 |
| 10 | 1.8457 | 110.742 | 109.02 | 9.98 |
| 15 | 1.7544 | 105.264 | 116.10 | 6.40 |
| 20 | 1.8026 | 108.156 | 119.57 | 5.93 |
| Average (all) | 1.75625 | 105.375 | 109.652 | 7.20 |
| Average (excl. 5°C/min) | 1.8009 | 108.054 | 114.896 | ----- |

Table 4.1 The values of the area over the curve as well as the corresponding amount of heat released under different curing rates.

From tabulated results in table 4.1, at different heating rates the Tg is usually around 7.2°C in average which is logically considered low due to lack of curing, therefore this can be considered as the starting Tg at the beginning of curing process. Results from table 4.1 could demonstrate that the value of the Tg as well as the total heat

released from the material is independent of the rate of heating applied to the material. This heating rate influences the peak temperature which is increasing as the heat rate is high as well as the shape of the exotherm which is getting broader at base in case of low heating rates indicating that more time was needed in order to release the total heat from the material as the activation energy is considerably low as can be shown in *fig.4.6*.

4.1.2 ISOTHERMAL TESTS

By carrying out a series of isothermal tests under different temperature ranges, a reliable model can be established. Different relations between the conversion degree/conversion rate and time could be easily deduced under any given temperature using the results of the already established model. Besides a direct relation between conversion degree/conversion rate and time can be deduced for the temperature used in the testing, then the compatibility between the curves from the tests and that from the model could help in testing the reliability of the used model.

4.1.2.1 Experimental Procedure:

In an isothermal test a specimen of 10-15 mg is placed inside the chamber along with the reference specimen under isothermal temperature for a given time (specified by the user based on experience) till a plateau is reached indicating the maximum amount of heat released by the specimen under this isothermal temperature. Logically the heat produced from an isothermal temperature test should be less than the amount of heat calculated from a dynamic scan depending of course on this isothermal temperature as well as the curing time.

4.1.2.2 Tests & Results:

Investigating the behaviour of the material at different isothermal temperatures ranges. A series of tests was carried out for different temperatures varying between 35°C and 150°C. The maximum heat released from the material under each temperature can be

deduced by calculating the area behind each curve to get the heat flow released under each temperature.

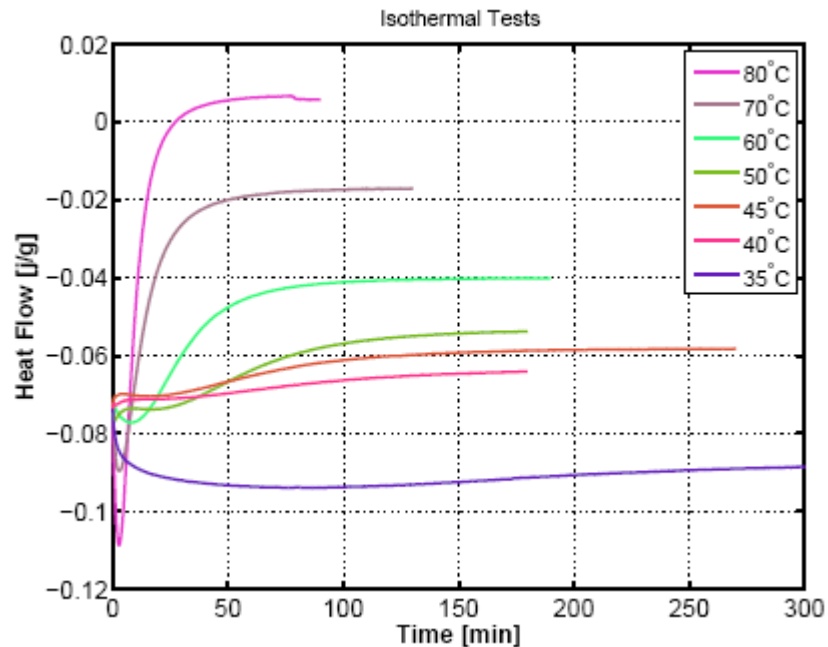


Fig. 4.8 Heat flow during an isothermal test under different isothermal temperatures

Fig 4.8 shows that as the temperature is being decreased, the behaviour of the material changes as the plateau is getting lower which indicates a release of less heat from the material and consequently giving a lower degree of cure. This could be due to the lack of activation at lower temperature. A peak can be always noticed during the isothermal test, this peak can be an indication of the behaviour of the material whether it is autocatalytic or n^{th} order. The peak in the beginning of the test is being shifted, which means that the behaviour of the specimen starts as n^{th} order behaviour then is tending more towards an autocatalytic behaviour again due to the lack of activation from an external heat source, which also takes more time to reach a desirable degree of cure. Two different ranges are proposed in *fig. 4.9* and *fig. 4.10* in order to differentiate between the behaviour of the material under moderate and low isothermal temperatures.

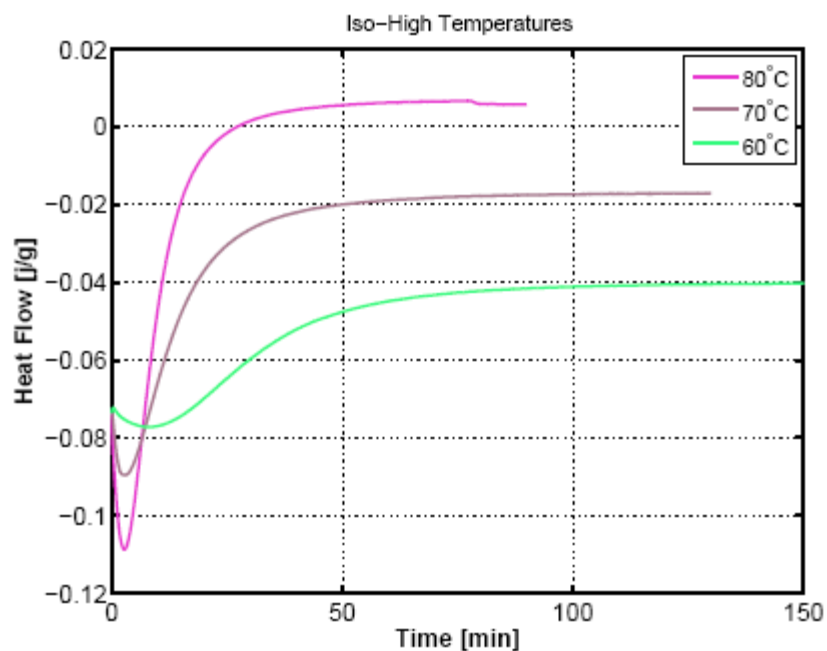


Fig.4.9 Heat flow for the high range of temperatures

Fig 4.9 shows the moderate temperature range between 60°C and 80°C. The behaviour of the material in this range seems to be more nth order; this can be interpreted due to the sufficient activation energy given to the specimen provided by these temperatures. The peak at the beginning of the 80°C test is happened to be at the very beginning of the test and being shifted with the decrease of isothermal temperature indicating the tendency of the material towards a “mixed” behaviour (nth – autocatalytic). Logically the plateau is lowered with the isothermal temperature as the specimen could not release more heat due to lower activation energy.

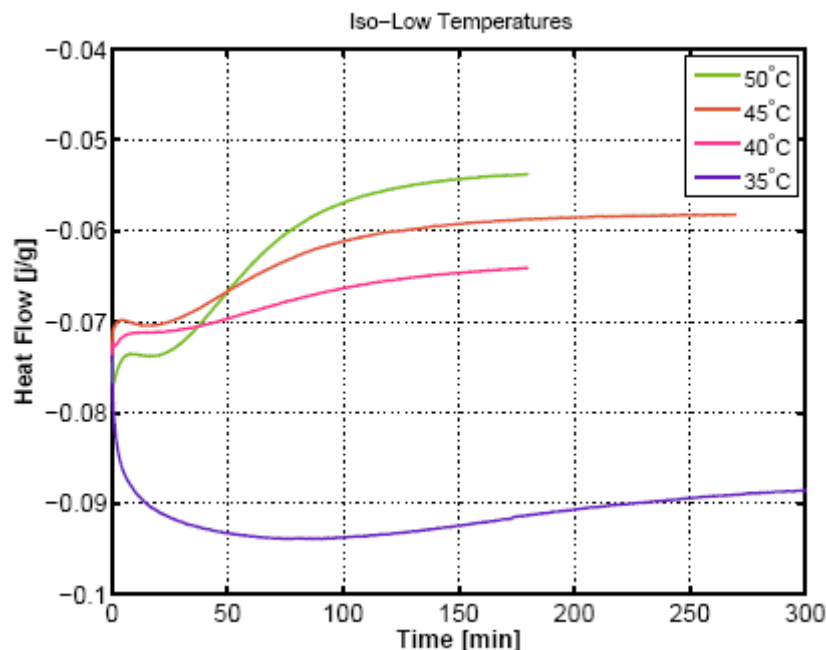


Fig. 4.10 Heat flow for the low range of temperatures

Fig 4.10 shows the behaviour of material under low isothermal temperatures. For lower temperature a behaviour tending to be more autocatalytic can be noticed as well as a lower plateau indicating less heat released. This behaviour can be interpreted due to the lack of activation so the material tries hard to activate the reaction and release more heat in order to get a further curing. The isothermal test for low temperature is found to be time consuming; this can be well noticed for 30°C isothermal temperature and lower, where this test can take more than eight hours and more. Also a complicated behaviour is being noticed in the beginning of the 30°C test which could be due to the lack of activation following a low temperature range. Therefore a complete test (reaching the plateau) for a low temperature till 10°C will be carried out using a different approach, using a temperature control chamber where the temperature can be controlled for different time laps then a dynamic scan can be carried out to get the residual heat, by subtracting the residual heat from the total heat (previously calculated from dynamic scan of uncured specimen), then the degree of cure for a given time can be calculated, by repeating the same procedure for different periods, a curve which is relatively close to the real one can be plotted. During this procedure a dewar filled with liquid nitrogen is used to immerse the specimen in it between the two tests (temperature control in the chamber

and a dynamic scan using the DSC machine) in order to stop the reaction inside the capsule so that the loss of part of the curing can be avoided or at least minimized.

| Temperature (°C) | Area | Heat Released (J/g) | Conv. Degree (%) | Notes |
|------------------|--------|---------------------|------------------|-----------------------|
| 150 | 0.1799 | 10.794 | 9.99 | |
| 120 | 0.3524 | 21.114 | 19.54 | |
| 100 | 1.2078 | 72.468 | 67.066 | |
| 80 | 1.2709 | 76.254 | 70.57 | |
| 70 | 1.2662 | 75.972 | 70.31 | |
| 60 | 1.3678 | 82.068 | 75.95 | Highest curing degree |
| 50 | 1.3566 | 81.396 | 75.33 | |
| 45 | 0.9509 | 57.054 | 52.80 | |
| 40 | 0.5999 | 35.994 | 33.31 | |
| 35 | 1.0930 | 65.58 | 60.69 | |

Table 4.2 Data deduced from isothermal test under different temperatures.

Table 4.2 sums up the final results from different isothermal tests showing the heat flow released during each test, and which can be calculated from the area behind the isothermal curve. Also the final degree of cure after each test is calculated by dividing the maximum heat flow released during each isothermal test by the total heat released from the material previously calculated using DSC scan (108.054 j/g).

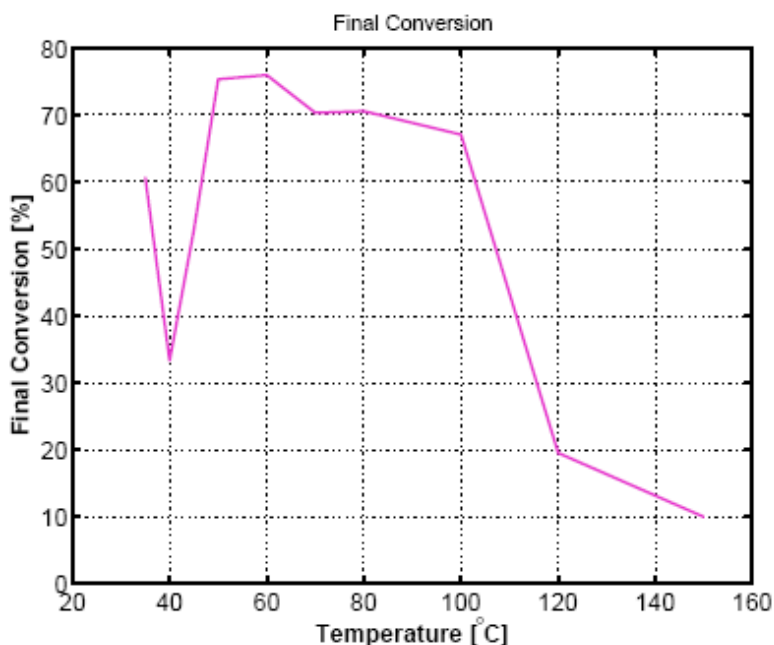


Fig.4.11 The final curing rate curve for different isothermal temperatures

Fig 4.11 shows the final curing degree behaviour under different isothermal curing temperatures ranged from 35°C – 150°C, the highest reachable curing degree is in the range between 50°C – 60°C which is illogic, this could be due to the limitation of heat-flux DSC where part of the initial data can be lost at high temperatures as the test is getting faster than the data acquisition system implented inside the machine.

| 35°C | | 40°C | | 45°C | | 50°C | |
|----------------|-------------|----------------|-------------|----------------|-------------|----------------|-------------|
| Conversion (%) | Time (mins) | Conversion (%) | Time (mins) | Conversion (%) | Time (mins) | Conversion (%) | Time (mins) |
| 5% | 36.9972 | 5% | 11.8138 | 5% | 7.5088 | 5% | 4.1455 |
| 10% | 54.3272 | 10% | 24.5938 | 10% | 14.9805 | 10% | 8.6505 |
| 20% | 84.8705 | 20% | 53.4205 | 20% | 30.1355 | 20% | 17.6922 |
| 30% | 115.584 | 30% | 104.474 | 30% | 48.0305 | 30% | 26.8372 |
| 40% | 150.75 | 33.33% | 175.644 | 40% | 74.2355 | 40% | 36.7772 |
| 50% | 199.859 | | | 50% | 139.286 | 50% | 48.6872 |
| 60% | 331.306 | | | 52.83% | 266.442 | 60% | 65.1672 |
| 60.72% | 395.684 | | | | | 70% | 96.5105 |
| | | | | | | 75.37% | 177.3 |

| 60°C | | 70°C | | 80°C | | 100°C | |
|----------------|-------------|----------------|-------------|----------------|-------------|----------------|-------------|
| Conversion (%) | Time (mins) | Conversion (%) | Time (mins) | Conversion (%) | Time (mins) | Conversion (%) | Time (mins) |
| 5% | 2.6672 | 5% | 1.4155 | 5% | 0.98 | 5% | 0.2505 |
| 10% | 5.1872 | 10% | 2.6722 | 10% | 1.8222 | 10% | 0.5172 |
| 20% | 10.0672 | 20% | 5.2005 | 20% | 3.4155 | 20% | 1.1305 |
| 30% | 15.1172 | 30% | 8.0788 | 30% | 5.1038 | 30% | 1.9138 |
| 40% | 20.7972 | 40% | 11.7605 | 40% | 7.1172 | 40% | 3.0405 |
| 50% | 27.9472 | 50% | 17.2422 | 50% | 9.8755 | 50% | 4.9838 |
| 60% | 38.5972 | 60% | 28.0238 | 60% | 14.6605 | 60% | 9.9972 |
| 70% | 61.7172 | 70% | 92.5788 | 70% | 34.0105 | 67.10% | 39.3305 |
| 76.03% | 162.127 | 70.34% | 125.132 | 70.60% | 44.3372 | | |

| 120°C | | 150°C | |
|----------------|-------------|----------------|-------------|
| Conversion (%) | Time (mins) | Conversion (%) | Time (mins) |
| 5% | 0.5105 | 5% | 0.8305 |
| 10% | 1.3572 | 10% | 6.6672 |
| 19.63% | 19.2572 | 10.18% | 10.0138 |

Table 4.3 Different curing degrees under different isothermal temperatures and the corresponding time per gram

Table 4.3 shows roughly at each isothermal temperature how long it takes (in minutes) to reach a specific curing degree with a step of 10% of cure. This table can be profitable in order to know when exactly during the year the material can be applied and how long it

will be taking to reach a desirable curing degree. This extracted specification will be later related to the mechanical properties of the material.

Three different relations, involving different material properties, could be deduced from these tests. Besides giving direct information on material behaviour under isothermal temperature, it could help confirming the applicability of the model to be constructed later with the tests. These three relations are:

- *Time and Conversion*: Stating the time needed to reach a certain degree of cure, and then the acceptability of this conversion degree can be tested when related to mechanical properties of material.
- *Time and Conversion Rate*: Giving a good idea on the rate (how fast) by which the material cures under each isothermal temperature.
- *Conversion Degree and Conversion Rate*: Complementary relation to the previous two which helps understanding at which curing period the rate is high and vice-versa. For instance indicating if the rate is fast or not till reaching a conversion degree of 50% and how is the performance at higher degrees.

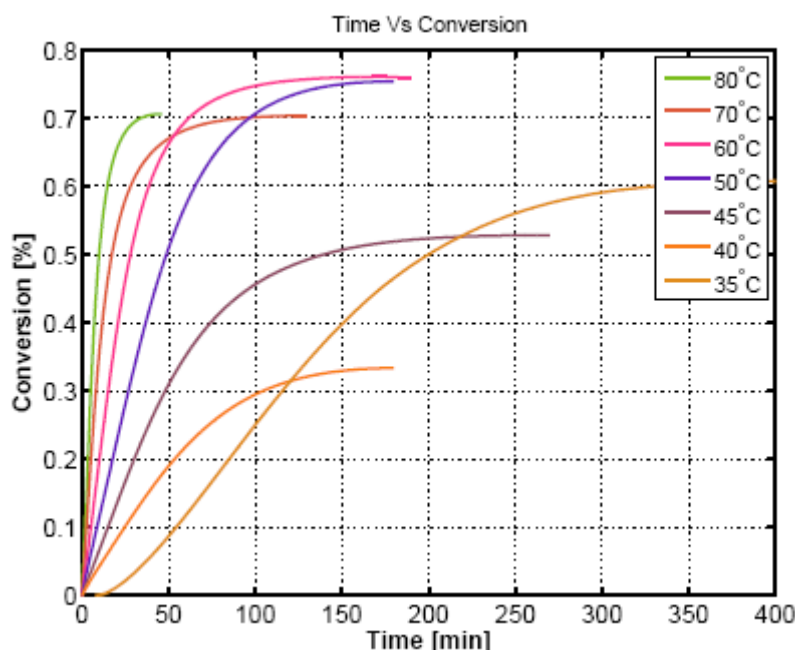


Fig. 4.12 Conversion (Curing degree) Vs time under different isothermal temperatures.

Fig 4.12 shows the relation between the conversion degree and time. Conversion degree can be calculated by dividing the heat flow at certain time by the total heat flow previously calculated from a DSC scan. In this plot it can be noticed that logically for

lower curing degrees, the material takes more time to reach the final curing degree (plateau for test results) as the provided activation energy is getting low along with the isothermal temperature. Therefore a steeper slope is always predictable for higher temperatures. Two illogic behaviours can be noticed, the first is that the final curing degree for 50°C and 60°C is higher than that of 70°C and 80°C. This can be interpreted due to the slow data acquisition during faster tests. The second is the behaviour of the 35°C test. For very low curing temperature, the behaviour of the material becomes very complicated o be interpreted. Therefore further research for low curing temperatures should be carried out.

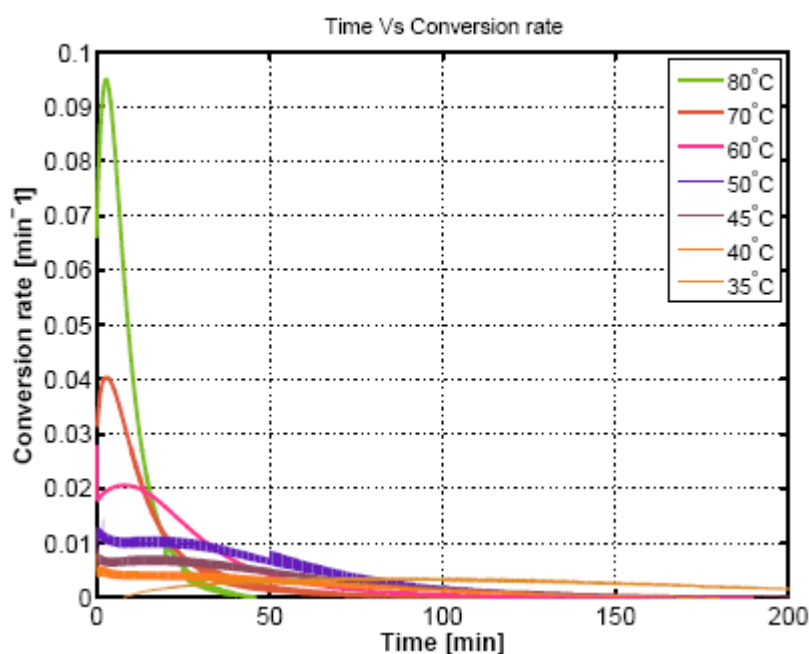


Fig. 4.13 Conversion rate Vs time under different isothermal temperatures.

Fig 4.13 shows the relation between conversion rate and time. Conversion rate is defined as the difference of conversion degree divided by time step. In this plot, the rate of curing for high temperatures was found to be so fast with the highest curing peak being reached at the beginning of the test. Along with lower curing temperatures, the material curing rate seems to be not only decreasing but dropping gradually. Also more time is needed in order to reach the peak of the curing rate. This curve is another indication on the importance of the activation energy which works on accelerating the curing process of the material.

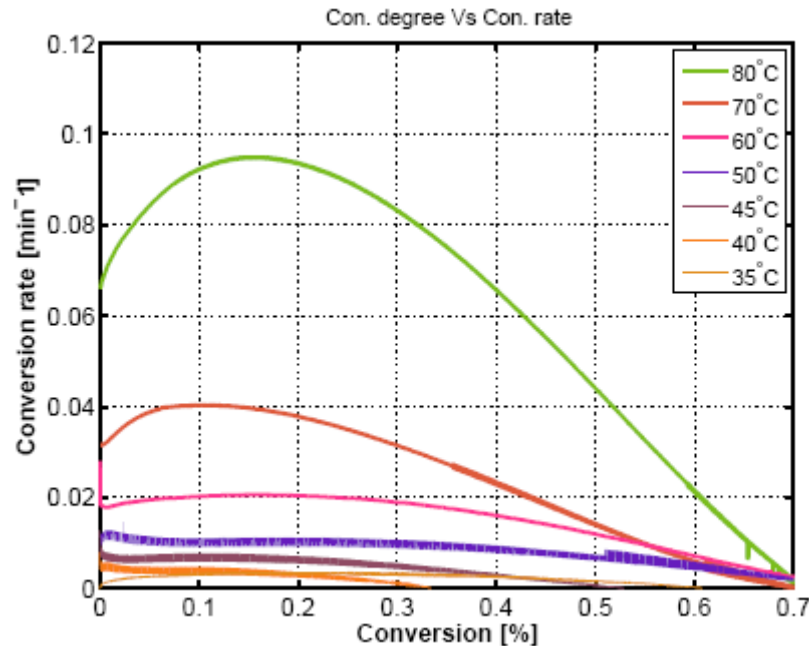


Fig. 4.14 Conversion (Curing degree) Vs conversion rate under different isothermal temperatures.

In fig 4.14 the relation between conversion degree and conversion rate can be shown, this plot indicates that for higher temperatures the rate reached the maximum at a curing degree around 15% then starts decreasing gradually till reaching maximum curing degree. This also indicates that the material takes more time to cure after reaching the maximum curing rate. For lower temperatures starting from 50°C and below, it seems that the curing rate stays constant during the whole curing process. Therefore the relation between conversion rate and conversion degree shows that the behaviour of the material changes from higher to lower temperatures, which confirms that the material behaviour is not a pure one and it's a "mixed" between the two different behaviours, n^{th} order and autocatalytic, and which should be considered during the modelling of the material behaviour.

The same three plots were presented for a high temperature range between 100°C and 150°C. Although this range is out of the scope of this research (bridge joints applications), it can help in better understanding the behaviour of material under different temperature ranges.

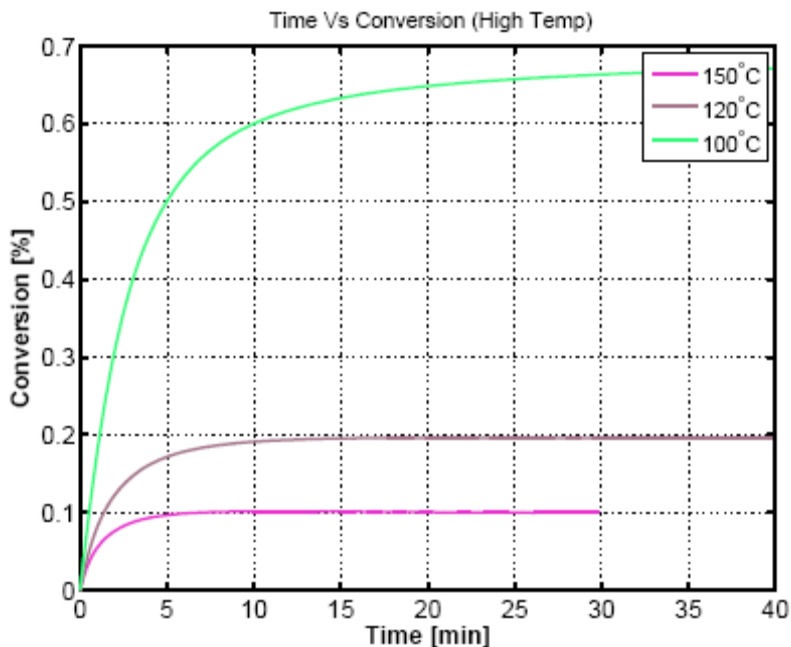


Fig. 4.15 Conversion (Curing degree) Vs conversion rate for high range isothermal temperatures.

Fig 4.15 shows the same problem as fig 4.12 concerning the slow data acquisition of the heat-flux DSC system. As the temperature is getting higher, the reaction is faster and the machine could not follow the data recording, therefore part of the initial data were lost.

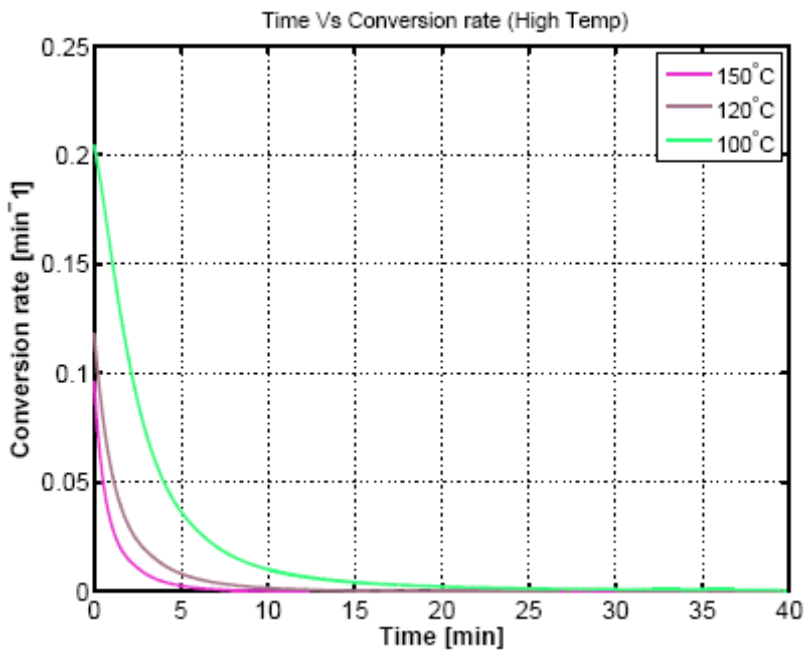


Fig. 4.16 Conversion (Curing degree) Vs conversion rate for high range isothermal temperatures.

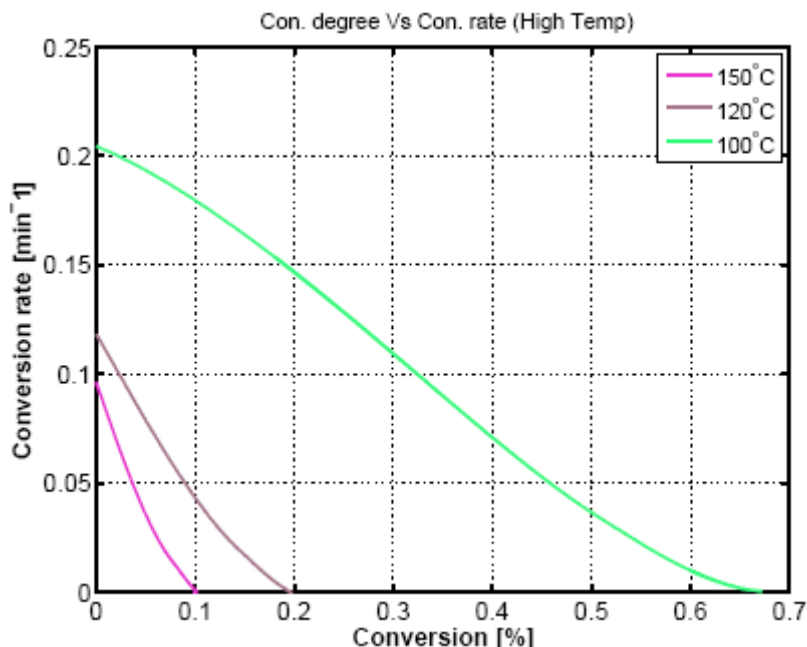


Fig. 4.17 Conversion (Curing degree) Vs conversion rate for high range isothermal temperatures.

In fig 4.16 and fig 4.17 the peak of the maximum curing rate could not be shown, again due to the loss of initial part of the data.

4.1.2.3 Modelling:

The modelling aims to predict relations between conversion degree/conversion rate and time under any given isothermal temperature, therefore modelling is considered as the intermediate phase between the test results and the curves to be predicted under any given isothermal temperature according to fig 4.18

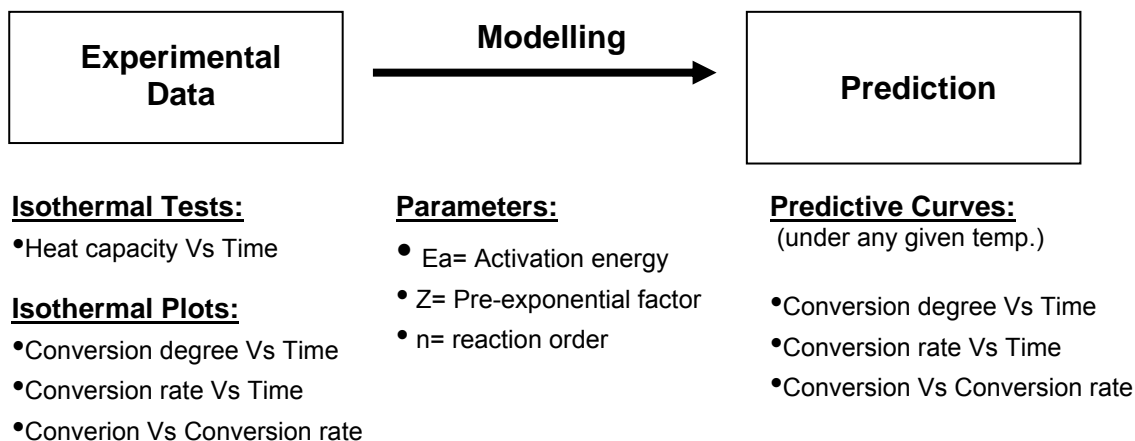


Fig. 4.18 Modelling process objective.

The general model of Brodcharts and Daniels is being used in order to plot the predictive curves under any given temperature, it aids in the calculation of three different parameters (n, Ea and Z); where Ea is the energy needed to activate the interlocking of molecules (curing process reaction) and n is the reaction order corresponding to the speed of the reaction.

$$\frac{d\alpha}{dt} = Z \cdot \exp\left(\frac{-E}{RT}\right) \cdot (1 - \alpha)^n$$

Where, da/dt = reaction rate (1/sec)
 a = fractional conversion
 Ea = Activation energy (j/mol)
 Z = Pre-exponential factor (1/sec)
 R = gas constant = 8.314 j/mol K
 n = reaction order

$$\int_{t_0}^{t_{99}} dt = \left(\frac{1}{Z \cdot \exp\left(\frac{-E}{RT}\right)} \right) \cdot \int_{\alpha_0}^{\alpha_{99}} \frac{d\alpha}{(1 - \alpha)^n}$$

$$t_{i+1} - t_i = \left(\frac{1}{Z \cdot \exp\left(\frac{-E}{RT}\right)} \right) \left[\frac{-(1 - \alpha_{i+1})^{1-n}}{1-n} + \frac{(1 - \alpha_i)^{1-n}}{1-n} \right] \dots\dots (1)$$

From results of at least three tests, values of n, Ea and Z can be obtained, as three values of n are calculated for each isothermal temperature, therefore the average can be calculated. Also a relation between Ln k and 1/T (in Kelvin) as shown in *fig 4.19* can be plotted, then Z and Ea/R can be found as the intercept and the slope directly for the regressed points.

For EPOXY SIKADUR 30, four isothermal results for temperatures between 50°C and 80°C, where for each curve, using the previous equations, different values were calculated, tabulated as follows:

| | 80°C | 70°C | 60°C | 50°C | n _{av} |
|---------------------|-------------|-------------|------------|-------------|-----------------|
| n | 0.75143 | 1.1769 | 0.67334 | 0.56027 | 0.790485 |
| Ln K | -2.184 | -2.3995 | -4.5458 | -4.1342 | |
| norm of res. | 1.8413 | 0.7805 | 9.6325 | 4.2499 | |
| K | 0.112590268 | 0.090763324 | 0.01061168 | 0.016015472 | |

Table 4.4 Calculation of different parameters from four different isothermal tests

Then using different values of Ln K plotted against 1/T, four points are plotted (one for each isothermal test) and a basic curve linear fitting is carried out to get the Z as the intercept and the Ea/R as the slope as shown below.

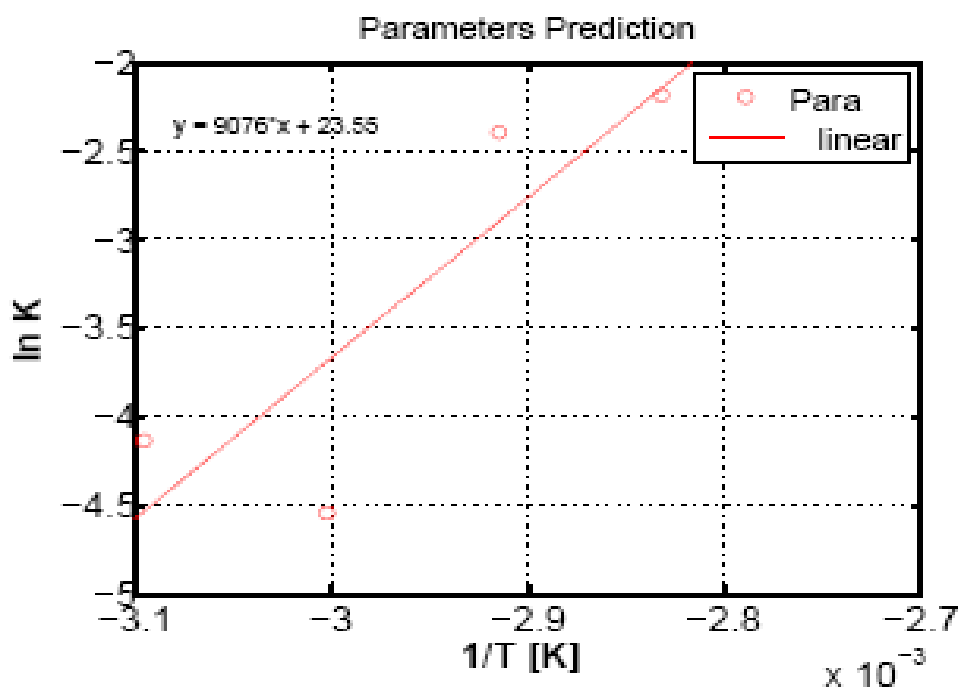


Fig. 4.19 Curve fitting for predicting modelling parameters.

Fig 4.19 shows the linear fitting for all four points (each point calculated from one isothermal test). It can be noticed that the fitting is not satisfactory especially for third point as the average norm of residuals is 1.0674. This resulted fitting weakens the reliability of such a model. This could be due to the different behaviour of material, as the behaviour changes gradually from nth order to autocatalytic under such range of temperatures as aforementioned. Therefore it is recommended to fit smaller ranges of temperatures, for instance 70°C, 75°C and 80°C where a closer behaviour could be guaranteed. Ln Z and Ea/R can be estimated as follows:

$$\begin{aligned} \text{Ln } Z = 23.555 & \rightarrow Z = 1.69749 \text{ e}^{10} \text{ min}^{-1} \\ \text{Ea/R} = 9076.3 & \rightarrow \text{Ea} = 75.46 \text{ KJ/mol} \end{aligned}$$

Finally using the integrated equation (1), and substituting the already calculated values of n, Ea and Z, at any given isothermal temperature Therefore the time can be calculated at any conversion degree and vice-versa, thus giving the following plots:

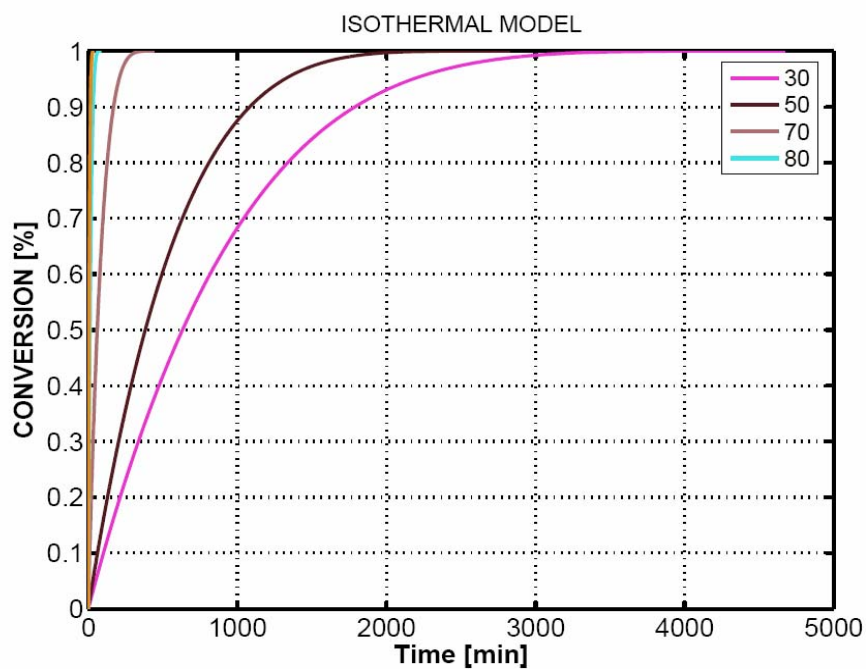


Fig. 4.20 Predicted curves between conversion degree and time.

Fig 4.20 shows the relation between conversion degree and time calculated by the Brodchart and Daniels model for different isothermal temperatures. In this plot The most important thing to be noticed, is the non-conformity of this model for low temperatures, as we can notice that we reach 100% conversion under 30°C which is illogic. The time needed to reach this final curing degree seemed to be reasonable but could not be confirmed using the isothermal tests as they are limited to short period testing procedure.

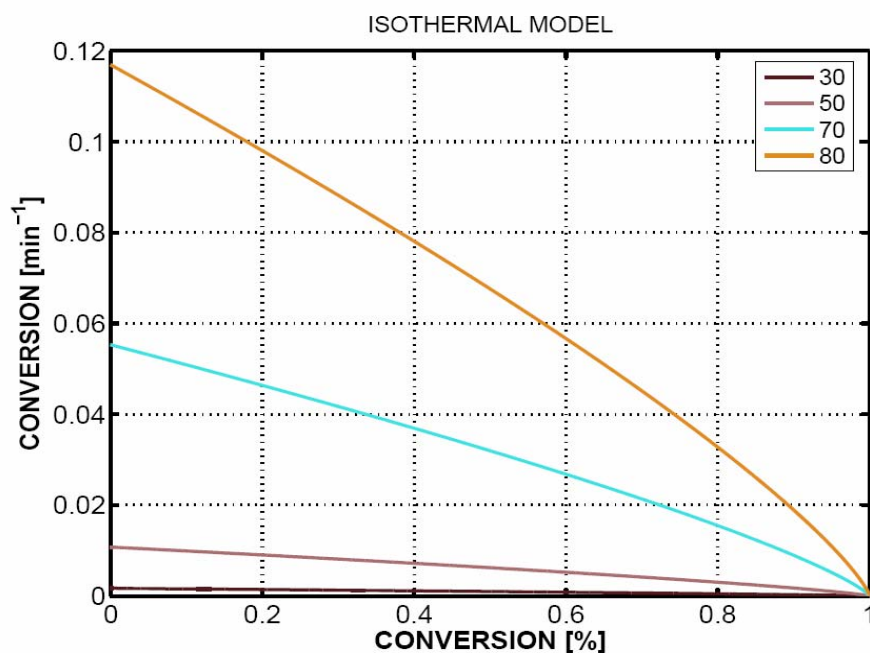


Fig. 4.21 Predicted curves between conversion rate and conversion degree.

Fig 4.21 shows the relation between conversion degree and conversion rate calculated by the means of the Brodchart and Daniels model for different isothermal temperatures. It can be noticed how this plot gives a behaviour that is different from the one produced from testing, as the maximum conversion rate is given at the very beginning of the test and then drops gradually till the maximum curing degree. Also the maximum conversion rate value is found to be not conservative as for instance under 80°C isothermal temperature, the model gives a peak of 0.12 min⁻¹ while the test results gives a maximum rate lower than 0.1min⁻¹.

The reliability of such model is tested for different temperature ranges by comparing both results from the model and the test. Two different temperature ranges are considered in this comparison, 50°C to 60°C and 70°C to 80°C.

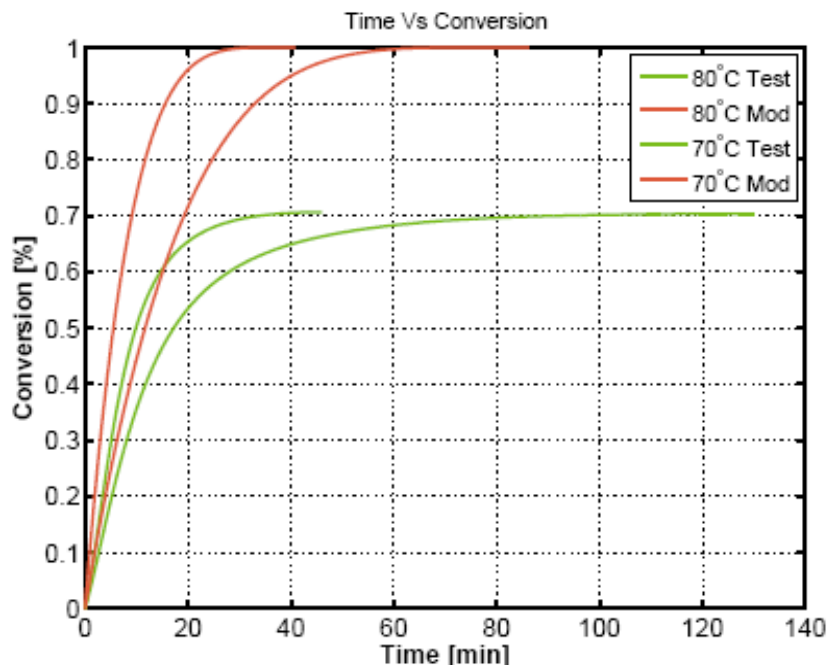


Fig. 4.22 Comparison between predicted curves and tests for high temperatures.

Fig 4.22 shows the comparison between model and test results for 70°C and 80°C. It is noticed that behaviour of the material under testing is much more conservative than that from the model. The material reaches a maximum curing degree of 0.7 (during testing) under such temperatures at time not less than 40 minutes, While the model gives a degree of cure of 1 at a time of almost 30 minutes which is not corresponding to reality.

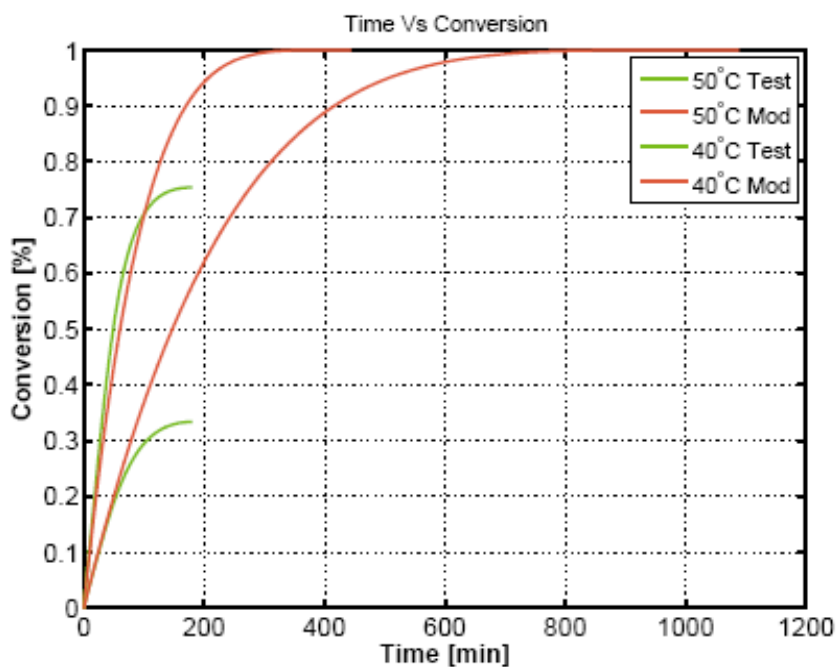


Fig. 4.23 Comparison between predicted curves and tests for low temperatures.

Fig 4.23 shows other comparative results for 50°C and 60°C. It is noticed that behaviour of the material under testing has been more improved than that from the previous range with respect to the rate of curing (slope). But still this model gives a degree of cure of 1 for any isothermal temperature during the test which sounds illogic. This 100% curing degree can be reached only on the long-term as the time factor plays an important role in such case.

Finally, This model should be well-adjusted for such range of testing (35°C-80°C), as the material's behaviour becomes more complicated the behaviour of the material as it is believed is a mixed and complicated behaviour between n^{th} order and autocatalytic. A new proposed method can be taken out in order to overcome the hurdle of 100% curing at any given isothermal temperature. A relation between the slope (the rate of increase) and the plateau (final curing degree) can be obtained from the already carried out tests, and by integrating this relation in the model, more representative curves could be plotted for lower temperatures using this model

4.1.3 Tg Analysis

The main objective of this test is to build a reliable relation between the glass transition temperature of the material and time, consequently a relation between Tg and the conversion degree. Three main temperatures were chosen to investigate the behaviour of the Tg of Epoxy sikadur 30 with time; the temperatures are shown as well as the choice can be justified as follows:

- 80°C: considered as the highest possible temperature that could be achieved on a bridge situated in Switzerland.
- 22°C - 25°C: considered as the average ambient temperature all over Switzerland during the year.
- 10°C: considered as the minimum accepted temperature under which the material could be applied in order to guarantee a minimum degree of cure as well as minimum accepted mechanical properties

4.1.3.1 Experimental Procedure:

In this series of testing an isothermal test is carried out and stopped at a certain time, then a dynamic scan with a constant rate of 15°C/min between -50°C – 400°C is followed for the previously tested specimen after immersing the specimen into liquid nitrogen for 20-40 minutes in order to stop the reaction (curing process), different points (at different time stops) were plotted for the main three temperatures mentioned previously above. The Tg is the first inflection point advancing the exothermic peak, it was calculated using the software accompanying the DSC machine as follows in the next figure.

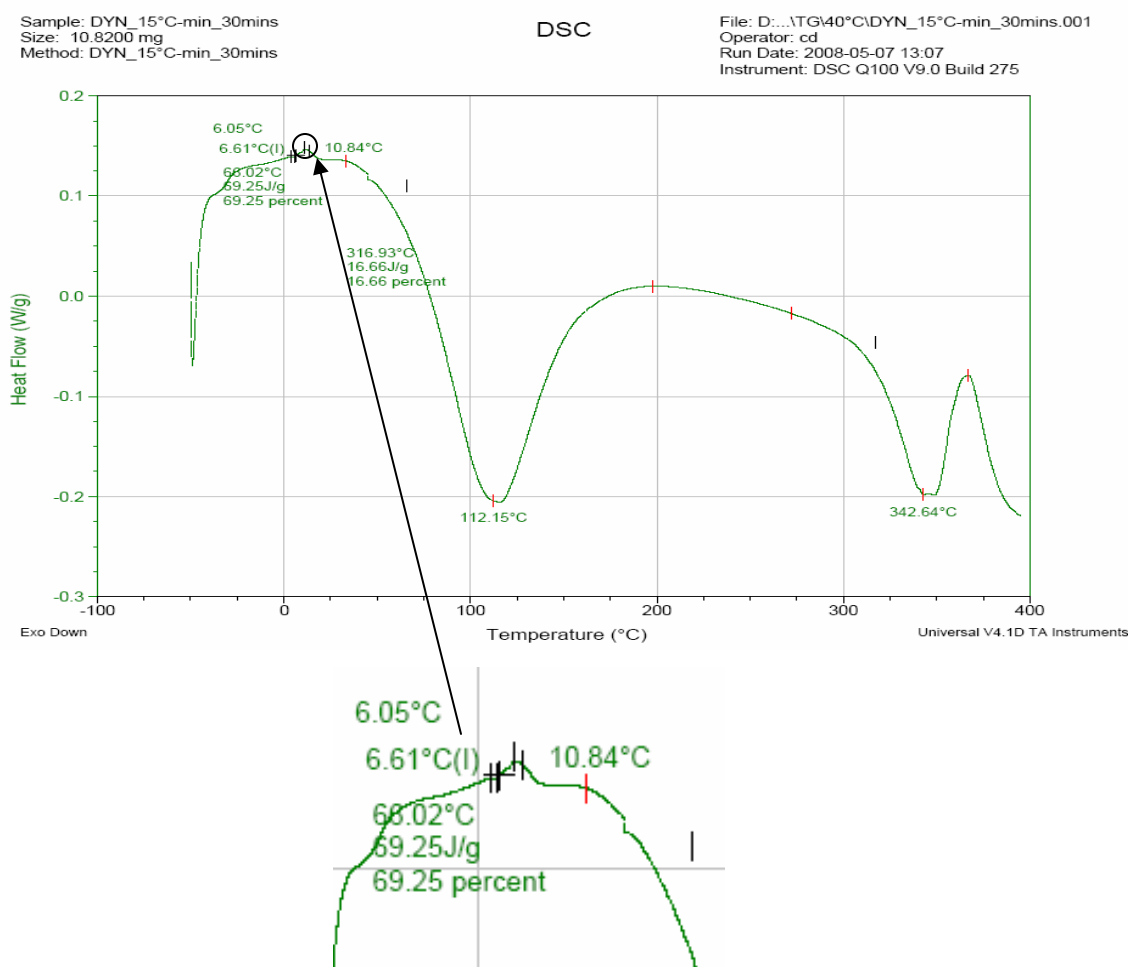


Fig. 4.25 Tg analysis using the DSC machine software.

4.1.3.2 Tests & Results:

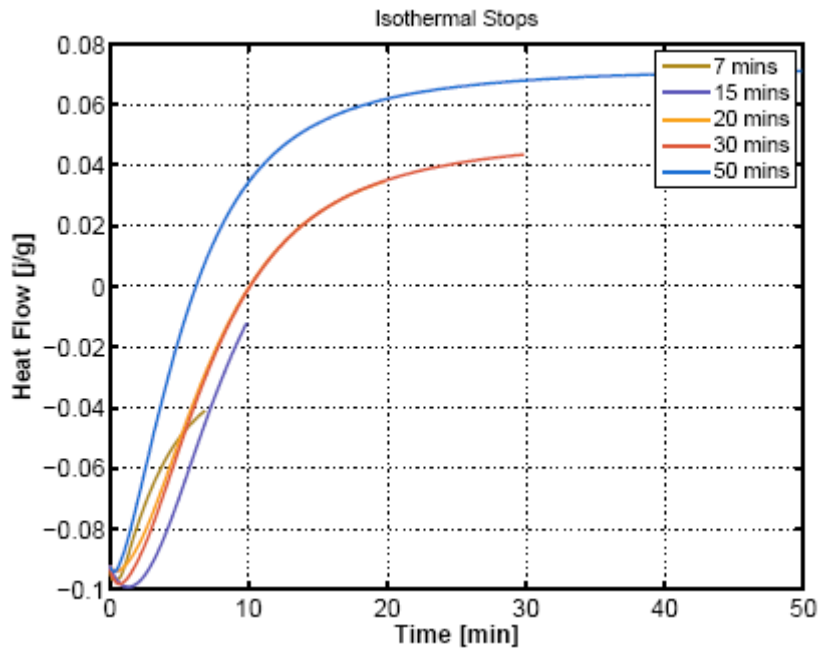


Fig. 4.25 Heat flow Vs time at different time stops at 80°C isothermal temperatures.

Fig 4.25 shows the first phase of Tg tests, indicating the isothermal tests at different time stops. The slope of all the tests seemed to be close which indicates the consistency of the results.

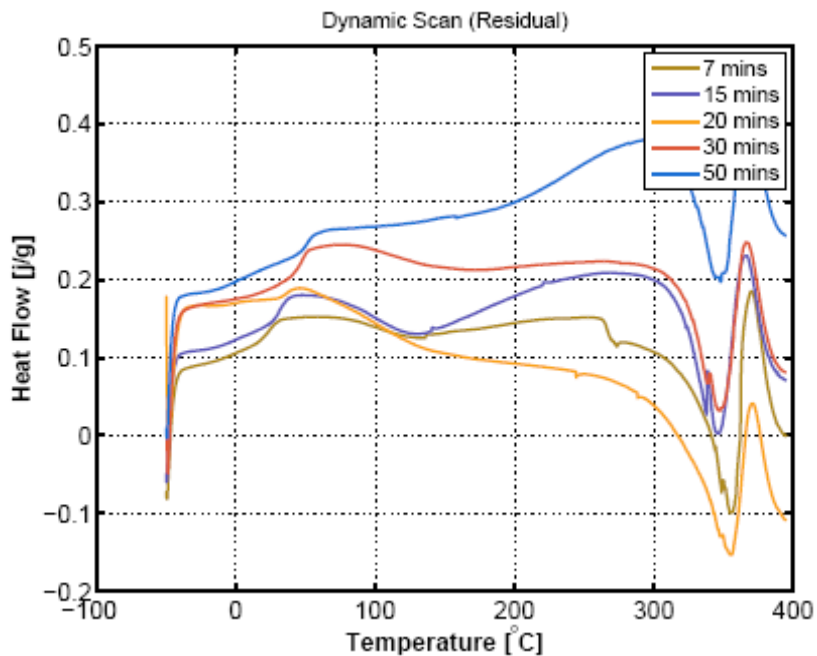


Fig. 4.26 Dynamic scan after different time stops under 15°C/min rate of heating.

Fig 4.26 shows the second phase of Tg tests, the dynamic scan providing the residual heat after the isothermal stops. Also the evolution of Tg can be recorded during this test.

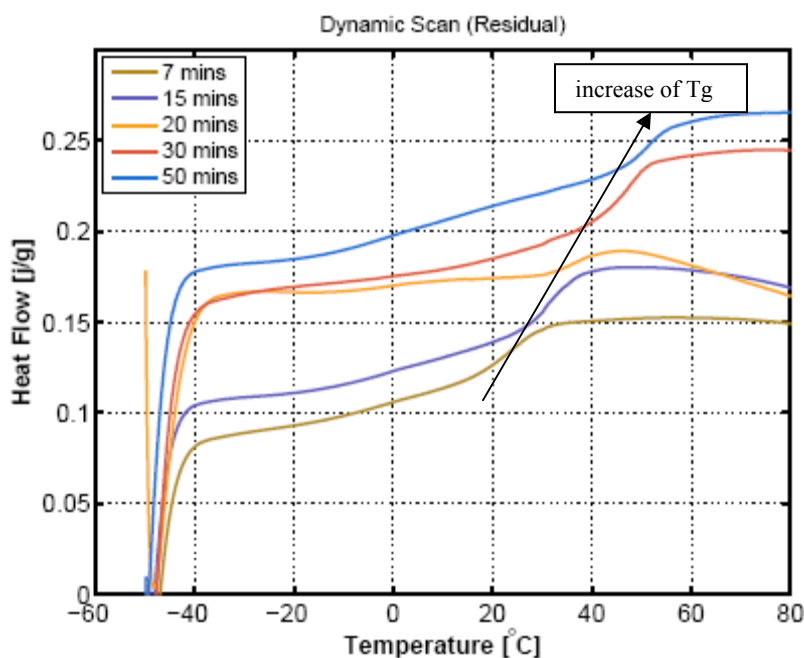


Fig.4.27 Increase of Tg as the material gets more cured under isothermal temperature.

The evolution of the Tg can be shown in fig. 4.27 where the glass transition temperature keeps on increasing as the specimen is getting more cured, which means that the material is hardened during isothermal test and needs higher temperature to reach Tg where the material loses part of its properties at that specific temperature. Tables 4.5, 4.6 and 4.7 as well as the accompanying graphs demonstrate this evolution of Tg as well as conversion for the three different temperatures mentioned above.

| Time | Weight (mg) | Area(iso) | Area(dyn) | Peak Temp | Con (%) | Tg |
|------|-------------|-----------|-----------|-----------|----------|-------|
| 3 | 12.49 | 19.56 | 54.43 | 111.49 | 0.181021 | 15.77 |
| 5 | 12.76 | 12.12 | 21.72 | 116.86 | 0.112166 | 18.62 |
| 10 | 14.16 | 31.08 | 18.88 | 122.65 | 0.287634 | 22.07 |
| 15 | 13.65 | 56.448 | 20.84 | 132.26 | 0.522405 | 30.61 |
| 20 | 16.62 | 58.902 | 4.028 | 133 | 0.545116 | 36.08 |
| 30 | 15.44 | 72.978 | 4.517 | 162 | 0.675385 | 47.35 |
| 40 | 14.24 | 78.78 | 2.142 | 142.64 | 0.72908 | 55.14 |
| 50 | 12.25 | 72.63 | 7.49 | 186.64 | 0.672164 | 51.62 |

Table 4.5 Results for Tg analysis under 80°C isothermal temperature

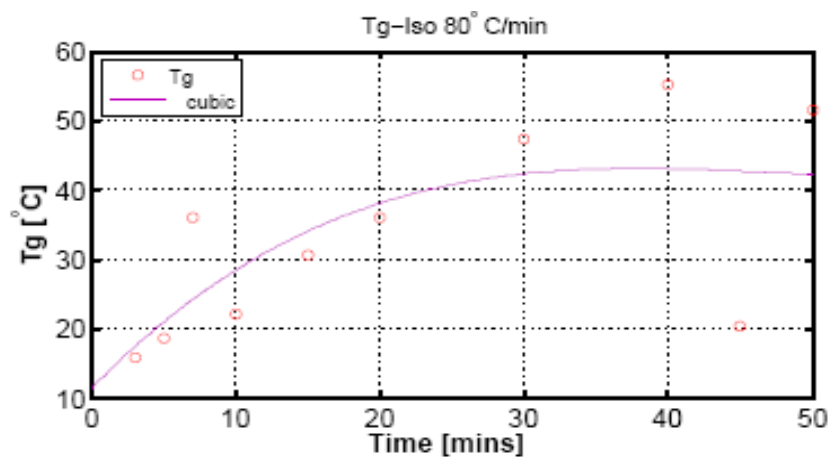


Fig 4.28 Evolution of Tg along time due to further curing under 80°C.

Table 4.5 and fig 4.28 show the results for Tg tests under 80°C. A consistent fast increasing behaviour of Tg can be noticed although the small time gap between first and last test which is less than one hour. For high temperatures, the curing processes happened to be so fast and consequently the increase of Tg.

| Time | Weight (mg) | Area(iso) | Area(dyn) | Peak Temp | Con (%) | Tg |
|------|-------------|-----------|-----------|-----------|----------|-------|
| 30 | 11.55 | 39.474 | 68.58 | 115.08 | 0.365317 | 6.34 |
| 60 | 11.65 | 53.984 | 54.07 | 114.12 | 0.499602 | 12.68 |
| 120 | | 68.294 | 39.76 | 112.91 | 0.632036 | 24.24 |
| 240 | 11.26 | 79.184 | 28.87 | 116.98 | 0.732819 | 27.76 |
| 540 | 10.67 | 91.034 | 17.02 | 117.13 | 0.842486 | 29.65 |
| 480 | 12.98 | 99.796 | 8.258 | 122.9 | 0.923575 | 30.29 |
| 900 | | 89.854 | 18.2 | | 0.831566 | 37.97 |
| 1020 | 15.08 | 103.833 | 4.221 | 124.38 | 0.960936 | 40.1 |
| 1180 | | 101.533 | 6.521 | 116.69 | 0.939651 | 41.77 |
| 1440 | 13.24 | 105.945 | 2.109 | 127.43 | 0.980482 | 44.89 |

Table 4.6 Results for Tg analysis under 25°C isothermal temperature

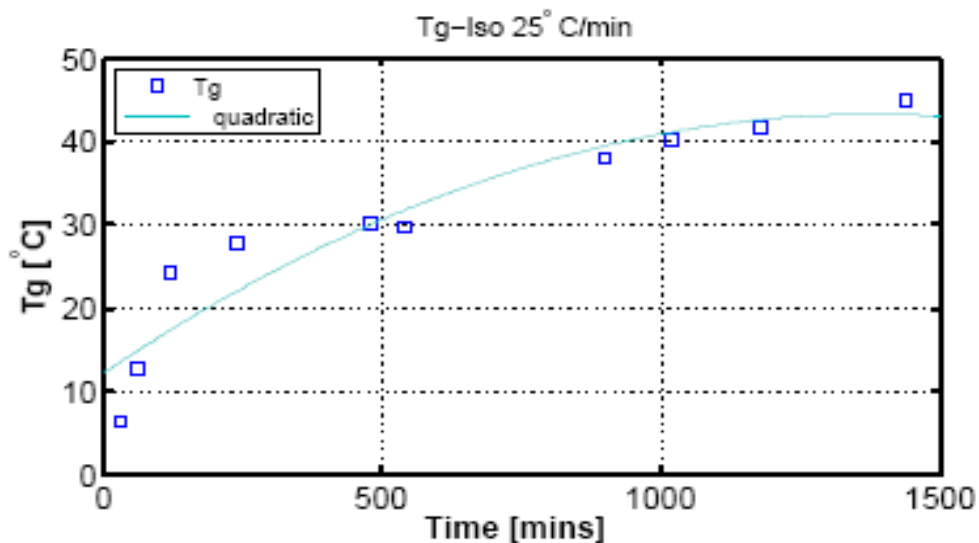


Fig.4.29 Evolution of Tg along time due to further curing under 25°C.

Table 4.6 and fig 4.29 show the results for Tg tests under 25°C. Again a consistent increasing behaviour of Tg can be noticed for this test, but it seemed to be time consuming comparing to the previous series (at 80°C) where a Tg of more than 50°C is reached in 50 minutes while during this test a whole day is needed to reach a Tg of 45°C. Although this time consuming defect, the final results under 25°C are found to be acceptable.

| Time | Weight (mg) | Area(iso) | Area(dyn) | Peak Temp | Con (%) | Tg |
|------|-------------|-----------|-----------|-----------|----------|-------|
| 60 | 12.62 | 31.05 | 76.95 | 91.26 | 0.287356 | 15.9 |
| 120 | 11.99 | 26.27 | 81.73 | 108.82 | 0.243119 | 15.97 |
| 240 | 11.77 | 27.41 | 80.59 | 107.22 | 0.253669 | 24.25 |
| 300 | 13.82 | 40.93 | 67.07 | 108.56 | 0.378792 | 24.81 |
| 900 | 11.53 | 97.62 | 10.38 | 122.54 | 0.903437 | 29.14 |
| 1080 | 10.27 | 87.09 | 20.91 | 114.3 | 0.805986 | 56.9 |
| 1200 | 12.03 | 100.094 | 7.906 | 114.48 | 0.926333 | 23.32 |
| 1320 | 8.32 | | | | | 21.15 |
| 1440 | 11.61 | 108 | ----- | ----- | 0.9995 | 53.99 |

Table 4.7 Results for Tg analysis under 10°C isothermal temperature

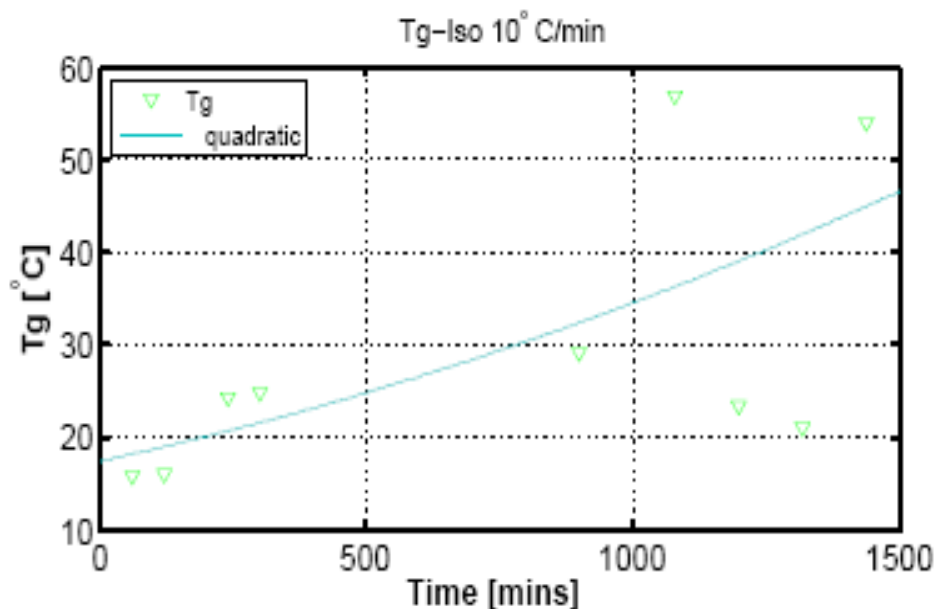


Fig. 4.30 Evolution of Tg along time due to further curing under 10°C.

Table 4.7 and fig 4.30 show the results for Tg tests under 10°C. In this test the behaviour of the material found to be inconsistent and difficult to interpret as the results are dispersed. This test is highly dependent on the pre-conditioning of the specimens; a preconditioning chamber was used to cure the material at different time stops under 10°C.

Resulting from Tg analysis, the consistency between the degree of cure and the increase of Tg sounded logic as the material possess a higher Tg when it is more cured i.e. in stiffer (solid) state. The behaviour of the evolution of the Tg can differ from one curing temperature to another, but finally it should be similar for certain ranges with a slight difference in values. From basic fitting of three different curves above (fig 4.28, fig 4.29 and fig 4.30), it can be shown that the degree of cure that can be reached during tests in general is between 40°C – 50°C. The time needed to reach such Tg is highly dependant on the curing temperature, for instance we reach this range in less than an hour under a curing temperature of 80°C while after almost one day for 25°C curing temperature. Also it can be shown that the increase of Tg is more consistent for high temperatures (80°C – Cubic fit) than that of lower ones (10°C/25°C – quadratic fit). Some unexplainable data couldn't be analyzed or interpreted such as reaching a higher Tg at 10°C than that at 25°C after one day, so all tests that seemed illogic were completely excluded. Sometimes

the preparation and the quality of taking out the testing procedure of a big importance in influencing the results.

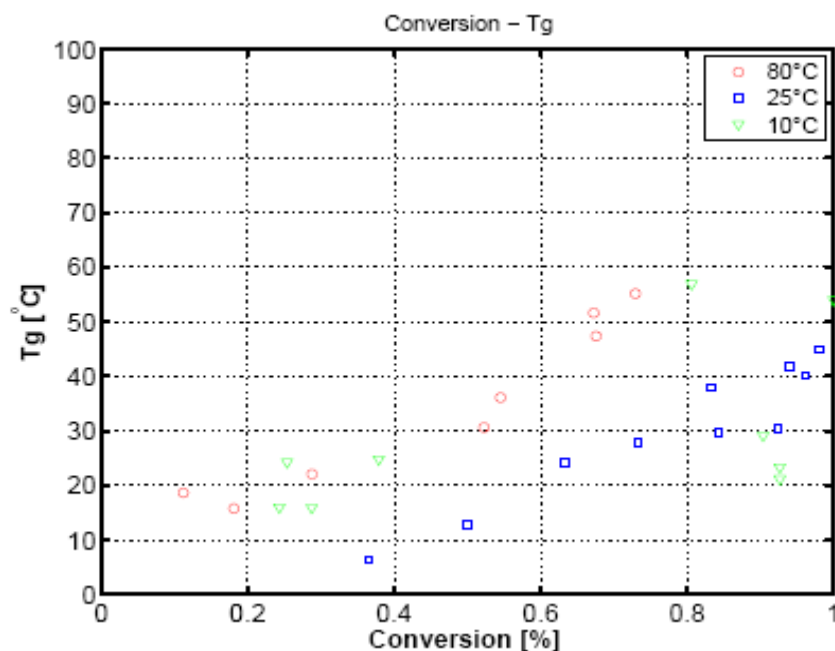


Fig.4.31 Relation between Tg and Conversion for different temperatures.

Fig 4.31 shows the relation between Tg and the Conversion degree extracted from the three previous relations (Table 4.5, Table 4.6 and Table 4.7). It can be figured out the consistency of increase between both parameters at 80°C and 25°C while the behaviour sounded less consistent at 10°C, this is due to the complicated behaviour of adhesives under very low curing temperatures. This would force many restrictions on the use of adhesives during low temperature seasons.

4.2 Mechanical Tests:

In this project, only the basic mechanical properties of the material were investigated i.e. tensile and compressive properties. The objective of executing these groups of tests is to establish relation between stiffness/strength of the material and Tg/curing degree in order to assure the sufficiency of both strength and stiffness provided by the material in the joints in resisting or transmitting the different loads. The required properties are highly dependent on different parameters such as the type and dimensions of joint, structural function, quality of the material and the quality of the execution.

Mechanical tests will be based on different standardized codes, mainly ASTM D 638, therefore testing specimens and procedure will be taken out according to these standards.

A DSC scan is accompanied with every testing condition in order to relate the mechanical properties to the physical characterization of the material i.e. getting the influence and evolution of the curing degree (α) and the glass transition temperature (T_g) on the basic mechanical properties of the material.

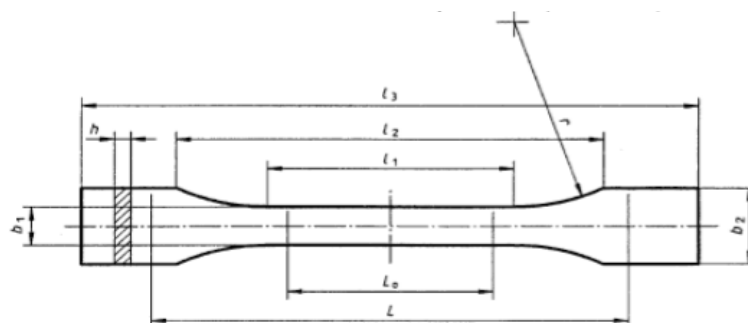
4.2.1 Tension Tests:

All types of epoxies are almost considered as brittle materials, which possess a relatively low tensile resistance compared to its high compressive strength. This fact makes it sometimes delicate to use epoxies in some bridge joints subjected to tension loads. This leads the engineer to have recourse to more ductile adhesives such as polyurethane.

4.2.1.1 Test specimens:

The test specimens according to the ASTM D 638 standards of type (I) is that shown in *fig. 4.32* with the given dimensions. Type (I) is preferred for rigid and semi-rigid plastics and also as the material is having a thickness of less than 7mm (a specimens with 4mm thickness were formulated for this test). The aim of this dog bone specimen is to force the failure in the middle of the specimens so that the influence of grip stress is avoided at both ends of the specimen [26].

Specimens were prepared in aluminium moulds fabricated with the given dimensions below, each series of specimens, in one mould, are directed for one environmental condition of testing. Surfaces of specimens should be proper as much as possible i.e. free of visible flaws, scratches, or imperfections [26].



| | | ASTM D 638, Type 1 | ISO 527, Type 1A |
|-------|--------------------------|---|------------------|
| l_3 | Length overall | 165 ± 1 mm / 6.50 ± 0.2 in. | 150 ± 2 mm |
| b_1 | Width of narrow section | 13 ± 0.5 mm / 0.50 ± 0.05 in. | 10 ± 0.2 mm |
| l_1 | Length of narrow section | 57 ± 0.5 mm / 2.25 ± 0.02 in. | 80 ± 2 mm |
| b_2 | Width overall | 19 ± 0.5 mm / 0.75 ± 0.05 in. | 20 ± 0.2 mm |
| L_0 | Gage length | 50 ± 0.25 mm / 2.0 ± 0.01 in. | 50 ± 0.5 mm |
| L | Distance between grips | 115 ± 5 mm / 4.5 ± 0.2 in. | 115 ± 1 mm |
| r | Radius of fillet | 76 ± 1 mm / 3.0 ± 0.04 in. | 20 - 25 mm |
| h | Thickness of specimen: | | |
| | Unfilled systems | 4 - 7 ± 0.4 mm / 0.15 - 0.28 ± 0.02 in. | 4.0 ± 0.2 mm |
| | Filled systems | 7 ± 0.4 mm / 0.28 ± 0.02 in. | 10 ± 0.2 mm |

Fig. 4.32 Standard tension test specimen according to ASTM D 638.

Strain gauges were glued to the specimens in order to record the strains due to tensile load. Two types of strain gauges were used; strain gauges shown in *fig 4.33a* (with a 120 Ω resistance) were used to get the strains in the longitudinal direction, while other strain gauges (with a 350 Ω resistance) were used to record the strains in both longitudinal and transverse directions so finally Poisson's ratio can be calculated.

One of these fabricated specimens was used to get the degree of cure (α) of the material, at the time of the tensile strength test, using a DSC machine in LTC lab. This degree of cure is obtained by running a DSC scan to get the residual curing as explained explicitly in the previous chapter (for T_g).

A number of two tests were carried out and in case of clear imperfections or unexpected failure due to voids or low quality of fabrication, so that the percentage of differences of any parameter should be less than 10%.

4.2.1.2 Machinery:

A testing machine of a max capacity of 5KN was used to test the specimens under tensile load. The expected failure load is found to be low, compared to other adhesives, due to the brittleness of epoxies in general. The machine is connected to two different softwares.

The first one was to record directly the relation between the load and displacement. The second software (Catman ver. 4.5) was used to record all strains produced in the specimen due to tensile stresses and it is connected to the machine via spider 8 where different channels for strains, load and displacement can be found, and help the transmission of data to the software.

An inductive transducer is used to check the displacement recorded during the test by the Catman software.

4.2.1.3 Experimental Procedure:

According to the ASTM D 638, the dog-bone specimens mentioned above were placed in a loading machine (max. load capacity of 5 KN) shown in *fig. 4.33b*. Specimens should be well aligned between the two grips of the machine. A constant rate of loading of 1mm/min is chosen (between the range proposed by the ASTM D 638) to carry out all the tests. This rate of loading should be modified according to the type of loading to which the different joints in a bridge, but this is out of the scope of this report in order to avoid any complications due to the integration of more parameters. All tests were carried out in ambient condition after specimens were cured at different curing degrees and after different curing periods.

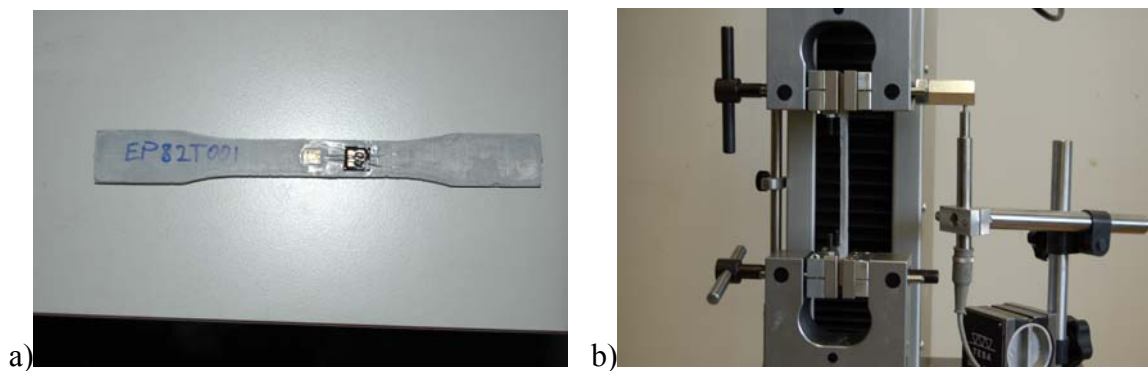


Fig.4.33 a) Tension test specimen, b) Testing machine.

4.2.1.4 Test Results:

A brittle failure is noticed for all epoxy specimens that can be shown in *fig 4.34a* and *fig 4.34b*. A tension crack is initiated at the weakest section of the specimen (crack is forced at the middle). In some specimens a failure is noticed near the grips (tab failure) as shown

in *fig 4.34c*, this could be because of the existence of micro voids on the surface as in *fig. 4.34d* or due to pores inside the specimen as shown in *fig 4.34f*.. Therefore it can be concluded that the cracking and failure is much more related to the quality of fabrication. That was a reason why an acceptable difference between specimens failed under the same condition should be taken into consideration.

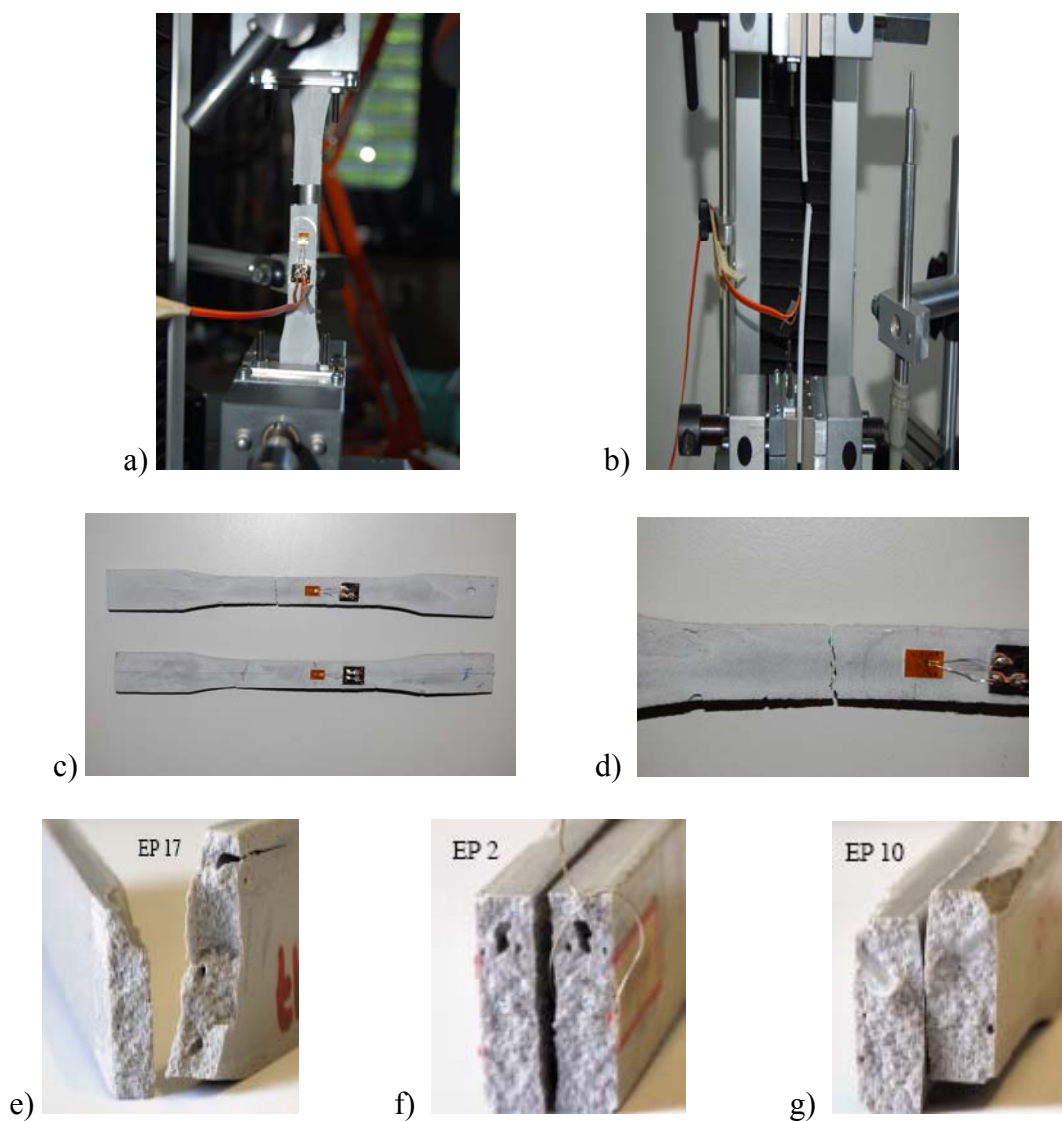


Fig 4.34 a),b) Specimen fixation and testing c),d) different failure mechanisms(cracking behaviour) e),f),g)Failure behaviour inside the specimen .

After starting the test, the displacement during a rate of loading of 1mm/min applied to the specimen was recorded till failure. A relation between load-displacement is plotted

for different curing temperatures, as aforementioned in the Tg analysis above, at different curing time (Time stops). Every test was accompanied by a dynamic scan analysis in order to record the degree of cure of the material under at failure as well as the Tg so that a relation between Tg, Degree of cure and strength/stiffness of the material can be easily established, all results are tabulated and can be shown also in the figures below.

| 10 °C | Physical properties | | | | Sp. No | Mechanical properties | | | | |
|-------|---------------------|------------|-------------------|---------|--------|-----------------------|---------------|----------------|-----------------|---------------|
| | Curing time | Heat (j/g) | Curing degree (%) | Tg (°C) | | Ultimate Load (N) | Maximum displ | Average UL (N) | Stiffness (GPa) | Possion Ratio |
| B | 16 | 83,65 | 77,45 | 23,5 | 1 | No Data | | 46 | No Data | - |
| | | | | | 2 | 46 | 43,161 | | | |
| C | 24 | 90,05 | 83,34 | 22,8 | 1 | 297 | 11,7 | 297,067 | 0,3 | - |
| | | | | | 2 | 294 | 7,5 | | 0,3 | - |
| | | | | | 3 | 300,2 | 7,13 | | 0,4 | - |
| D | 48 | 90,74 | 84,01 | 35,91 | 1 | 477,5 | 3,9 | 464,8 | No Data | - |
| | | | | | 2 | 461 | 1,99 | | 3,9 | 0,32 |
| | | | | | 3 | 455,9 | 6,23 | | 1,9 | - |
| E | 72 | 100.46 | 93.15 | 24.91 | 1 | 552 | 2,02 | 672.825 | No Data | - |
| | | | | | 2 | 497 | 1,78 | | 3,4 | 0.3 |
| | | | | | 3 | 1077,3 | 1,22 | | 9,3 | 0.23 |
| | | | | | 4 | 565 | 1,47 | | 4,5 | 0.31 |

Table 4.8 Mechanical and physical properties for specimens tested under tension at 10°C curing temperature.

Table 4.8 groups the final testing results for specimens cured at 10°C and tested after different curing times. Generally the results from this test are found to be relatively low, for instance specimens tested after a 16 hours curing, don't possess any resistance, while those tested after 72 hours curing reached an average ultimate tensile load of 673 N which could be not eligible for all applications to which the material is directed. It can be noticed that logically the increase or decrease of the stiffness is following that of the strength. The displacement found to be not constant for specimens of the same conditions even if the ultimate maximum load is somehow close, this could be more or less related to the fabrication quality, as some specimens were defected by micro-voids. Poisson's ratio found to be close for each testing condition, test E3 is excluded as the loading rate for this test was different from all the other tests.

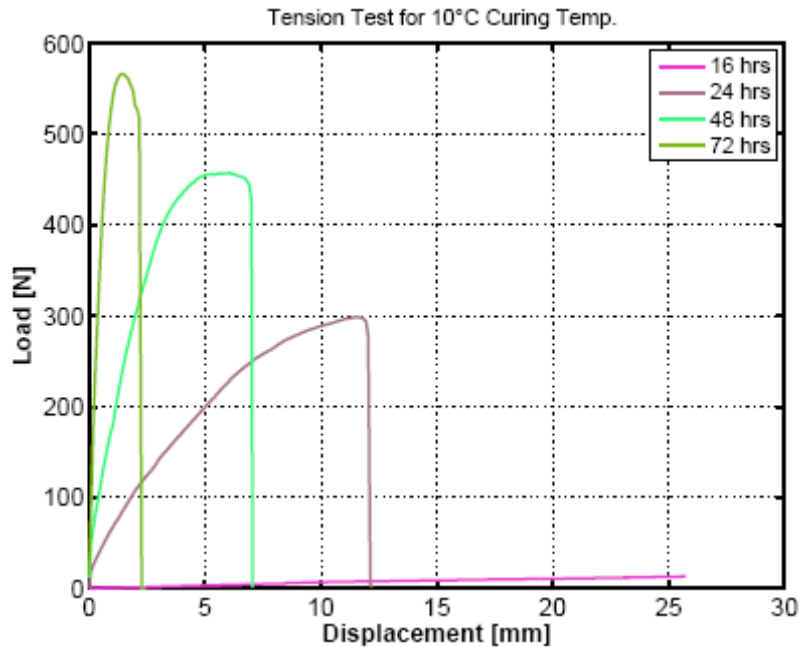


Fig. 4.35 Specimen behaviour at different curing times at 10°C curing temperature.

Fig 4.35 shows the tensile behaviour of specimens tested at 10°C and after different curing time. It can be noticed that the behaviour is more or less influenced by the curing of the material, for instance specimens cured for 16 hrs possessing very low tensile strength shows a completely non-linear behaviour, while those cured for more time having not only the tensile strength increased but also their behaviour starts improving producing a linear part at the beginning of the test then the non-linear phase starts depending on the curing and consequently the ultimate tensile strength of the specimens. During taking out the application, a curing of epoxy at 10°C could be insufficient, therefore sometimes heating of the material will be needed in order to reach a sufficient curing degree and consequently an acceptable ultimate tensile strength then material can be left to further cured at 10°C.

| 25 °C | Physical properties | | | | Sp. No | Mechanical properties | | | | |
|-------|---------------------|------------|-------------------|---------|--------|-----------------------|---------------|----------------|-----------------|---------------|
| | Curing time | Heat (j/g) | Curing degree (%) | Tg (°C) | | Ultimate Load (N) | Maximum displ | Average UL (N) | Stiffness (GPa) | Possion Ratio |
| A | 5 | 88,41 | 81,86 | 18,32 | 1 | 105,9 | 17,57 | 145 | 0,4 | - |
| | | | | | 2 | 184,1 | 13,74 | | 0,3 | - |
| B | 10 | 91,94 | 85,13 | 24,95 | 1 | 485,3 | 3,56 | 482,85 | 0,6 | - |
| | | | | | 2 | 480,4 | 2,18 | | 0,7 | - |
| C | 24 | 96,07 | 88,95 | 40,07 | 1 | 944,5 | 1,45 | 856,17 | 5,9 | - |
| | | | | | 2 | 822,8 | 1,89 | | 2,7 | - |
| | | | | | 3 | No Data | | | No Data | - |
| | | | | | 4 | 801,224 | 0,99 | | 7,8 | 0,22 |
| D | 48 | 101,58 | 94,06 | 51,48 | 1 | 1152 | 1,12 | 1099,233 | 10,5 | 0,22 |
| | | | | | 2 | 1182 | 1,24 | | 9,5 | 0,16 |
| | | | | | 3 | 963,7 | 0,88 | | 9 | 0,24 |
| E | 72 | 89.28 | 82.66 | 44.87 | 1 | 619,388 | 0,54 | 979.082 | 9,9 | - |
| | | | | | 2 | 1338,776 | 1,37 | | 10,9 | - |
| | | | | | 3 | 1113.673 | 1,04 | | 10.8 | - |
| | | | | | 4 | 1152.857 | 1,16 | | 9.4 | - |

Table 4.9 Mechanical and physical properties for specimens tested under tension at 25°C curing temperature.

Table 4.9 groups the final testing results for specimens cured at 25°C and tested after different curing times. It can be shown that Tg as well as the ultimate tensile strength at 25°C are much improved comparing to that at 10°C, for instance after 48 hours ultimate tensile strength is improved by 58% while the Tg increased by 32% although the curing degree remains so close for both cases. Displacements are found to be much lower than those at 10°C although the ultimate tensile load has increased, this can be due to the brittleness resulting from a closely fully cured specimens. Stiffness of the material has logically increased with the ultimate tensile strength. Poisson's ratio seems to be decreasing at 25°C which indicates the decrease of longitudinal strains compared to those at 10°C.

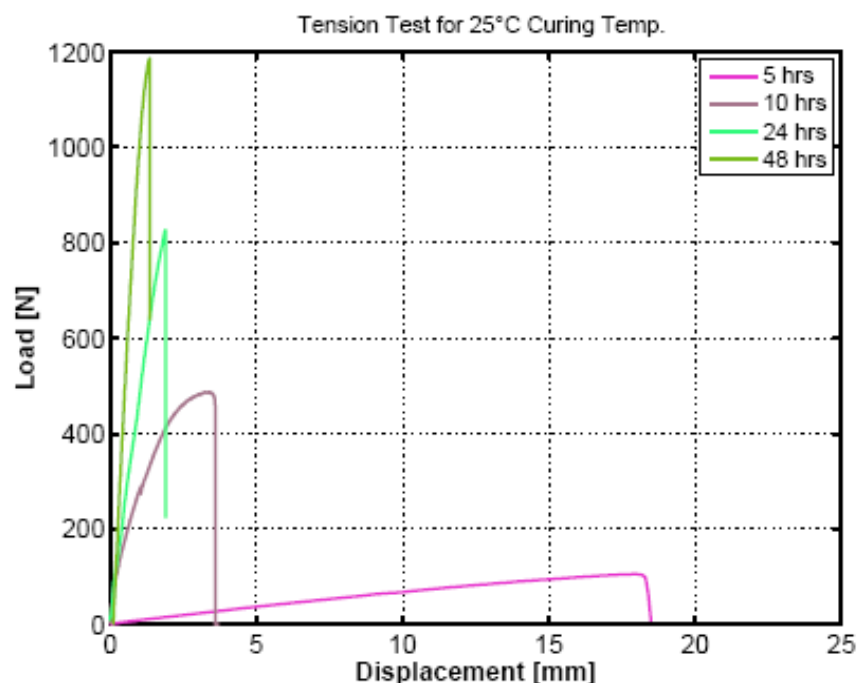


Fig. 4.36 Specimen behaviour at different curing times at 25°C curing temperature.

Fig 4.35 shows the tensile behaviour of specimens tested at 25°C and after different curing time. A tendency for a linear behaviour can be shown in this figure compared to that at 10°C where ultimate tensile strength is higher and displacements are getting smaller according to more brittle material resulted from a different curing condition. The same trend shown above, with specimens being cured for longer time giving more linear behaviour can be noticed here. This condition (curing at 25°C) represents a very reasonable and logical one, as the ultimate tensile strength seems to be sufficient for a bridge application, also a “self-curing” process at 25°C can be achievable at different periods all over the year.

| 80 °C | Physical properties | | | | Sp. No | Mechanical properties | | | | | | |
|-------|---------------------|------------|-------------------|---------|--------|-----------------------|---------------|----------------|-----------------|---------------|------|------|
| | Curing time | Heat (j/g) | Curing degree (%) | Tg (°C) | | Ultimate Load (N) | Maximum displ | Average UL (N) | Stiffness (GPa) | Possion Ratio | | |
| A | 2 | 100.46 | 93 | 29.19 | 1 | 1473 | 1.904 | 1446.5 | 8.9 | 0.21 | | |
| | | | | | 2 | 1420 | 1.806 | | | | | |
| B | 4 | - | 100 | 59.64 | 1 | 1527 | 1.933 | 1578.50 | 9.3 | 0.14 | | |
| | | | | | 2 | 1630 | 1.822 | | | | 10 | 0.2 |
| C | 8 | - | 100 | 54.54 | 1 | 1035 | 0.982 | 1082.70 | 13.8 | 0.35 | | |
| | | | | | 2 | 1148 | 1.216 | | | | 8.6 | 0.30 |
| | | | | | 3 | 1065.102 | 1.118 | | | | 9.2 | 0.27 |
| D | 24 | - | 100 | 47.94 | 1 | 1511.224 | 2.271 | 1624.49 | 9 | 0.24 | | |
| | | | | | 2 | 1737.755 | 2.098 | | | | 10.5 | 0.2 |

Table 4.10 Mechanical and physical properties for specimens tested under tension at 80°C curing temperature.

Table 4.10 shows the final testing results for specimens cured at 80°C and tested after different curing times. It can be noticed that under such high curing temperature, a closer results to that obtained at 25°C can be achieved at shorter curing periods; this is for sure due to the high activation energy provided to the material in order to accelerate the curing process. A 100% cured specimens can be obtained after 4 hours at 80°C curing temperature which is judged as being so fast, also a high Tg exceeding 50°C can be achieved. Reasonable ultimate tensile strength can be achieved rapidly, for instance the strength obtained after 2 hours at 80°C is 33% higher than that obtained after 72 hours at 25°C. For achieving such curing condition, a forced heating of material in site is needed as it is going to be hard to reach such ambient condition in Switzerland. Also the calculated stiffness of the specimens found to be higher than those calculated for the two previous conditions, but it remained almost constant for all tests at 80°C.

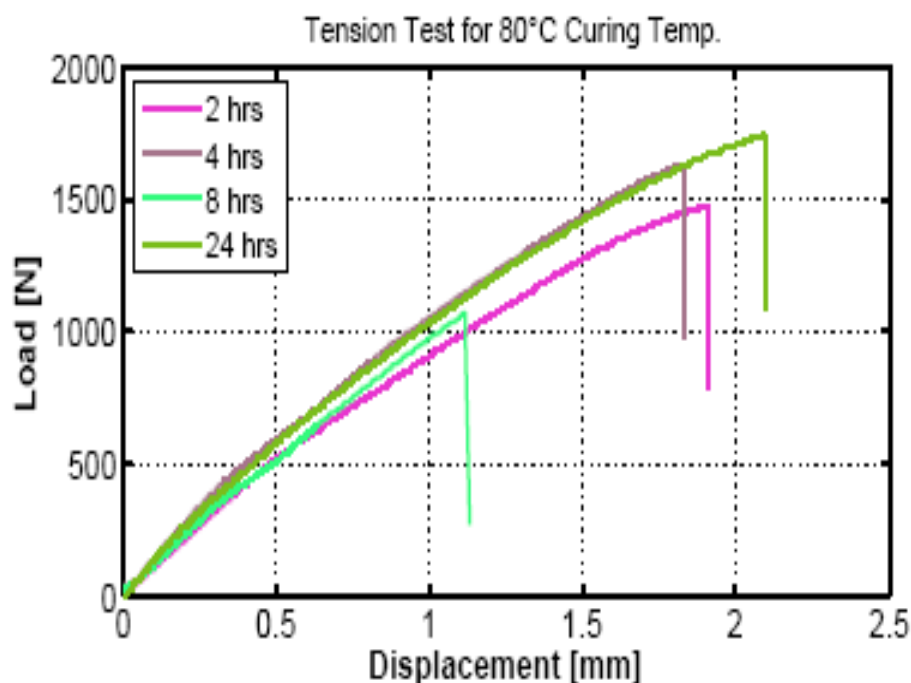


Fig. 4.37 Specimen behaviour at different curing times at 80°C curing temperature.

Fig 4.35 shows the tensile behaviour of specimens tested at 25°C and after different curing time. It can be noticed for such curing condition that the behaviour of the material is so close after different curing periods. This can be also remarkable by a close stiffness for all specimens although an increase of ultimate tensile strength can be noticed for longer curing periods. Linearity of the behaviour of these specimens is to be highlighted.

Finally From the previous figures it can be noticed that the behaviour of the material is changing between linearity and non-linearity according to the temperature of curing and consequently the degree of cure, as for high curing degrees at high temperatures a more linear behaviour can be figured out, on the other hand the behaviour tends to get more non-linear for lower degrees of cure particularly for low curing temperatures. Also a remarkable increase of strength and stiffness is noticed for high curing temperatures conditions also dependent on the period of curing.

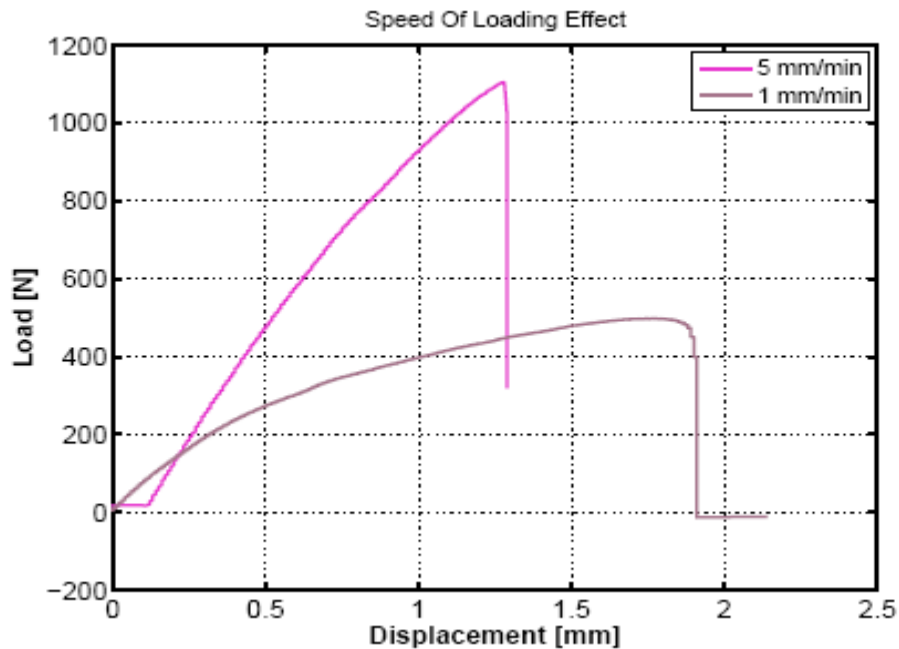


Fig. 4.38 Impact of rate of loading on the behaviour under tension at same curing condition.

Fig 4.38 shows another important parameter that influences the behaviour of the material under tension, is the rate of loading, two different loading rates are compared in fig below; the standard loading rate 1mm/min due to ASTM D 638 and a faster loading rate of 5mm/min representing a higher impact of vehicles passing on a bridge. It was found that a higher loading rate gives better behaviour of the material with higher failure load and more linear behaviour favouring the stiffness as well as shown also in the previous table (specimen E3), on the other hand the 1mm/min loading rate gives a highly non-linear behaviour especially for lower curing temperatures.

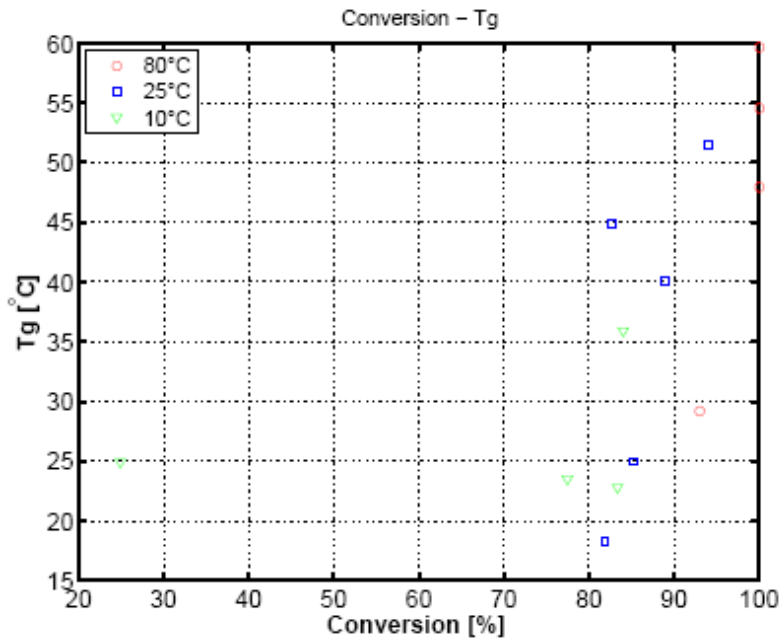


Fig. 4.39 Relation between Tg (mechanical) and degree of conversion.

Fig 4.39 shows the relation between Tg recorded from dynamic scan of mechanical tests specimen and conversion degree. A consistent behaviour can be noticed for both 25°C and 80°C curing conditions as the Tg increases with the increase of conversion degree, but not in a linear manner. A 100% conversion can be rapidly achieved for 80°C accompanied by a slower increase in Tg as shown. On the other hand dispersed results are noticed for 10°C.

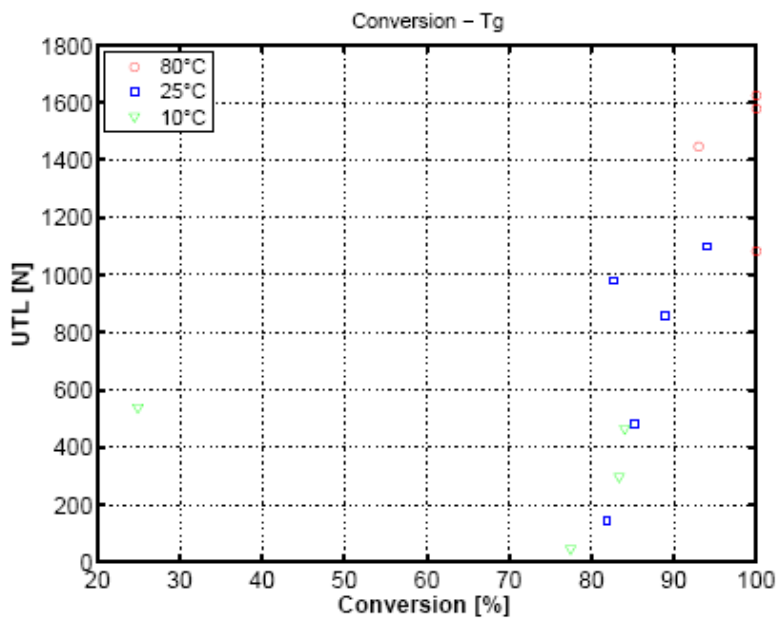


Fig. 4.40 Relation between ultimate tensile load (UTL) and degree of conversion.

Fig 4.40 shows the relation between ultimate tensile strength of mechanical tests specimen and conversion degree. Again a consistent behaviour for both 25°C and 80°C curing conditions can be noticed with a reasonable increase in strength. For 10°C curing condition, a very low tensile strength can be achieved even after 72 hours curing although a reasonable conversion degree more than 90% can be obtained.

From *fig 4.39* and *fig 4.40* it can be noticed that the relation between Tg- Conversion degree- UTL is almost consistent for most of the executed tests, but the rate of increase of Tg with time is not linear with that of conversion degree i.e. not directly proportional, this can be noticed also from the previous physical characterization which can be shown in *fig.4.31* above.

4.2.2 Compressive Tests:

Compressive strength of epoxies are expected to be high, which is beneficial in bridge application as most of the joints in bridges are subjected to whether pure compression or compression accompanied by other different loads. So a high compressive strength is needed particularly for structural joints, in order to resist all different loads from the bridge such as imposed dead loads and live loads.

4.2.2.1 Test specimens:

According to ASTM D 638, specimens in the form of parallelepiped were chosen for the compressive strength tests; the dimensions as shown in *fig. 4.41a*. All surfaces should be parallel and dimensions should be constant all over the specimens, so it should be controlled before testing using a trimmer in order to avoid any influence of non-uniformity of specimens on the results [25].

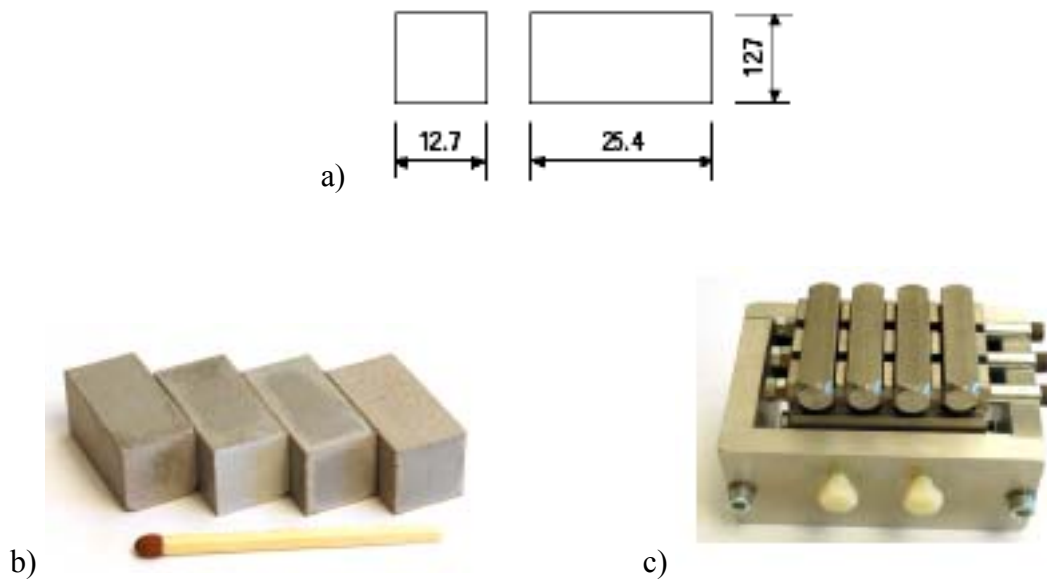


Fig. 4.41 a) Compression test specimen's dimensions, b) Test specimens c) Moulding of test specimens^[20].

Specimens were fabricated in the mould shown previously, by applying a quantity of material with a ratio 3:1, as previously discussed, in the openings of this mould, then metal parts shown in *fig 4.41c* are used to press the material and smoothen the surface of specimens, finally specimens were left to harden for a certain time, then un-moulding took place.

4.2.2.2 Experimental procedure:

The specimen is aligned in a vertical position between the grips of the machine (W+B 500) i.e. the specimen is placed almost within the centrelines of the two grips in order to guarantee a pure compressive load and avoid any moment that could act on the specimen and consequently could influence the results.

A constant rate of loading is applied to the specimen until failure; parameters such as load and displacement were recorded. Three different loading rates were applied to different tests in order to get the difference in behaviour as this loading rate, as mentioned above in tension test, is much connected to the type of load to which the joint on a bridge is subjected. The different loading rates as well as the number of specimens tested for each case is summarized in the *Table 4.11* below:

| specimen | loading rate (mm/min) | Number of specimens | Total Number |
|---------------------------------|-----------------------|---------------------|--------------|
| EP11 EP12 EP13 | 0.13 | 3 | 12 |
| EP2 EP3 EP5 EP6 EP7 | 1.3 | 6 | |
| EP8 EP9 EP10 | 13 | 3 | |

Table 4.11 Specimens classification according to the rate of loading.

4.2.2.3 Test Results:

It was noticed during the testing procedure, while the specimen was under loading, the crack started at the specimen surface and then propagated with further loading of the specimen until the specimen failed; finally a splitting tension failure is noticed as shown in *fig. 4.42* below [20].



Fig. 4.42 Cracking behaviour in compressive strength test [20]

The relation between load and displacement was then plotted for different loading rates, in order to show its influence on the material properties notably the stiffness of the material, the evolution of material properties along with the increase of the rate of loading are grouped in *Table 4.12* as follows:

| specimen | loading rate (mm/min) | | | | | |
|----------|----------------------------|--|----------------------------|--|----------------------------|--|
| | 0.13 mm/min | | 1.3 mm/min | | 13 mm/min | |
| | Ec (N/mm ²) | $\sigma_{c,u}$ (N/mm ²) | Ec (N/mm ²) | $\sigma_{c,u}$ (N/mm ²) | Ec (N/mm ²) | $\sigma_{c,u}$ (N/mm ²) |
| EP11 | 5407 | 73 | | | | |
| EP12 | 5961 | 74 | | | | |
| EP13 | 6581 | 75 | | | | |
| EP2 | | | 5444 | 76 | | |
| EP3 | | | 6063 | 73 | | |
| EP5 | | | 5592 | 81 | | |
| EP6 | | | 7202 | 81 | | |
| EP7 | | | 5645 | 78 | | |
| EP8 | | | | | 5659 | 91 |
| EP9 | | | | | 5914 | 90 |
| EP10 | | | | | 6472 | 90 |

Table 4.12 Regrouping results (Young's modulus and max. allowable stresses) for compressive strength results^[20].

It is obvious that an increase in the material properties is accompanied to the increase of loading rate, as an increase of young's modulus and the failure load is found to be higher for a rate of loading of 13 mm/min that that for 0.13 mm/min and 1.3 mm/min, for example a 22% and 17% increase in stiffness can be noticed for 13 mm/min comparing to 0.13 mm/min and 1.3 mm/min respectively.

A different behaviour in the curve load – displacement can be noticed due to applying different loading rates, as a tendency to a more linear behaviour is obvious for higher loading rates as shown in *fig.4.43*, as the material did not have the time to get to the non-linear phase, also a relatively slight increase in the failure load can be noticed.

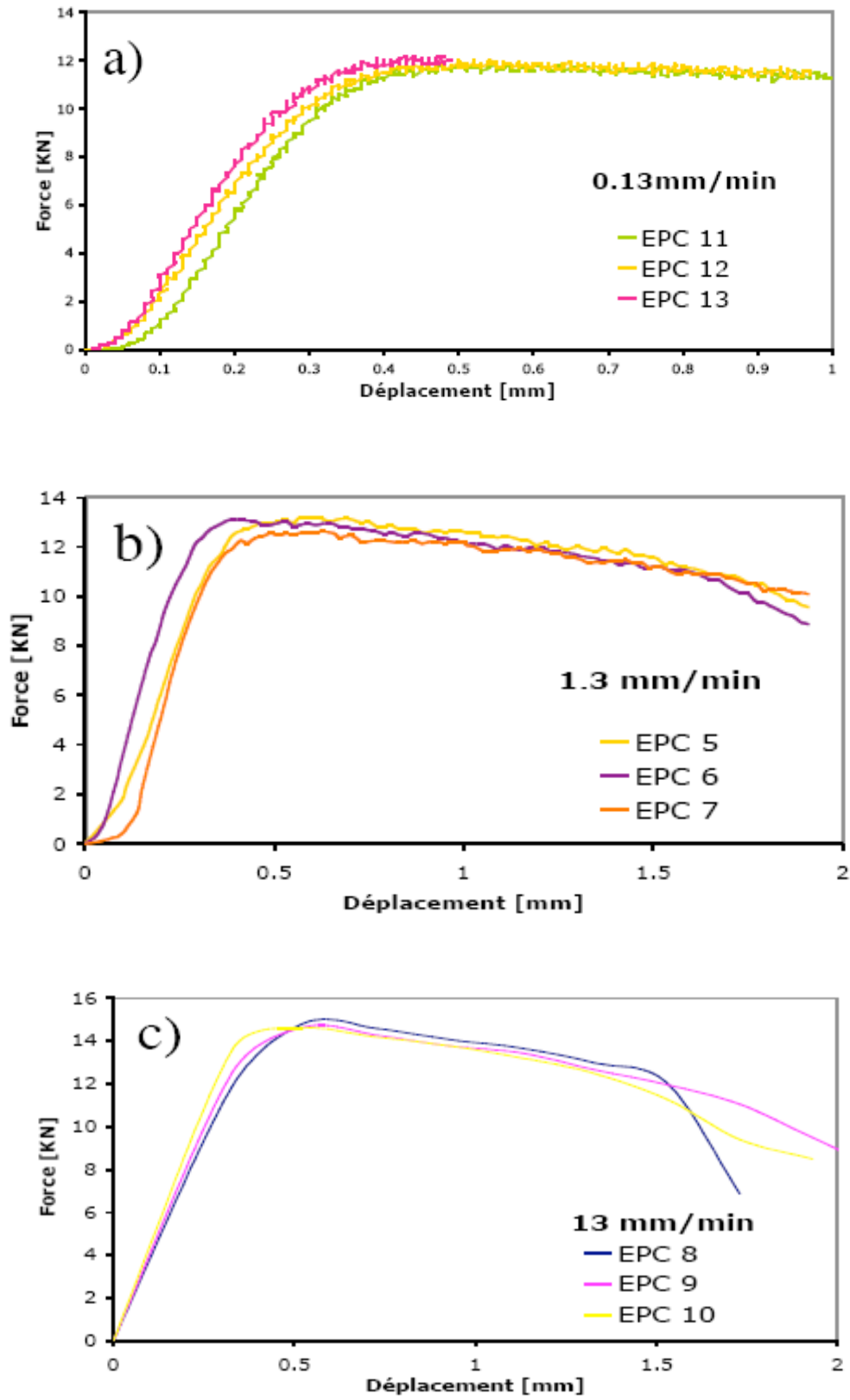


Fig. 4.43 Compressive behaviour of material under a) low b) moderate c) high rate of loading^[20].

5. Application

The main objective of this research on the physical and mechanical properties of adhesives and the relation between them is to build a strong knowledge that could assist engineers in making the right choice of adhesives during their use in the joints of bridges. As mentioned before in chapter 2, adhesives are widely used in the works of strengthening and repair of structures, but when it comes to the use of adhesives in the joints of bridges, it becomes more delicate, as the behaviour of adhesives is complicated and is influenced by several external factors like temperature which comes at first place, also other factors such as humidity, salinity as well as other factors.

In this chapter, different types of joints in a bridge will be studied profoundly within the limits of the results obtained in the previous chapter, so basically both tensile and compressive strengths will be the main two guiding factors, but other material properties such as shear strength, modulus of elasticity. could not be excluded during the study of these joints.

5.1 Advantages of the use of adhesives in bridges:

As mentioned above, several applications were carried out on the use of adhesives in bridges, most of these applications are already judged applicable others still need to carry out further studies; the recourse for adhesives in bridges was for the following main reasons:

5.1.1 High strength material

Structural adhesives are distinguished from other adhesives by being high strength materials that are designed to support loads. Such adhesives are often subjected to cycling high and low temperatures and aggressive environments (a review of different weathering conditions to which a structure is subjected will be discussed later). They are generally used for bonding rigid structures, although a degree of flexibility is required in the adhesive to counter the effects of movement, impact or vibration.

5.1.2 Workable material

Adhesives can be easily applied in structures, usually they are applied manually by skilled labour as they should be applied carefully and conscientiously, adhesives' execution should be well adapted to the type of adhesive in use.

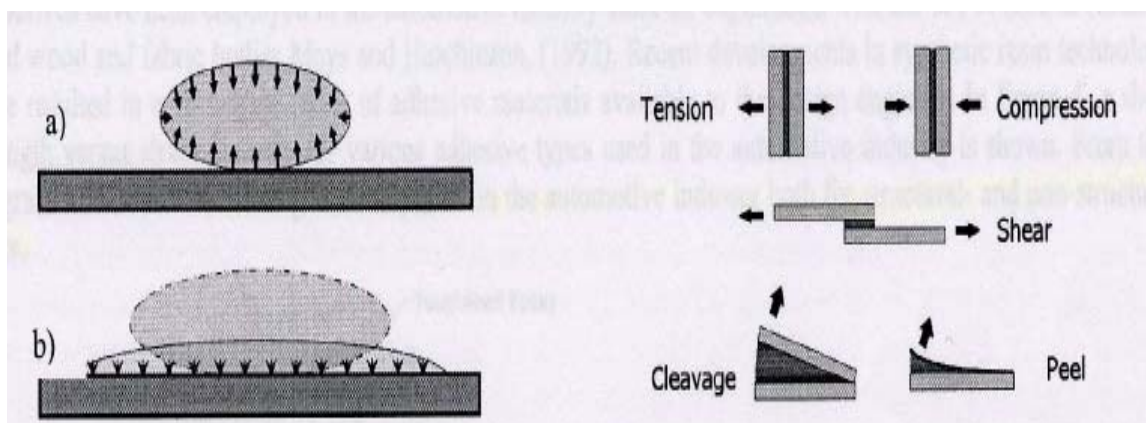
5.1.3 Easy maintenance

Adhesives are materials possessing a reasonable lifetime, also one very good advantage of adhesives is the facility of maintenance, and adhesives can be easily removed and replaced with new material.

Besides all these advantages that adhesives possess as a challenging structural material, some disadvantages can not be ignored such as influence of humidity, salinity. That is why the selection of the right adhesive represents a very important step that should be done conscientiously by the structural engineer.

5.2 Selection of the right adhesive:

The successful performance of a bonded material is dependant upon the adequate adhesion between two or more constituents. The strength of the bonded joints depends not only on the cohesive strength of the adhesive, but also on the degree of adhesion to the bonding surface. One of the disadvantages of adhesive bonding is that the surfaces need to be clean in order to obtain a satisfactory degree of contact and therefore adhesion. This is explained in *fig. 5.1* if the surface tension value of the liquid is greater than the surface surface-free energy of the substrate the liquid molecules stay bound together; conversely, when the surface free energy value of the substrate is higher than that of the liquid it allows the liquid to uniformly wet the surface as shown in *fig. 5.2*. The purpose of surface preparation is to remove contamination and weak surface layers, to change the substrate surface geometry. Different materials need different surface treatment, for example when bonding to concrete the surface is often sandblasted, then properly cleaned and often a primer for the bond system is used to enhance the bond [6].



*Fig.5.1 the importance to wet the surface
Before bonding*

Fig. 5.2 Different forces acting on bonded joint

In addition, the design of the bond joint may dictate the adhesive to use; depending on the joint design varying forces will be applied to the bond, i.e. peel versus shear, cleavage and compression, as shown schematically in *fig 5.2*. Also bond thickness and bond area will affect the ability to transfer the load. A bonded joint is preferably loaded in shear. It is also important when choosing the right adhesive to investigate the environment where the adhesive is going to be used as well as the exposure conditions. The ability of an adhesive to maintain adhesion while exposed to harsh environments varies as does their chemical resistance. All these factors will be discussed later in this chapter after a quick overview of different joints in bridges.

Before reviewing each joint separately figuring out the type of loads to which it is subjected as well as the preferred adhesive to be used, Different factors should be taken into consideration such as different exposure conditions on a bridge.

5.3 Exposure Conditions on a bridge:

Three main climatic conditions could be influencing the exposure of bridge elements and consequently the joints, these three conditions could affect the salinity rate in joints as well as the humidity, they can be reviewed as follows [27].:

A) Salty fog: influencing mainly the inferior face if the cantilever in a bridge deck, which could not be as dangerous in a bridge as there is no joints in this position.

B) Splash: could be dangerous for the borders of a bridge, which could influence the humidity of joints such as parapet and guard rail fixations (Discussed below).

C) Direct contact: affects the upper surface of the deck, so a good retaining system is indispensable for joints such as deck joints, parapet joints and guard rail fixation, as their exposure to such condition would probably reduce the mechanical properties of the material, particularly if ductile, due to the increase of humidity.

The mechanical properties are dependant on the degree of relative humidity and rate of salinity in joints, which could decrease the mechanical properties in joints as well as the composition of the adhesive in use.

5.4 Joints in bridges:

Different types of joints can be executed in bridges using structural adhesives; the ones under research by CCLAB/EPFL can be shown in the following figures:

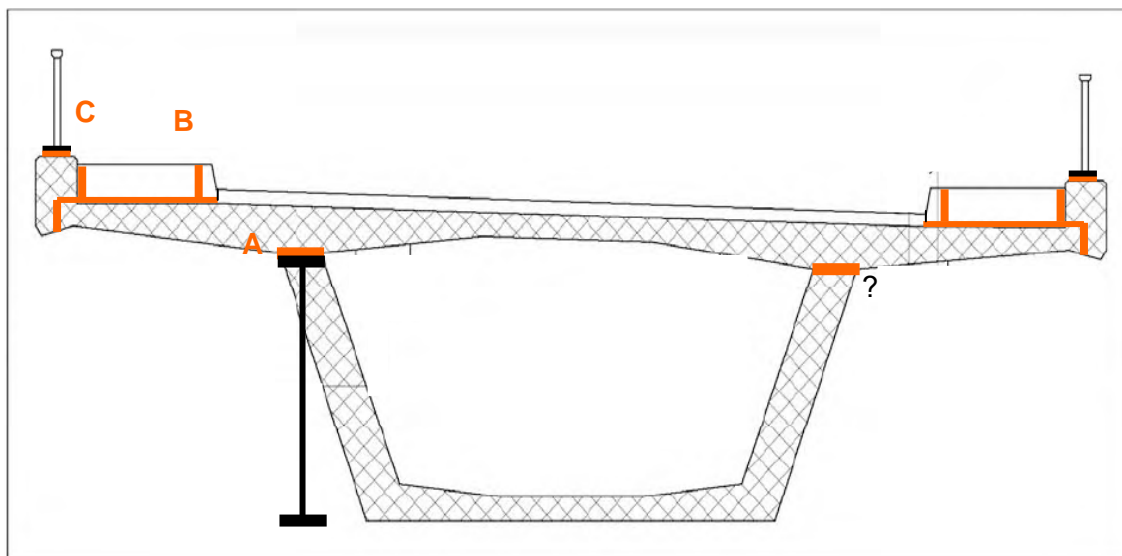


Bild 1 Beispiel Querschnitt Hohlkastenbrücke

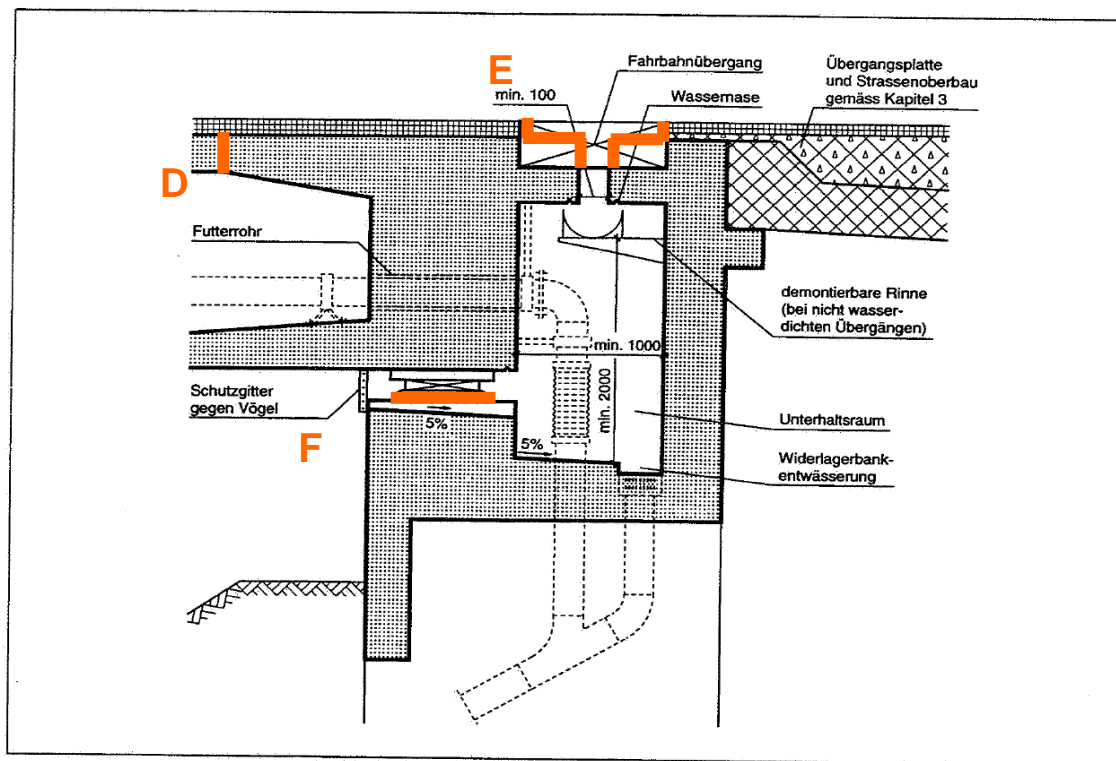


Abb. 2 Beispiel Brückenende

Fig. 5.3 Different types of joints proposed in this report.

- Where; A = Girder – deck joints in composite bridges
- B = Parapet joints
- C = Guard rail fixation
- D = Deck joints prestressed
- E = Expansion joints fixation.
- F = Bearing joints

5.4.1 Girder deck joints:

Girder-deck joints are structural joints of primarily importance, as they connect the two main load supporting members of the bridge superstructure; the deck and the girder, so any failure of these joints could simply lead to a total collapse of the structure. These joints are subjected mainly to sectional compressive and shear forces, also they are affected by creep and fatigue but fortunately subjected to low temperature and humidity ranges which could limit the effect of the heat variations on the joint, but the shrinkage of material should be considered due to curing of the material, as the volume of the material injected between the deck and the girder should be sufficient to ensure a strong bond with

both concrete deck and steel girders. Also the area and thickness of joint can be adjusted to meet design requirements and to provide a sufficient material that can resist different imposed loads considering different load and geometry factors such as bridge span, material used as well as other factors.

Given that such joints were applied and cured in ambient condition then a maximum admissible compressive stresses of 77.8 Mpa are provided by the material, this is the average value of a medium loading rate of 1.3 mm/min as for such a joints, it is only subjected to imposed loads of the structure as well as the live loads of trucks which can be simulated by moderate loading rate, which is also the standard rate according to the ASTM. Practically for ultimate limit state design the minimum area of epoxy joint can be calculated using the maximum admissible stresses and by knowing the total loads to be transmitted to the substructure, also other conditions are to be fulfilled such as a) a reasonable thickness of joint for better charge distribution is required, b) the joint area calculated should be complying with the area of the upper flange in case of I-beam girders for instance. Finally, a simple formulation of the area can be shown as follows:

$$\frac{F}{A} \leq \sigma_{c,u}$$

Where; F = Total load to be transmitted from both dead and live loads

A = Area of the epoxy joint

$\sigma_{c,u}$ = Maximum admissible stresses in epoxy

For example a joint of 300*300 mm² can sustain a load of almost 7000 KN, which is found more than reasonable in bridges taking in consideration the thickness for the distribution of these forces.

Another force that should have been taken into consideration is the shear forces, but unfortunately results for shear strength in epoxy are still in preparation phase.

5.4.2 Parapet joints:

A parapet joint is a very delicate joint, but very useful in case of bridges as the parapet is the most exposed part to splash water which requires a regular maintenance, generally for

maintenance the concrete of the parapet around the reinforcement hook is removed and a new concrete is placed, which requires a bond between old and new concrete elements. Parapet joints are semi-structural joints, that carry statically only the parapet's own-weight, but it is subjected to impact which is another factor that should be planned for further research, the parapet joints are subjected to flexural stresses in case of accident which causes an impact so the upper part of parapet will be subjected to tensile stresses whilst the lower part will be subjected to compressive stresses. Finally a model of both Impact and compressive or tensile stresses should be simulated in order to get a better idea about the behaviour under such stress combination. It is believed that the combination between impact and compressive stresses would be the worst case as with compression the brittleness of the material is higher as the deformability of the material is almost restrained, so in this case a more ductile and deformable material is needed to be used in order to absorb the energy generated from the impact. The design of these joints is dependant also on the material used for the sidewalks and the "vehicle restrain system" as well as its height.

5.4.3 Guard rail joints:

These are structural joints that are subjected mainly to tension accompanied by peeling as well as shear stresses, as for a parapet joint a deformable ductile material such as polyurethane is preferred to be used in such joints as it is mostly exposed to impact forces, the own weight of the guard- rail which exerts compression force on the joint can be neglected. Another parameter that should be taken into consideration is the high temperature and humidity ranges to which this type of joints can be subjected; it is indispensable to study the environmental and exposure conditions for each bridge case independently in order to understand the influence of these variations on the joints as it could force thermal stresses on the joints which should not be neglected.

5.4.4 Deck joints:

Deck joints are structural joints similar to those of deck-girder joints, subjected mainly to shear and compression, so a stiff brittle material such as epoxy is preferred, the only difference is that these joints are more exposed to environmental conditions particularly if

the road surfacing was not of a good quality. These joints are subjected to creep and fatigue as well, which require more research in this field.

5.4.5 Expansion joint fixation:

This is a very traditional application in bridges, expansion joints are semi-structural joints that consist of a pair of metal plates that are usually fixed to the concrete using hook reinforcement, so in case of maintenance the concrete around the hook should be removed which cause complications to the engineer when casting new concrete, so gluing the plates in the concrete could represent a good solution which facilitates the maintenance of the joints as well as guarantee a strong fixation for the expansion joint.

These joints are directly exposed to continuous live load of vehicles, so a resistible joint should be formulated in order to be able to get through different environmental variations; this could be another reason why for an expansion joint a more flexible and slow curing resin like polyurethane can be successfully implemented. Also fatigue study is very important in this type of joints as they are subjected to dynamic loads from the trucks passing on the bridge.

5.4.6 Bearing joint:

Bearing joint is another classical application for adhesives in bridges, these structural joints are designed to transmit loads, notably compression and shear, form the main supporting element to the substructure, and so a refined design for the joint is needed, giving a sufficient area to resist the loads as well as a sufficient thickness for a better load distribution.

| Joint | Type | Loads | Considerations | Notes |
|-------|---------------------------|---------------------------------|--|----------------------------|
| A | Girder – Deck joints | Compression - Shear | Creep – Fatigue – Bond between elements | Structural / critical |
| B | Parapet joints | Flexure (compression – tension) | High temperature and humidity ranges - Impact | Semi-structural / Critical |
| C | Guard rail fixation | Shear - Compression | High temperature and humidity ranges – Impact - peel | Structural |
| D | Deck joints prestressed | Shear - Compression | High temperature and humidity ranges – Creep - fatigue | Structural |
| E | Expansion joints fixation | Tensile | High temperature and humidity ranges – Fatigue - Peel | Semi-Structural / Critical |
| F | Bearing joints | Shear - compression | | Structural |

Table. 5.1 Different types of joints summary.

Table 5.1 summarizes the important information and details concerning each type of joint, including the loads to which such joint is subjected, other important considerations as well as the criticality of each joint.

6. Conclusion and future research:

Although the adhesive behaviour is found to be complicated, it seemed to be a good applicable material that can facilitate different joints formulations and maintenance in bridges. It became clear now how the choice of the adhesive is very important in formulating resistible joints.

The applicability of joints and a good performance are ensured if and only if the suitable type of adhesive is chosen as well as a refined design is carried out. The choice of whether apply a ductile or brittle adhesive is highly dependant on the application to which it is specified for example using ductile and flexible adhesive for joints subjected to impact which could help in the absorption of energy released due to this impact.

Finally the factors affecting the choice and design of adhesive can be summarized as follows:

- Position and type of joints in bridges
- Type of loads and forces to which the joint is subjected
- The physical and mechanical characteristics of the chosen adhesive
- The environmental and exposure conditions to which the joint is subjected
- The possibility of a regular maintenance of the joint

Physical characterization of the material helps in a better understanding of behaviour of adhesives under different temperature ranges. This is achieved by investigating the curing behaviour (conversion degree and conversion rate) as well as the evolution of the glass transition temperature following the curing process.

A model is proposed to predict the curing behaviour under any given temperature. It was found to be providing results that are not conform with the tests results as checking the compatibility between the model's results with the test results show that for low temperatures, this model gives curves that are far from reality (testing), depending on the behaviour of the material as it is believed is a mixed and complicated behaviour between nth order and autocatalytic. For lower temperature it seemed that the model can simulate more or less the rate of curing as at least it could be possible to simulate the behaviour of

the curve with a similar slope i.e. the rate of increase of curing but not the final curing degree as this last parameter should be integrated by the designer in the model, on the other hand for higher temperature it sounded less precise in predicting the material's behaviour, so the model should be well adapted to suit a mixed behaviour of the material. That is why these models are mainly used in case of 100% curing is expected.

Investigating the mechanical properties of epoxy gives a good idea about the range of strength and stiffness provided by the material in both compression and tension. This helps the engineer to make the right choice of adhesive for a specific application. Mechanical properties of adhesives found to be more or less related to physical properties especially the curing temperature and time. Finally it is recommended, for both tensile and compressive strengths, that joints' execution takes place at a minimum curing temperature of 25°C in order to get a sufficient strength for load sustainability.

Future work should be taking place in order to collect reliable information on the characteristics and behaviour of these materials under different environmental and mechanical loading conditions as well as the combination between both, such as the shear strength, resistance to impact, peel, creep, humidity...Etc. Also testing in different environmental conditions is needed as all the executed mechanical tests in the scope of this project were carried out in ambient condition.

References:

1. G.C Mays and A.R Hutchinson, *Adhesives in civil engineering*.
2. W.J Sichina, *Better DSC isothermal cure kinetics studies using power compensation DSC*.
3. W.J Sichina, *Prediction of epoxy cure properties using pyres DSC scanning kinetics software*.
4. W.J Sichina, *Characterization of epoxy resins using DSC*.
5. TA Instruments, *A review of DSC kinetics methods*.
6. B.Taljsten, *The importance of bonding – An historic overview and future possibilities*, Department of civil engineering, Technical university of Denmark, Denmark.
7. J.Y. Lee, H.K. Choi, M.J.Shim and S.W.Kim, *Kinetic studies of an epoxy cure reaction by isothermal DSC analysis*.
8. H.K.D.H Bhadeshia, *Thermal analysis techniques*. University of Cambridge, materials and science metallurgy.
9. H.K.D.H Bhadeshia, *Differential scanning calorimetry*. University of Cambridge, materials and science metallurgy.
10. *Effet de microclimat sur l'initiation de la corrosion de l'acier d'armature dans les ouvrages en béton armé*. EPFL
11. Mangeng Lu and Sangwook Kim, *Kinetics and thermal characterization of epoxy-amine systems*, Department of chemical engineering, university of Seoul.
12. Liangfeng Sun, Ioan I. Negulescu, Su-seng Pang and Arthur M. Sterling, *Characterization of epoxy prepreg curing process*, Department of mechanical engineering, Louisiana state university.
13. G. Wisanrakkit and J.K. Gillham, *The glass transition temperature (T_g) as an index of chemical conversion for a high-T_g Amine/epoxy system: chemical and diffusion-controlled reaction kinetics*, Department of chemical engineering, Princeton University.
14. B.G. Min and Z.H. Stachurski, *Cure kinetics of elementary reactions of a DGEBA/DDS epoxy resin:1. Glass transition temperature versus conversion*, Department of material engineering, Monash University, Clyton, Victoria, Australia.
15. A. Schiraldi, P.Baldini and E.Pezzati, *Epoxy polymers: Glass transition / cure degree correlation*.
16. Darren A. Riedlinger, Nanijian Sun and Charles E. Fraizer, *T_g as an index of conversion in PMDI- Impregnated wood*.
17. Y. Lei, Q. Wu, K. Lian, *Cure kinetics of aqueous phenol-formaldehyde resins used for oriented strandboard manufacturing: Analytical technique*
18. J.H.Flynn, *A general differential technique for the determination of parameters*, scientific thermal research and data analysis.
19. A. Cherdoud-chihani, M. Mouzali et M.J.M. Abadie, *Paramètres cinatiques de systèmes Epoxy/Acide par analyse calorimétrique différentielle (DSC)*.
20. Sarra Ben Houala, *Essais mécaniques sur résines d'epoxy et de polyuréthane*, Ecole polytechnique fédérale de Lausanne.
21. R.F Mander, *Use of resins in road and bridge construction and repair*.

22. Thomas Keller and Herbert Guertler, *Composite action and adhesive bond between fiber-reinforced polymer bridge decks and main girders.*
23. Thomas Keller, *Influences of advanced composite materials on structural concepts for bridges and buildings*, Swiss federal institute of technology, Lausanne, Switzerland.
24. Thomas Keller, Julia de Castro and Martin Schollmayer, *Adhesively bonded translucent glass fiber reinforced polymers sandwich girders.*
25. ASTM D 638, *Standard test method for compressive properties of rigid plastics.*
26. ASTM D 638 *Standard test method for tensile properties of plastics.*
27. E. Bruewiler, *Structures existantes 1*, Ecole polytechnique fédérale de Lausanne.
28. Wikipedia.org