Protection of topside against the arctic environment

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Declaration of Authenticity and Author's Rights

This thesis is the result of the author's original research. It has been composed by the author and has not been previously submitted for examination which has led to the award of a degree.

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Abstract and key words

The integrity of the floating platform represents the main research topic of offshore engineering. As offshore engineering is moving to the Arctic, new issues and challenges will be raised, mostly related to the unusual Arctic environment. To maintain a high level of safety, the topside of the floating platform should be protected against the Arctic environment. This protection must present a low maintenance and a high efficiency.

The past investigations in the field of integrity in arctic offshore engineering are generally related to the structural integrity, fracture mechanics and fatigue analysis. The icing maintenance has been recently studied for the shipping industry in order to simulate the icing on a structure and to determine the most appropriate method to remove it. However, the prevention against cold temperature effects and icing on the floating platform deck has not been extensively studied.

Polymer engineering represents one of the most active research fields in material engineering. Polymers have been extensively studied during the last 40 years. They are currently used for various applications in a lot of industries. The polymer material could present very different properties, depending on its molecular structures, and therefore could be used in different situations.

The protection against cold temperature and icing has been recently studied for curative maintenance. However, an efficient preventive protection against cold temperature and icing still has to be determined. As it is not always possible to increase the thickness of metal parts, an appropriate polymer may represent an efficient and reliable solution.

The purpose of this project is to determine the feasibility of using one or more polymers to protect an engineering active system against the Arctic environment by reducing the heat transfer and the risk of icing and increasing the hydrophobic property. As there is not any accurate model to simulate the behaviour of a polymer for a large range of temperatures, two serials of experiments will be realised. After producing small sized samples, a differential scanning calorimetric test will be carried, followed by a dynamic mechanical analysis. Then, the properties related to the extreme cold temperature will be studied to determine the efficiency of a polymer coating against the arctic environment.

Key word: arctic engineering, heat transfer, icing, hydrophobic, glass transition temperature, differential scanning calorimetric, dynamic mechanical analysis, storage modulus, loss modulus, low maintenance

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Aims

The main purpose of this thesis is to study the feasibility of using polymer materials to protect the engineering active systems, particularly offshore structures, offshore facilities and topside equipment against the Arctic environment. To achieve this objective, the project is developed around three main tasks:

- Identification of issues and challenges related to the Arctic Environment.
- Identification of appropriate materials able to face such issues and challenges and determining main properties of those materials.
- Performing serials of experiments to assess or confirm properties of materials aforementioned and defining a realistic and efficient solution to avoid icing, water infiltration and loss of heat.

1 Literature Review

1.1 Introduction

The hydrocarbon industry is always looking for new fields to explore and produce oil and gas. There are currently two new "exploring directions".

The first is the ultra-deep water. The offshore and subsea industry is now able to access ultra-deep water and provide reliable solutions to produce oil and gas.

The second is the arctic and the Antarctic Exploration and Production E & P, which will be developed in this thesis. The Oil & Gas E & P in Arctic and Antarctic zones represents real technical challenges due to harsh conditions most of the year such as cold temperature, wind and restrained access (a few weeks to a few months). The Hibernia Oil Platform (Jeanne d'Arc Basin – North Canada) is designed to operate with 5 months access per year, where a complete arctic project is accessible for less than 2 months a year. The restrained access to a few months a year governs maintenance frequency. Under some weather conditions (cold temperature associated with wind), maintenance and more particularly corrective maintenance might be cancelled and avoided. The limitation of maintenance frequency or the lack of corrective maintenance will shorten the Arctic offshore platforms and/or topside equipment life cycle (even when this is limited to 10 or 15 years) that makes oil & gas E & P less competitive.

On the other hand, working in severe conditions due to cold weather requires the preparation of operation crews and protecting them against the cold.

Based on what was said before, the development of new materials constituted of polymers has become more and more justified to protect facilities, equipment and workers operating in cold weather such as in the arctic and Antarctic zones.

The 21st century will face a considerable increase of oil and gas demand due to the increase of energy demand linked to rapid population growth. Hence, the Oil & Gas Industry will be obliged to invest in cold and very cold regions to satisfy the growing needs of energy and to develop new materials to protect facilities as mentioned before.

1.2 Exploration of the arctic environment

The Arctic is a polar region located in the geographic northern part of the Earth. It is generally admitted that the Arctic region is limited by the Arctic Circle. The Arctic consists of an ocean (the Arctic Ocean) with some ice-covered areas surrounded by permafrost. Alternatively, the Arctic region can be considered the northern part of the Earth where the warmest month is below 10 °C. The Arctic region regroups eight countries: Canada, United State of America (Alaska), Russia, Sweden, Iceland, Finland, Norway and Denmark (Greenland). The Arctic Regions have been inhabited since the 2500 BC and were regularly visited by the Vikings during the Middle Ages. The Arctic Ocean became regularly explored during the 16th and 17th century as the English, French and Spanish Navies were looking to find the Northwest Passage to connect Europe to America without crossing the Atlantic Ocean. The modern exploration of the arctic environment started during the nineteenth century. The purpose of these exploration missions was mostly to increase the knowledge about the arctic environment and also increase the domination of new lands in order to control the shipping traffic and the potential resources of the Arctic underground. The arctic environment became more attractive for energy companies during the twentieth century when major oil and gas fields had been discovered, particularly in Alaska, northern Canada and Siberia. During the 80’s, the production of oil and gas from onshore fields was developed. But, as in other regions, the oil and gas industry is slowly moving offshore. Some offshore shallow water projects were realized in northern Norway and northern Canada, where the environmental conditions could be considered as arctic conditions. However, these projects are using fixed platforms, mostly concrete gravity based structure platforms. The most famous project with an accurate and regular evaluation of the platform and the production is the Hibernia project. It is important to notice that some region could present the Arctic environment outside of the Arctic area. It is the case for the northern part of the Caspian Sea, which often presents the same meteorological characteristics as the Arctic regions.

1.3 Main issues related to cold temperature and harsh environment

The arctic environment and more specifically cold temperature has a lot of consequences on floating platforms, which can affect their integrity, maintainability and operability through some issues or phenomena listed below.

The notion of cold temperature is not objective. It can be considered as cold by someone or a system, and warm by someone else or another system. In some arctic regions the temperature changes all year long from -70°C to +15°C . In other regions such as North Canada, North White Sea… the average temperature changes between -70°C and -20°C all year long. This level of temperatures causes a lot of concerns:

- Decrease of the efficiency of some systems
- Decrease of the availability of some systems
- Decrease available time for maintenance
- Modification of properties of Structural Material
- Decrease the available time for inspection and survey
- Modification of main properties of coating used on the platform
- Decrease the efficiency of the crew for outside work

As shown, cold weather could generate issues related to human factors and to properties of material. The human factors could partly be overcome by an appropriate training and the use of appropriate individual protection. However, even with an intensive training and an appropriate protection, the cold will still have an impact on the efficiency of the crew and on every task requiring crew members.

The cold temperature also has a significant impact on the properties of material. It is important to rank material into two different categories. Some materials are used for structural purposes and others are used for coating and surface protection purposes. For a structural material, most of the issues are related to the decrease of the elasticity of the material and the creation of a high number of plastic fractures. The decrease of elasticity will increase the rigidity and the brittle behaviour and risk of failures that reduce the life cycle of the material. Plastic fractures could seriously damage the structure, particularly in the case of water infiltration.

For coating and surface protection materials, cold temperatures will result in their deterioration by the creation of plastic fractures and the emergence of erosion and corrosion. The plastic fractures occur through the creation of numerous creases that reduce the capacity of the coating to efficiently protect the surface of the material. The erosion occurs faster with cold temperature, especially with icing. The erosion reduces the thickness of the coating material and consequently its thermodynamic efficiency.

The decrease of thermodynamic efficiency intensifies the heat transfer and consequently accelerates the corrosion of structure and equipment. This last phenomenon is responsible for the shortening of the life cycle of the structure, equipment, and facilities.

A more complex phenomenon was reported. The accumulation of ice on a structure will generate ice-induced vibrations, specifically when the ice sheets pass through the legs of the structures (Yue, 2008). These excessive vibrations can increase the risk of failures of deck units and risk fatigue failure.

1.4 De-icing methods

The accretion of ice on structures, as seen on Fig 1.1, causes regular maintenance and production stops in Oil & Gas offshore E&P in cold weather zones. The removal of ice solution is difficult, time consuming and costly. As a result, several studies are done by SINTEF's Polar Group to improve anti-icing properties of materials, to assess ice accretion and to develop de-icing methods.

The icing process can be divided into different phases. These phases were well described and studied on wind turbine blades (Kraj, 2009). Four phases are normally described: the pre-icing phase, the operational-icing, the stopped-icing and the posticing. At the end of the fourth phase, the wind turbine remained non-operational due to residual damages. It may become operational.

Correlations between anti-icing properties of a material and its hydrophobicity have been established, and it has been concluded that a high hydrophobicity (contact angle of 90°) generally induces good and durable anti-icing properties.

To assess the ice accretion, SINTEF's has developed a one-dimensional model IceMod for plane and cylinder surfaces. IceMod is continually in development to be extended to 2D simulation and to 3D structures.

De-icing methods could be organized into three different categories: chemical, mechanical and thermal.

- Chemical de-icing:
  - Low adhesion coating surfaces
  - Freezing-point depression fluids

Chemical de-icing methods are expensive, require a lot of time and cannot provide a long term protection. They are extensively used in aeronautical engineering in order to protect aircrafts from icing during the flight.

- Mechanical de-icing:
  - Drilling, cutting, sawing
  - High-pressure jet
  - Pneumatic devices

The mechanical methods are efficient but require a lot of time and cannot prevent future icing. Also, the drilling and sawing methods can decrease the integrity of the structure and cannot be done during very cold weather.

A semi-active solution was studied in order to increase the mitigation of ice by increasing the level of vibration applied to the iced structures (Mroz, 2008). This solution might require a lot of energy, particularly for large structures, but can represent an interesting solution for non-offshore structures (pillars and beams).

However, this solution has only been tested numerically, and the lack of a precise model of ice material was pointed out. The results should be verified experimentally.

- Thermal and electrical de-icing:
    - Heaters
    - Electrolytic protection
    - Electro-pulses techniques

The thermal method consists of heating the structure or equipment.

The electrical protection method uses electro-pulse systems to destroy ice on the protected surface. A series of regular “electrical pulses” could protect a large surface of a ship or a platform. The electro pulse system might be used on a drilling platform if the energy generator is coupled with the drilling system. The electro pulse system could also be used on a production platform, using the energy produced by the energy generator (using the gas extracted from the crude oil). But the electro pulse system could not be used on a wind turbine or a small ship, as they might not be able to provide the required energy.

Thermal and electrical methods require a lot of energy to be managed properly and for continuous maintenance to be efficient. They cannot be used to de-ice or protect a floating structure not able to provide the required energy to make those methods usable. This is the case for logistics vessels, transportation boats, and non-manned platform.

Figure 1-1 Icing on a deck

1.5 Offshore Arctic projects

Three major Oil & Gas Offshore developments have been conducted within the Arctic Circle in three major areas: Sakhalin Island (Far East Russia), Jeanne D'Arc Basin – Hibernia Platform – in North Eastern Canada and Cook Inlet in Alaska, as seen in the Figure 1-2.

The development of other projects is on-going. Some of them are in the design stage (Shtokman – Russia), or construction stage (Yamal – Kara Sea – Partly offshore).

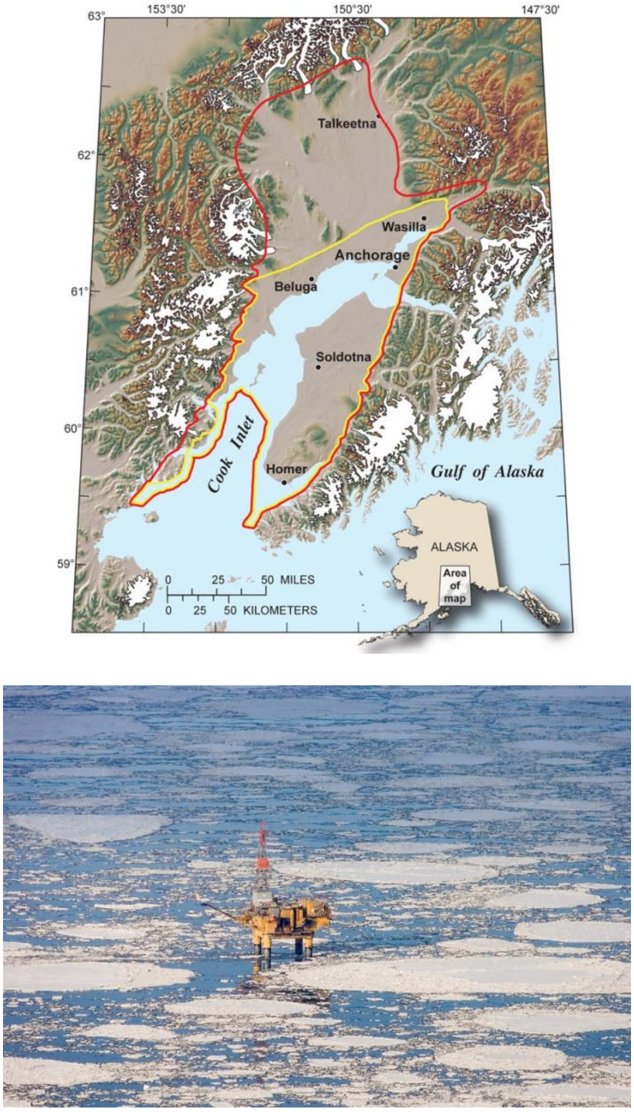


Figure 1-2: Cook Inlet Platform – Alaska (Cook Inlet includes more than 16 platforms)

Hereafter, two projects will briefly be described: the Hibernia Project, which has been in production since 1997, and the Shtokman Project, the design of which is ongoing.

1.5.1 Hibernia Project

The Hibernia project is an offshore arctic project, using a gravity based structure GBS platform to realize the exploration and the production of the Hibernia field.

The Hibernia platform (Figure 1-3) is a fixed one. It is located in shallow water of 80 m depth at 315 kM East-Southeast of Saint John's, Newfoundland, Canada. The Hibernia topside extends 50 m out of the water. The entire structure has an approximate weight of 1.2 million tons. The development of the field started in 1987 and the production in 1997.

The Hibernia platform is operating in a semi-arctic environment, which is considered fully arctic during a few months per year. The Hibernia platform was therefore designed for these arctic conditions and has some unique features to allow a full year production:

- Wellhead, made of two mobile drilling derricks, partially closed, in order to protect the crew
- Processing unit, which separates oil, gas and water and injects some of the gas and water
- Mud unit, which produces and pumps the mud through the drill pipe and the drill holes
- Utilities modules, which contain the required equipment necessary to generate the power, produce the heat, run the ventilation and distribute the water
- Accommodations, which represent the living units for the crew and are totally insulated against cold in order to protect the crew
- A concrete gravity base structure designed to withstand the impact of sea ice and icebergs
- The platform contains several production storage tanks and magnetic ballasts

The Hibernia has the possibility of performing a complete maintenance operation or an integrity analysis. Also, there is always a supply vessel at a commuting distance in order to supply the crew with necessary goods but also to perform some fast maintenance operations.

Although the Hibernia platform is not in complete isolation, it still requires some protection and maintenance due to the arctic environment.

Figure 1-3 Hibernia platform

1.5.2 Shtokman project

The Shtokman project (Russia – Barent Sea – Kola Peninsula) is at design stage. Its development is intended to start by 2017.

The Shtokman, Condensate and Natural gas field is located in the northwestern part of the South Barents Basin in the Russian sector of the Barents Sea at more than 600 kilometers of the Kola Peninsula.

The Shtokman field is considered one of the largest non-associated gas fields in the world. Its development requires a 320 m length floating platform unit FPU for gas separation and processing. The FPU is not intended to include any storage capacities. Gas will be directed by subsea pipe to shore located close to Murmansk city at 600 kM from the field in order to be liquefied and exported as a liquefied natural gas. Although Shtokman field is not located in a high probability iceberg area due to shallow water, the FPU cannot sustain an impact with a large iceberg. The FPU, risers and flowlines systems can be disconnected to avoid an iceberg and to prevent any emergency due to the arctic environment. The main issue faced by the Shtokman project is partly due to the arctic environment and partly due to the long distance between onshore base support and the field (more than 600 km).

The Shtokman platform should normally face an arctic environment for 6 to 8 months per year with regular maintenance and a regular supply (Russian Authorities plan to use nuclear icebreakers to insure logistics and maintenance during ice periods). As with the Hibernia platform, the Shtokman FPU is not in full isolation. However, the topside and equipment are designed to remain in operation year round. Some of the equipments will be heated, and others will be coated to keep them in service.

1.6 Mechanisms of Heat Transfer

Since the purpose of this research is to define an efficient method to protect a platform topside or a ship deck against cold weather, it is necessary to review some basic thermodynamic laws, and particularly heat transfer theory. There are three types of heat transfer:

- The conduction: transfer of heat caused by temperature gradient between 2 parts of the same solid or 2 solids in contact (fluids are less conductive than solids. Their conductivity increases with temperature and pressure).

- The convection: transfer of heat by fluid movement (gas or liquid). The convection is defined by heat transfer between one solid and one fluid (liquid or gas). The convection is experienced every day when we interact with air and feel the cold. A simple convection problem is often represented by a surface exposed to a static fluid or a pipe exposed to a steady dynamic fluid.

- The radiation: electromagnetic transfer of heat and the only one able to transfer energy in a complete vacuum.

The conduction represents the most efficient way to transfer heat from one solid to another. An insulation to be efficient requires having very low thermal conductivity. The heat transfer by conduction can be expressed by different equations, depending on the geometry of the system. The heat transfer is different for a simple wall and a pipe system. For a simple two-plan surface, in direct contact, the following equation, the Fourier Law in 1 dimension can be used. (Holman, 2010)

$$q = -kA\frac{\Delta T}{\Delta x} = -kA \times \frac{T_2 - T_1}{x_2 - x_1}$$

- q represents the heat transfer
- k is the thermal conductivity (W/m.K)
- T is the temperature of each solid, in Kelvin
- x is the distance between two points in the solid, in meters

- A is the area normal to the heat transfer

The following equation represents a basic heat transfer by convection between plane surface and static fluid with known temperature.

Convection equation (Holman, 2010)

$$q = hA \times (T_s - T_f)$$

- q represents the heat transfer
- h is the convective heat transfer coefficient (W/m².K)
- A is the area of the solid in contact with the fluid, in m²
- Ts is the temperature of the solid, in Kelvin
- Tf is the temperature of fluid, in Kelvin

It is important to note that the flow of the fluid has an important impact on the heat transfer. If the solid is warmer than the fluid, the heat transfer comes from the solid to the fluid. The temperature of the fluid will then be increased. However, if the fluid is not static but dynamic, which is the real situation, the flow of the fluid will be the main factor affecting heat transfer. A fluid with a fast flow will exchange more heat with the solid than a solid with a slow flow. Also, the convection applied to the engineering system, generating heat and exposed to air, should include the humidity of the air. A high level of humidity will increase the heat transfer, and a low level of humidity will reduce the heat transfer. As the purpose of this study is to identify appropriate material to reduce the heat transfer and avoid icing, no flow of dry or wet air will be considered.

The radiation represents the heat transfer generated by a solid emitting light. The light is composed of photons. The impact of the photons on a surface will generate energy and, therefore, heat. It is important to note that the radiation heat transfer is the only type of heat transfer that cannot be stopped by the vacuum. However, the heat transfer generated by radiation is so reduced compared to the conduction and the convection that it can be ignored during the calculation.

Radiation equation (Stefan-Boltzman Law) (Holman, 2010)

$$q = \epsilon \sigma A \times T^4$$

- q represents the heat transfer
- ϵ represents the emissivity of the body, always between 0 and 1
- σ is a constant, equal to 5.6697×10^{-8} W/m^2.K^4
- A is the area of the emissive body, in m^2
- T is the temperature of the emissive body, in Kelvin

In order to reduce the effect of cold temperature on the topside, it is necessary to reduce the heat transfer between the warm body (topside) and the cold one (cold environment). Thus, most of the simulations are done to determine heat transfer parameters and their values. Those results are important to define and to design the appropriate materials corresponding to the values' outcome from simulations.

1.7 Organisation of a platform, different units

The topside of a floating production exploration and production platform cannot be considered passive. Even though the technology brought by the Siberian pipeline installation could be used to increase the integrity of the platform, the topside cannot be compared to the Siberian pipeline. (Det Norske Veritas, Oil and gas processing systems, 2010).

The topside is mostly composed of four different units:

- The production and processing unit, which has to process the crude oil and represents the most complex unit on the topside (Low pressure processing and high pressure processing, security valves systems for oil, gas, water and sand).
- The electrical and control systems which have to produce the required energy and manage the distribution of water, electricity, heat and ventilation.
- A water and gas injection unit, which manages the constant injection of water and gas in the field in order to maintain an appropriate production pressure.

- Wellhead and mud units, which are made of one (sometimes more than one) drilling unit and a complex mud processing plant.
- Accommodations and offices unit, which is made by some accommodation and living modules and some offices modules.
- The flaring system, which has to burn the excess of gas in case of surpression.
- The export of hydrocarbon system, which has to manage the export of oil and gas to a tanker or a pipeline.

Even though the wellhead and mud unit are not always present on a production platform (FPSO), the study will include the drilling unit, as it requires specific protection against the arctic environment as well as a specific training for the crew (which has to do a full time operation for a few months).

The topside is also organised in segments. Each segment represents a number of components forming part of the pressure system, consisting of pipes and valves. A segment can be automatically closed-in by an emergency shutdown valve. The segment also defines the maximum volume of fluid or gas that can be released from that system in the event of a failure in any of the components. Some segment could contain liquid and gas; however, this situation is rare and must be analysed specifically.

The organisation in segments is necessary in order to perform an analysis for the same pressure. A segment inspection requires shutting down the inlet valve and the outlet valve after a vacuum procedure. Thus, maintenance operations will be faster and more reliable.

2. Methodology of work

2.1 Properties of material and organisation of materials

Different materials could be considered for usage as a protective coating on a platform. The engineering material could be organised in three categories. The first category regroups all the metals. The second category regroups the ceramic materials and the last category regroups the polymer materials.

Metals are considered an arrangement of positive ions, surrounded by a large quantity of non-associated electrons. Metals present a large range of different properties and could be used in a lot of application fields. However, metals have some common properties: they generally are good electrical and heat conductors. They cannot be used as an insulator to reduce the heat transfer. Also, even if the transformations of metals are well known, installing or replacing a large metallic part with a complex shape represents a complex maintenance operation. This might not be realised on time during a non-icing period (short arctic summer).

Ceramics are non-metallic solids, inorganic, and prepared by transformation, which requires a heating and cooling process. Ceramics generally have crystalline, or partial crystalline, structures. However, some ceramics can be amorphous (glass is an amorphous structure). Ceramics were the first material to be formed by humans. Ceramics are hard and a strong material in compression but cannot sustain shearing and tension stresses. Two of the most important properties of ceramics are their resistance to high temperatures and their relatively low thermal conductivity. Therefore, they are often used to insulate a material against high temperatures. Ceramics are brittle and often present some defects at a microscopic level, which can become a large fracture. In the present case, due to the arctic environment, it is likely to have a cycle of rain or snow followed by extreme cold temperatures. This can cause an important risk of infiltration of water into the defect. Water will then solidify due to the sub-zero temperature, which will increase the size of the defect, reduce the life cycle of the material and then reduce the integrity of the material. A protective coating made of ceramics can sustain a large range of temperatures but cannot sustain a long series of icing cycles.

A polymer is a macromolecule composed of a repetition of structural units. There are a large number of different polymers with a large range of properties, as even a simple modification of the molecule could lead to a complete new material with new properties. The preparation of a polymer is generally made with a solvent: the solid part of the polymer is dissolved in the solvent. Then, the solvent evaporates. The polymer is then cured and ready to be used. Polymers generally have weak mechanical properties and are rarely used for structural purposes. A particular category of polymer, the polyurethane materials, has some interesting properties in terms of heat transfer.

Therefore, a polymer, or a successive layer of different polymers might represent the most appropriate solution to protect a floating topside exposed to the arctic environment.

2.2 Glass transition temperature

An important property of a polymer material exposed to a large range of temperatures is the glass transition temperature. The glass transition temperature is the transformation of an amorphous polymer (or the amorphous regions of a semi crystalline polymer) from a hard brittle state to a molten and elastic state. If a polymer reaches and exceeds the glass transition temperature, its properties will change. In the present case, with a polymer material used between +100 C° and -70 C°, the glass transition temperature should be the lowest possible in order to maintain a relatively good level of elasticity for a large range of temperatures. In the glass transition temperature, the thermal expansion, the heat capacity and the shear modulus suddenly change.

However, it is important to notice that the glass transition cannot be considered a phase transition.

The glass transition temperature of a polymer, or a group of polymers organised in layers, can be determined by using different methods. Two of these methods are the differential scanning calorimetric test and the dynamic mechanical analysis. However, the dynamic mechanical analysis can only provide a range of temperatures. The differential scanning calorimetric can provide an accurate glass transition temperature generally with a diagram presenting the Heat Capacity against the temperature. Figure 2-1 represents an example of a glass transition temperature determined by a differential scanning calorimetric test and with a diagram Heat Capacity/temperature.

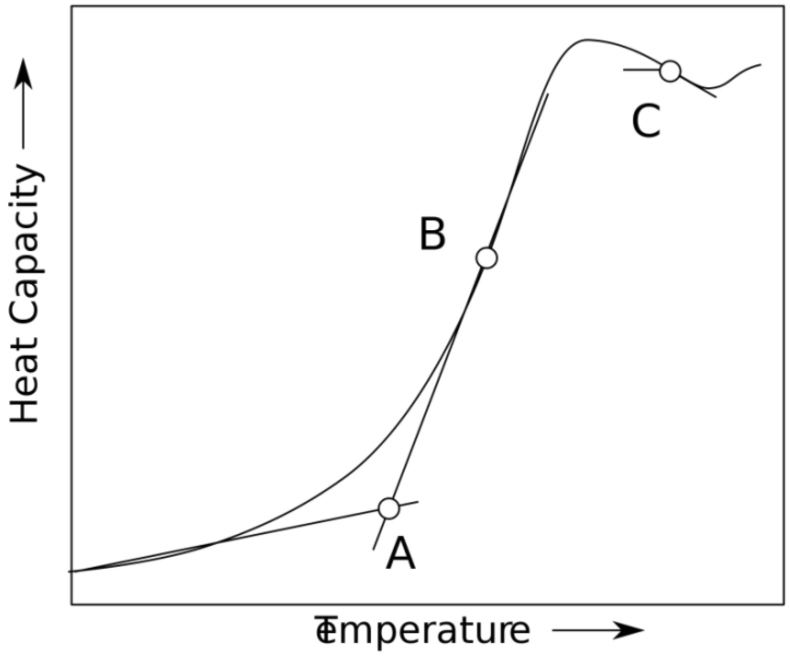


Figure 2-1 Glass transition temperature graph

2.3 Waterproof and anti-icing properties

The hydrophobic property represents another important property. Maintaining a low heat transfer is possible only if the coated material can maintain its thermodynamic and mechanical properties. An appropriate insulation material cannot perform its task correctly if it is flooded by water or any type of liquid. The conduction coefficient of water is relatively high, which tends to transmit heat and energy at a higher rate than the insulation material. Any micro fracture that leads the water to penetrate the material could decrease the performance of the material and increase the heat transfer. The possible consequences are:

- Increase the risk of icing into the material
- Increase the risk of direct damage to the material
- Increase the risk of corrosion to the protected material

The permeation of fluids could also represent an important issue for the protected material. The permeation of any type of fluid from the inside due to leaking or the outside due to damage in the outside layer would reduce the performance of the coated material. The permeation of fluid could seriously damage the protection layers by modifying the expansion of the layer for a specific temperature and by increasing the risk of icing inside the material.

The hydrophobicity of material is generally evaluated by calculating the contact angle between a drop of fluid and the surface of the material. The contact angle is generally measured through a drop of liquid where the liquid interface meets the solid surface. The contact angle is used to determine the shape of a drop of a specific fluid on a specific material. There is one contact angle per liquid/solid couple. The contact angle is the angle between the surface of the solid and the tangent of the drop. In the case of the system exposed to the arctic condition, the most important fluid is the water. Therefore, the material must be hydrophobic. If the contact angle is higher than 90°, the material is considered hydrophobic and cannot lead to the infiltration of water. If the contact angle is lower than 90°, the material is not hydrophobic, and the probability of water infiltration is high. The contact angle is measured with accuracy using a “contact angle camera”. For water, an eye observation could confirm if the material is hydrophobic or not by observing the shape of a water drop.

2.4 Worst case

As said previously, the platform is made of different units that have their own properties. It is not possible to study the consequences of the arctic environment on each unit. Instead of doing a linear analysis of each unit and equipment required on a floating platform, we tried to investigate the worst possible case. The worst possible case should be the one involving a high gradient of temperature with high and low pressure inside a highly complex system. Also, the worst scenario would represent a high risk of fracture due to the inside pressure and the consequences of the outside temperature. By its complexity, the worst possible case should also require regular and accurate maintenance.

On a floating platform, the worst case situation will be a processing system exposed to cold temperature. After receiving the crude oil, the main function of the processing system is the separation of oil, gas, water and sand. Depending on the quality of the crude oil, the processing could be extremely complex. In the case of a petrol/gas field (which tends to be more common), the processing unit should not only separate oil and gas, but also process the gas to separate the methane from some sulphuric gas, oxygen and hydrogen.

In the present case, the processing unit has to perform the main function (separation of oil, gas, water and sand) but also the complementary function (process the gas before transfer by pipeline). These processing operations are realised in a series of high pressure and low pressure thermodynamic systems. The variations of pressure required to perform a complete processing operation increases the maintenance. However, the maintainability of the processing system is relatively low as the system is extremely complex.

Also, the processing system represents a high differential/gradient of temperature, as the inside temperature could be up to 100°C, and the outside temperature in the arctic environment could be down to -60°C.

2.5 Insulation and protection of materials

To determine the appropriate solution in order to efficiently protect a processing unit operating under an extreme cold temperature (-70°C), which was identified as the worst possible case, it is necessary to analyse different possible protections for the processing unit or any offshore systems operating under an extreme cold temperature. Two different methods are identified (Manzini, 2010).

The first one is using a large metallic layer to create a "protective structure" around every system: all the systems are working in the same area and are covered by a large "roof" of metal, and the overall floating platform is protected. This method could be relatively simple; however, the free volume inside the platform is lost and will be extremely hard to maintain at an operating temperature. An integrated hull protection, presented in the Figure 2-2 cannot protect a topside.

Pros	Cons
Easy to design and manufacture	Large lost spaces
Could be applied to every floating platform	Large outside surface area
Simplified maintenance	Could not fit every requirement of the topside

Figure 2-2 Integrated hull protection

The second method can be considered the opposite of the first. Instead of protecting the overall topside, there is a specific protection for each unit coated directly onto the unit surface. The Figure 2-3 is an example of a outside layer protecting an metallic pipe. This method requires a complete analysis of the requirements of each unit and also requires more accurate maintenance. However, this method could provide a more specific solution for each unit operating on the topside.

Pros	Cons
Specific solution for each system	Complex design
Could be applied to every floating platform	Complex maintenance
	Require a complete analysis of the requirement for each unit

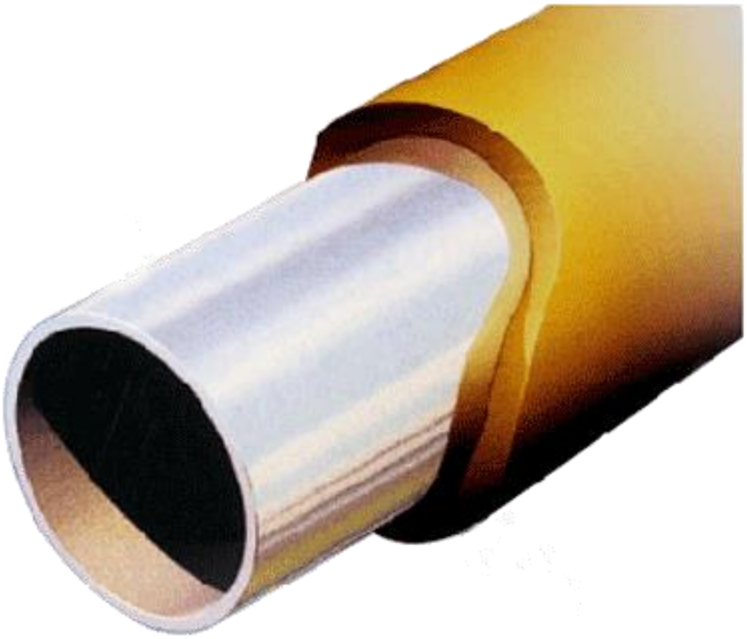


Figure 2-3 coating protection

The aim of this project is to prove the feasibility of the second method by selecting a few material samples and running a series of mechanical and thermodynamic tests.

2.6 The multi-layers concept

2.6.1 Consequences of the arctic environment on the maintenance

The maintenance of an offshore floating platform is generally considered more difficult than an onshore plant due to the complexity of the platform and restrained access as mentioned in chapter 1.

In the present case, the arctic environment modifies the maintenance operations by creating new issues or challenges which can be organised in three categories: environmental, technological and human.

The environment issues come directly from the arctic environment. The weather restrains the access of the platform by sea as the visibility is reduced. Any system will be able to perform its tasks without any help from a boat or ship. The snow and the ice also reduce the regularity of maintenance operations, particularly the preventive maintenance, as visual inspection will not be performed properly. The wind represents a particular issue because it reduces the possibility of performing any crane maintenance operation and any high height operation.

The technological issues come from the consequences of the arctic environment. Preventive maintenance and curative maintenance often require machines to perform the tasks. These machines generally work properly for a certain time but might not be able to perform the task after a long exposition to cold temperature. The preventive maintenance of welding, which requires regular inspections of welding, might not work because an outside weld might not be inspected properly if it is covered by ice or snow.

It is assumed that most of the equipment used on an arctic platform is designed and manufactured to be used under cold temperatures. However, after a lack of maintenance, due to the restrained access and the difficult weather, some equipment might not work properly. The cranes, particularly their transmissions and cables, might not be able to transport large weights. The pipes may be obstructed by hydrates and ice.

The human issues also come from the arctic environment. The arctic environment is cold and generally humid in offshore areas. The cold weather, associated with snow and ice, slows down any human work. The crews might not be totally comfortable working at -60°C, even with an appropriate protection. The visibility is often severely reduced, and any type of operation requires great attention to avoid any injury or fatality. Also, the human body requires a larger amount of energy to perform a task at -60°C. The crew members will likely feel tired after a few hours of work, even after simple inspection tasks. Also, the temperature will be felt differently by everyone due to the difference of physiology, but also due to the direct exposure to wind. The wind chill generally indicates the temperature felt by someone exposed to cold high-speed wind. For an exact outside temperature, the temperature felt by a human could vary up to 40°C (or -40°C), which means that even with a mild temperature, if the wind is fast enough, the crew could feel an uncomfortable cold temperature. The humidity also has the same consequences on the crewmembers, making a steady temperature that is not comfortable for the crewmembers, and then reducing their capacity to perform any type of maintenance operation.

In such conditions, the time required to perform maintenance operations increases and consequently oil and gas production decreases.

While on the other hand, the time required to perform maintenance operations increases. Crewmembers will have to work longer on the same tasks, which could be physically and psychologically challenging.

Therefore, the maintenance of any system must be simplified as much as possible and efficient. As seen previously, the main cause remains the arctic weather, particularly the cold temperature, which leads liquid water and snow to be ice. The main factor to focus on in order to simplify the maintenance is the temperature. By reducing the impact of the cold temperature on a system, the reliability will be increased and the maintenance will be simplified, and then faster. The crewmembers will be less exposed to the harsh arctic environment, and the production of oil and gas will be maintained. The availability of any system should be only slightly modified.

2.6.2 Ideas about maintenance: three/two layers concept

A single system should not have more than one complex function.

Different functions are to be performed to protect the processing unit or any other unit of the platform:

- Avoid heat loss to maintain the temperature of each unit
- Avoid surface icing
- Waterproof
- Avoid any minor fracture and defect (infiltration of water and icing could destroy anything…)
- Relative low thermal expansion/compression coefficient to avoid the protective material expanding or compressing because of the large thermal amplitude

In order to perform these functions with a high level of reliability, it is necessary to reduce the number of functions performed by the protection material.

Therefore, different layers must be used to protect a processing unit, a drilling unit, or any type of complex system exposed to extreme cold temperatures. An inside layer should deal with the issues coming from the inside of the system. And an outside layer should deal with all the issues coming from the arctic environment.

Function	Layer
Avoid heat loss and maintain temperature	Inside layer
Insulation against cold	Outside layer
Anti-icing	Outside layer
Waterproof	Outside layer
Relative elasticity and avoid fracture	Outside layer
Low thermal expansion and compression	Inside layer

2.6.3 Low maintenance concept: sacrificial outside layer

The arctic environment is one of the most extreme environments on earth. Even with the best material and geometry, as the platform shall operate on the same field for at least 20 years, maintenance and inspection operations are mandatory to be done regularly and cannot be avoided. Nevertheless, their number can be reduced by the use of a system of protective coating, the maintenance of which is easy.

The system of protective coating is used to reduce the heat transfer, avoid the infiltration of water and avoid the icing. In order to protect the inside layer and allow it to perform its function, at least one outside layer should be coated on it. The outside layer should be cheap, resistant, and easy to maintain. The arctic environment will slowly destroy the outside layer, which can be replaced easily, but will not affect the inside layer. In such conditions, the heat transfer is still reduced, and after a long no-maintenance period, only the outside layer should be replaced.

Table showing the impact of the arctic environment on the outside part of the protective material

Arctic environment	**Possible action**	**Consequences**
Snow	Melting into a liquid state Icing	Infiltration into fractures Increase size of fracture Reduce life cycle of the material
Rain	Icing	Increase size of fractures Reduce life cycle of the material
Ice	Melting into a liquid state	Infiltration into fractures Reduce life cycle of the material
Cold temperature	Icing of liquid water	Increase size of fractures Reduce life cycle of the material
Green water	Icing of liquid water	Increase size of fractures Reduce life cycle of the material
Hail	Melting into a liquid state	Infiltration into fractures Increase size of fractures Reduce life cycle of the material
Wind	Erosion of the material	Reduce life cycle of the material Reduce insulating properties

2.7 The selection of the different materials and different samples for testing

2.7.1 Polyurethane

The polyurethane is a polymer composed of a long chain of urethane.

The different types of polyurethane have a relatively low conductivity. Polyurethane based foam normally has a thermal conductivity of 0.02 W.m-1.K-1 (Prisacariu, 2011) and, therefore, is one of the best solid thermal insulators. Polyurethane can also maintain a good level of elasticity even under extremely cold temperatures. Even after a long series of icing-de-icing cycles, the risk of fractures is still reduced. Polyurethane also presents a high level of hydrophobicity, which reduces the risk of the infiltration of water.

In order to fulfil the requirements for a low-maintenance, non-icing thermal insulator material, the polyurethane represents the most appropriate solution. The rest of the project is then organised around creating low maintenance polyurethane and determining the main properties of a polyurethane based material protected by a cheap low maintenance material.

A low maintenance material defines a material able to maintain its properties for a long period of time with the least outside intervention or modification during its operation. The low maintenance property is necessary because of the reduced access of the arctic region and because of the difficulties of doing a series of inspection and maintenance operations under extremely cold temperatures and a large quantity of snow and ice (see chapter 1). A polyurethane based material generally requires only a few maintenance operations over a few years. However, a polyurethane based material is complex to install. Every modification or maintenance operation requires removing partially the polyurethane layer. In order to avoid removing the polyurethane layer, the polyurethane layer should be protected by a light, cheap resistance material. This material should be easy to install and should not require a long curing time in order to be installed in less than 12 hours on a large surface (few square meters).

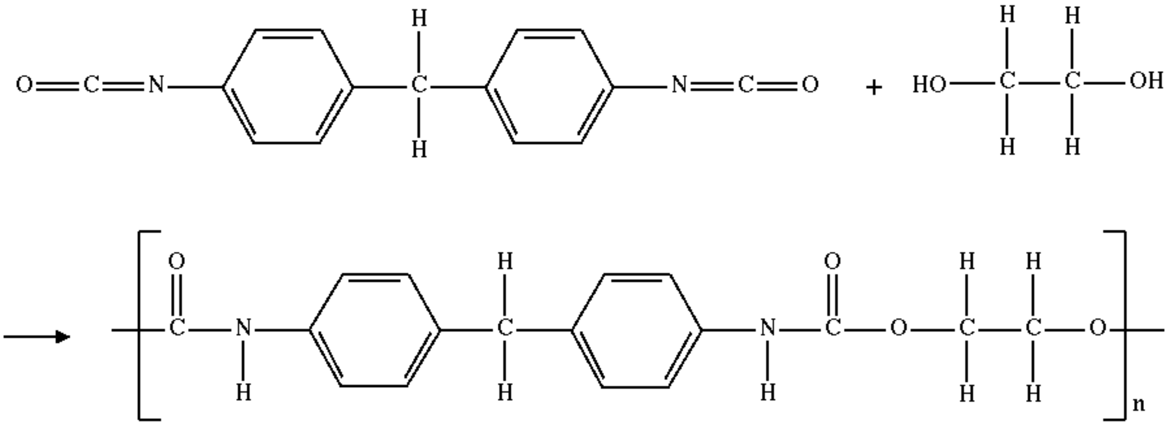


Figure 2-4 polyurethane chemical structure

2.7.2 Polypropylene

Polypropylene is a thermoplastic polymer often used for packaging and laboratory equipment. Polypropylene is supposed to be used as a second protective layer, directly onto the polyurethane layer and behind the outside layer. Polypropylene is generally tough and flexible. The density of polypropylene is around 0.900 g/cm³. Also the melting point is around 171 C°. Polypropylene is used as the middle layer as it has good resistance to fatigue. Also, polypropylene is often used to protect the pipe and is as a result available in a cylindrical shape, already manufactured so there is no need to melt the polypropylene and mould it before using it. The polypropylene is often hydrophobic and can also reduce the permeation of gas. The dissolution and curing of polypropylene generally uses a solvent such as halogenated hydrocarbons, higher aliphatic esters or ketones. (Brandrup, 1966)

Polypropylene has not been used for the experiments due to the complex chemical processing required. To cure a large quantity of polypropylene, it is necessary to dissolve the solid monomer in a solvent at a high temperature with a constant mixing for a few hours. The process must be steady and should not be disturbed by humidity or any type of outside parameters. It is useful to note that it was not possible to dissolve the polypropylene to cast it onto the polyurethane.

2.7.3 Epoxy

Epoxy is the common name of polyepoxide. It is a thermosetting polymer formed by two solid components. The first component is the epoxide resin, and the second component is the polyamine hardener. As it is formed of two chemical components, the epoxy is a copolymer. The epoxy is often used as a coating, adhesive or paint. It represents one of the best choices for an outside protective layer as it has important properties. (May, 1988).These properties are:

- Low price. The maintenance remains cheap.
- Easy to use. The epoxy does not require any complicated curing system and can be used by any maintenance technician
- Transparent. This is useful for inspection and allows the use of coloured paint to detect fractures and defects.
- Light. Its light weight doesn't represent a considerable mechanical stress for the under layer.
- Elastic. Its relative elasticity allows the under layer to have a relative thermal expansion without destroying the outside epoxy layer.
- Hydrophobic. Even if the epoxy is not as hydrophobic as the polyurethane, its hydrophobicity makes the infiltration process extremely slow.
- No preliminary forming. The epoxy is coated directly onto the material. For a maintenance operation, there is no need to remove the epoxy layer to repair or change a specific area.

3. Experiments

3.1 Aims and organisation of experiments

3.1.1 Organisation of the experiments

It is necessary to do tests as there are a lot of uncertainties around polymer behaviour and properties. Polymer properties are affected by different factors or parameters: temperature during curing, humidity and/or gas percentage inside the polymer before curing.

In addition, it is not possible to determine theoretically the thermodynamic and mechanical behaviour of the association of a few polymers.

The mechanical and thermodynamic behaviours of metals are well known, theoretically and experimentally. As the use of ceramic has been increasing over the last few decades, the behaviour of the most common ceramics and their properties are well known.

The properties of polymers are less known. The first reason comes from the composition of a polymer: a polymer is made by a long chain of carbons atoms with other different atoms. It is possible to create a new polymer and modify its properties by a chemical reaction. Theoretically, it is possible to create a large number of polymers with minor modifications to the same base. A minor chemical modification could create a completely new polymer with different properties.

The main consequence is the extreme difficulty of predicting the behaviour of a new polymer or a new association of polymers. There is no general law to determine by theoretical simulation the behaviour and properties of a new polymer used under an extremely cold temperature.

But it is necessary to determine which polymer and which association of polymers can be considered as the most appropriate solution to protect a system operating under extremely cold temperatures. Some properties need to be known and demonstrated to prove the viability of the polymer samples.

These properties are:

- Elasticity of the material
- Glass transition temperature
- Heat capacity of the material
- Waterproof capability
- Anti icing properties
- Storage modulus
- Loss modulus

All the experiments are made in the Advanced Materials Research laboratory of the University of Strathclyde. The AMRL is an interdepartmental laboratory with high level technology to analyse the properties of different materials. The applications can be found in the mechanical engineering field, civil engineering but also biochemistry and biotechnology.

A series of blank tests is necessary in order to calibrate the machine, determine the potential error and learn how to use the machine. Also, the blank test is used to determine the effective capabilities of the machine.

The differential scanning calorimetric is used to calculate the heat capacity of the material and glass transition temperature. The dynamic mechanical analysis is used to calculate storage modulus and loss modulus values. The hydrophobicity of material is determined using the contact angle of a drop of water onto the surface of the material.

3.1.1 Aims of the DSC

The DSC is the acronym for Differential Scanning Calorimetric test. The purpose of the differential scanning calorimetric test is to expose the sample to known heat in order to determine the heat flow through this material. The result is often a graph expressing the heat flow as a function of the temperature. In the present case, the differential scanning calorimetric test is not run at the room temperature, but for a large range of temperatures from -60 Celsius degrees to +70 Celsius degrees. The differential scanning calorimetric machine is coupled with a cooling system, which manages an accurate temperature by using a nitrogen injection directly onto the machine. The aim of the DSC is to determine the heat capacity of the material.

3.1.2 Aims of the DMA

DMA stands for dynamic mechanical analysis. The purpose of dynamic mechanical analysis is to measure the mechanical behaviour of material in a dynamic situation. Generally, with a standard dynamic mechanical analysis machine, it is possible to generate stress, strain, vibration, and modify the frequency, the amplitude and the time of the experiment. In the present case, the purpose of dynamic mechanical analysis is to determine the mechanical behaviour of material for a large range of temperatures. The dynamic mechanical analysis machine or DMA was coupled with a liquid nitrogen injection to regulate the temperature and compressed air injection to generate the motion of the system. The aim of the DMA is to determine loss and the storage modulus of material.

3.2 Protocol for S20 and S21

The experiments require doing a series of chemical preparations. Therefore, it is necessary to ensure a high level of safety and quality to reduce the risk of incidents, but also to increase the quality of samples.

In order to ensure the maximum security during chemical work, an S17 security form was filled and a security visit was realised in the chemical engineering and processing laboratory.

The preparation of materials cannot be realised without the S20 and S21 forms (also known as COSHH forms). They are compulsory forms to be filled in order to determine all risks associated with chemical work, but also to provide the necessary procedure to follow in case of an incident. The S20 and S21 forms are official documents and must be filled and approved by the researchers and the university responsible for the research.

3.3 Test samples preparation and description of the laboratories

The preparation of samples was carried out in the laboratory of the Chemical Engineering Department of the University of Strathclyde. All samples were prepared in exactly the same conditions. In order to maintain a stable temperature during the preparation of materials and constant humidity, they were carried in the same fume cupboard.

The polyurethane used is an industrial manufactured polyurethane; and presented in two components, respectively PU3436FA and PU3436FB. The mix ratio is 100: 20, with a pot life of 45 to 55 minutes at 25°**C.** The viscosity varies from 4200 to 5400 mPa.S and the shore hardness is around 80. The epoxy used is a dual component epoxy resin, with a curing time of 30 min at 15°C and manufactured by Sigma-Aldrich.

A specific list of equipment was made to ensure an efficient preparation of the samples. And the required apparatus was prepared in the fume cupboard. This apparatus is composed of:

- A Fume cupboard to maintain constant temperature and level of humidity
- An electronic balance to ensure an accurate measurement of the required quantity
- Five beakers to mix the different components
- A graduated cylinder to measure the volume used
- Stirring rods

- Five petri dishes
- A large scale blade to spread the polyurethane on a surface

The polyurethane was supposed to be transferred from the beakers to the petri dishes using pipets and bulbs. Due to the high viscosity of the materials, stirring rods were used.

Test programs were carried out in the Advanced Material Research Laboratory (AMRL). Two types of tests have been performed: the differential scanning calorimetric and the dynamical mechanical analysis, with each test using a specific machine. These tests required some specific equipment to produce samples and maintain the required temperatures:

- A differential scanning calorimetric machine
- A dynamical mechanical analysis machine
- A cutter to cut the sample
- An electronic balance to determine the weight of each sample
- A tank of nitrogen connected to the dynamical mechanical analysis machine

The apparatus to produce the multi-layer material is relatively simple. All the chemical reactions are made in the chemical engineering laboratory under strict supervision and always using appropriate protection (coat, gloves, and glasses). The chemical processes are realised in a chemical fume cupboard in order to evacuate the fumes and avoid any type of poisoning. Also, the fume cupboard allows controlling the temperature and humidity of the chemical environment. The polyurethane based material is the first to be prepared, as it has to be inside the layer directly in contact with the protected system. However, there are a large number of polyurethanes and different types of preparations. Few different preparation methods are tested in order to determine which one is the most appropriate to realise an accurate casting.

First, the two liquid components are mixed together with the appropriate ratio. As the polyurethane based material requires mixing two different components, there is a risk of having an air bubble in the mixture and a non-dissolved oxygen. The mixture should follow a degasing procedure to avoid the formation of bubbles during the curing. Actually, the bubbles could seriously affect the properties of the material because they will increase the heat transfer capacity of the material but also reduce the local mechanical strength of the material, which leads to water infiltration, and in case of icing, could lead to multiple micro fractures.

The degasing procedure used a pump. The material is exposed to low pressure and, therefore, tends to be “sucked”. The non-dissolved gases are separated from the material. As the material is black, it was difficult to observe the quality of the fluid. Even with a high differential of pressure, some bubbles did not leave the material. We therefore tried to apply a small vibration to the fluid, but the bubbles did not move. We then tried to cast the material by pouring it into a petri dish. The viscosity increased. And it was not possible to cast the material with accuracy. After a curing time of three days, the material had an irregular surface. Therefore, this method cannot be used to prepare the final samples.

Figure 3-1 polyurethane based material after degasing

In order to obtain a regular surface with a control thickness, another casting method was tested: a blade-casting machine. Using a blade and a glass plate, the mechanically activated machine pushes the blade to cast a film of 200 micrometres. Two different glass plates were used: one with a releasing agent and the second without a releasing agent. After a curing time of three days, it was observed on the first plate that the releasing agent almost dissolved the polyurethane film, which therefore cannot be used. On the second plate, the film was 200 micrometres, but cannot be removed. Also, the film presented a lot of air bubbles. Therefore, a 200 micrometres film is too thin to be safely prepared, removed and used for a mechanical test.

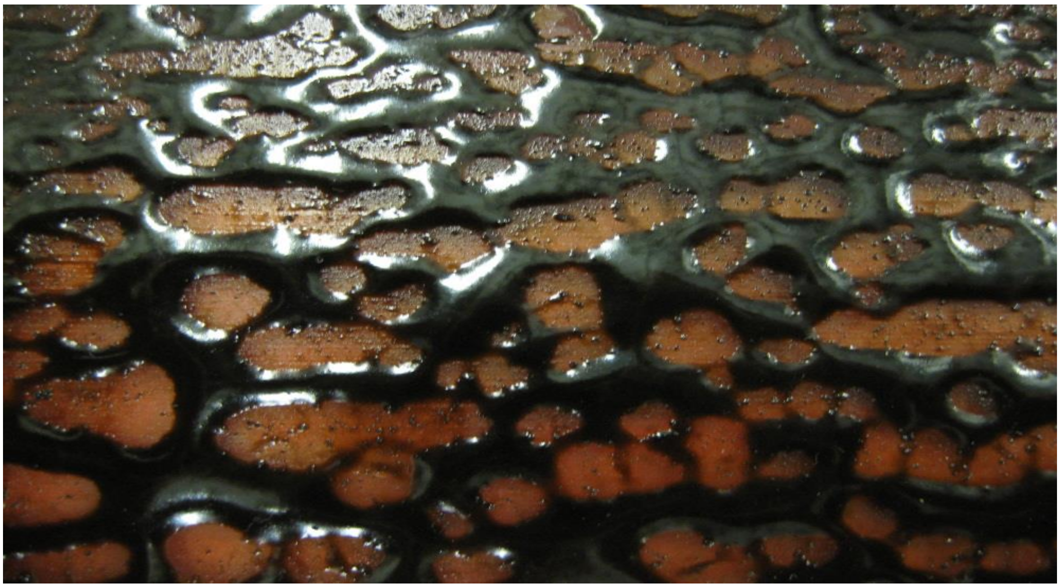


Figure 3-2 effect of using a releasing agent on a thin polyurethane layer

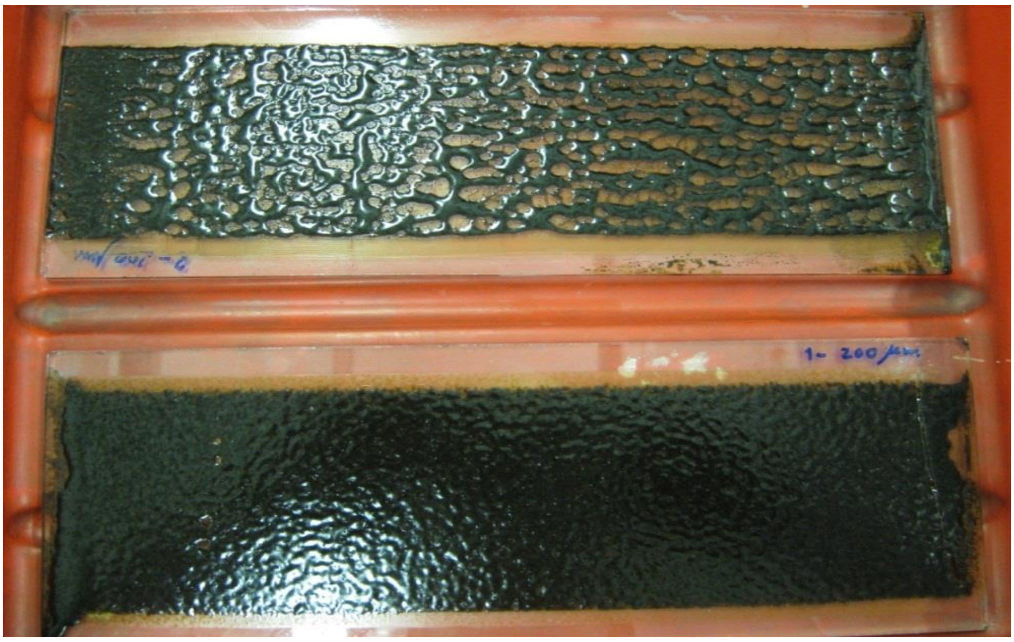


Figure 3-3 polyurethane based material coated with a 200 μm blade

The last method was different. After one minute of steady mixing of the two components, the polyurethane based material was not degased, but was directly poured into a petri dish in order to degas itself before the viscosity increase. After a curing time of three days, it was observed that the sample prepared with the last method presented the most regular surface without air bubbles and with a steady thickness. Therefore, the last method was used to prepare all necessary samples.

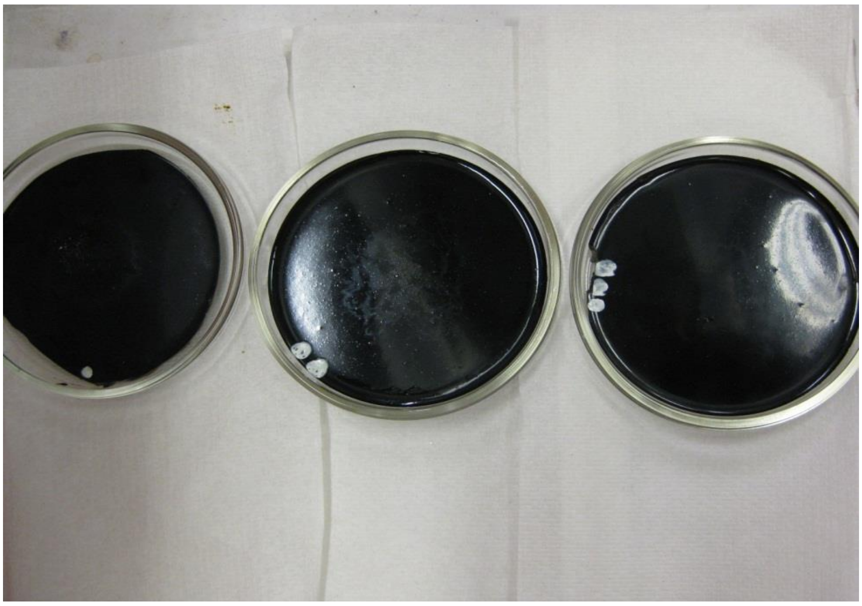


Figure 3-4 polyurethane based material poured without degasing

The epoxy is also made of two components. However, the viscosity of the epoxy is relatively high and cannot be poured directly onto the polyurethane based material. The curing time of the epoxy is extremely reduced, which makes the epoxy almost solid in less than ten minutes. This fast curing time is useful for a maintenance operation but represents an issue for a long and accurate chemical protocol. Therefore, it has been decided to prepare samples for mechanical and thermodynamic tests, and then cast the epoxy onto samples. The differential scanning calorimetric test used a small aluminium pan. The polyurethane is put into the pan, and the epoxy is casted directly onto it. The dynamic mechanical analysis required rectangular samples. The polyurethane is cut according to the required dimension (circular shape of 5 mm diameter and a thickness of 1 mm), and the epoxy is cast directly onto the polyurethane based material. These dimensions are required in order to fit the DSC machine.

3.4 Differential scanning calorimetric methodology

3.4.1 DSC protocol

The protocol for the differential scanning calorimetric tests could be divided into two parts. The first part is the preparation of the samples for the differential scanning calorimetric test, and the second part is the test itself. In order to follow an accurate DSC testing protocol, the standard ASTM D7426 was used as a guiding reference. However, due to the lack of time, the DSC testing was not entirely conducted according to the ASTM D7426 standard.

The first part is relatively fast, as the samples of the material have to be put in some small aluminium pan and closed by an aluminium tap. A small hole was drilled in the tap in order to prevent any pressure differential that may destroy the sample. Then the sample must be weighed to determine its accurate weight, which is necessary for the calculation of the heat capacity. Then the sample is put on the DSC machine. Another sample, an empty aluminium pan, has to be put close to the first sample. The heat flow through the material sample will be calculated by comparison between the empty sample and the material sample.

The second part is the test. A preliminary work had to be organised in order to determine the appropriate thermodynamic cycle to do the tests. As the purpose of the study is to determine the behaviour of the material for a large range of cold and hot temperatures, it was decided to perform a series of thermic cycles from -60 Celsius degrees (the minimum possible temperature for the Differential Scanning Calorimetric machine) to +70 Celsius degrees (which is the maximum possible temperature on the Differential Scanning Calorimetric machine).

3.4.2 Organisation of samples

As the casting of the polymer represented some difficulties, it was necessary to perform the differential scanning calorimetric tests on more than one sample of the same material. Two samples made of the same materials were produced. They were made of one layer of polyurethane based material of 1mm and one layer of epoxy of approximately 0.2mm.

For each sample, three different pans were prepared with the thickness required (1 mm thick polyurethane layer and 0.2 mm thick epoxy layer). No variation of thickness was measured. The differential scanning calorimetric tests were realised on six samples made from the same materials and coming from two different samples of polyurethane based material and epoxy. Two other samples were prepared in order to produce more accurate results for the differential scanning calorimetric tests. The first of these two samples was made exclusively of polyurethane based material in order to determine the behaviour of this material only, without epoxy. The thickness of this sample was approximately 0.8mm. The second of these supplementary samples was made of exclusively epoxy, to determine the behaviour of the epoxy without the polyurethane layer. The layer of the epoxy sample was approximately 1mm.

3.4.3 DSC raw results in terms of heat flows for 8 samples

This part presents the heat flow for each sample during the tests with the thermodynamics cycles and the glass transition temperatures. These graphs are representing the thermo dynamical behaviour of each sample compared to the reference. The polyurethane sample, not protected by the epoxy presents a rapid variation of heat flow for a linear variation of temperature. The epoxy sample also presents a quick variation of heat flow. However, the sample made of polyurethane protected by epoxy presents a smoother variation of heat flow, which indicates that the sample is less sensitive to variation of temperatures. On most of the graphs, it is possible to see two glass transition temperatures, which is due to the fact that the samples are made of two different materials.

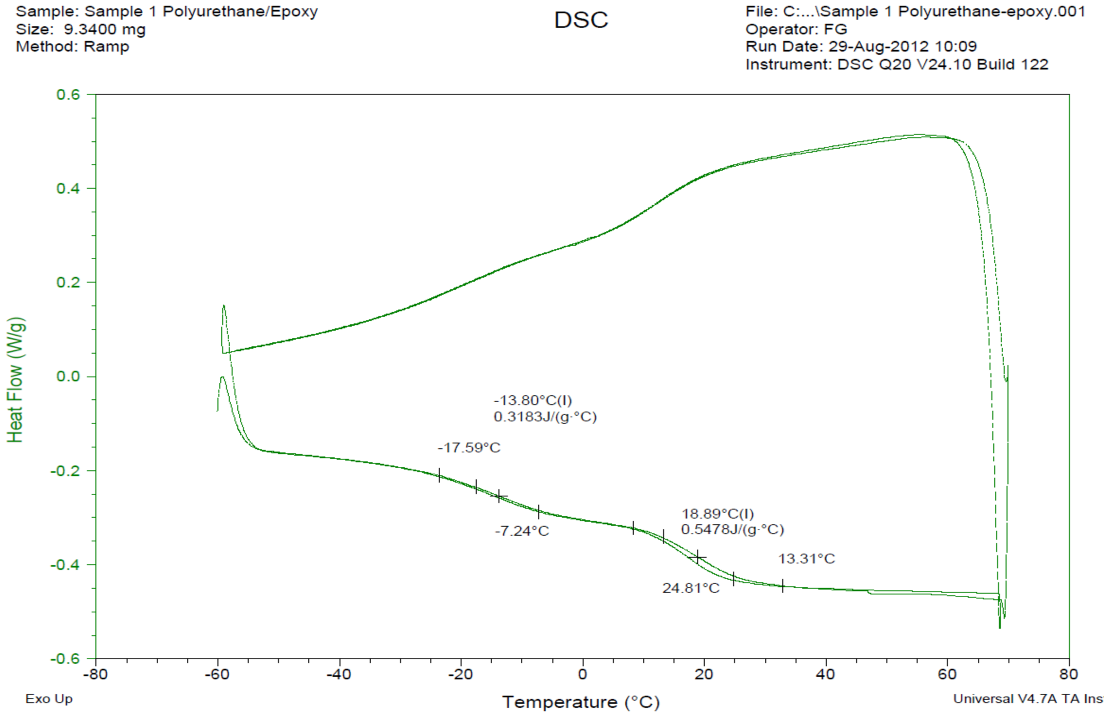


Figure 3-5 polyurethane-epoxy sample, thermodynamic cycle with glass transition temperatures

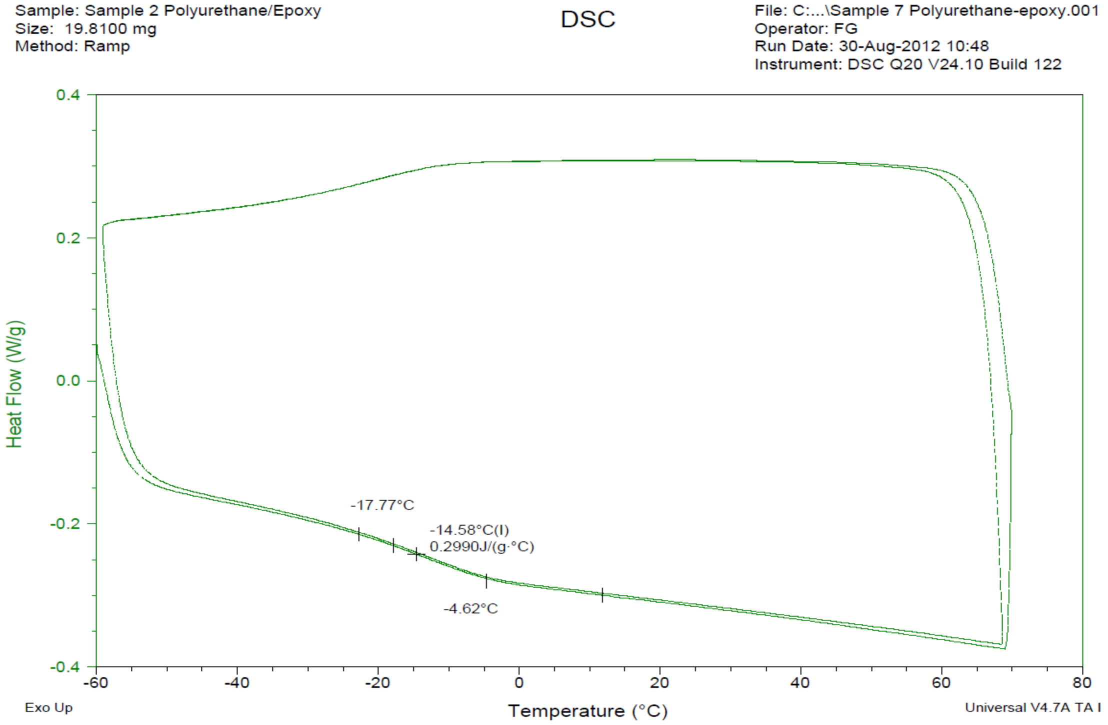


Figure 3-6polyurethane sample, thermodynamic cycle with glass transition temperatures

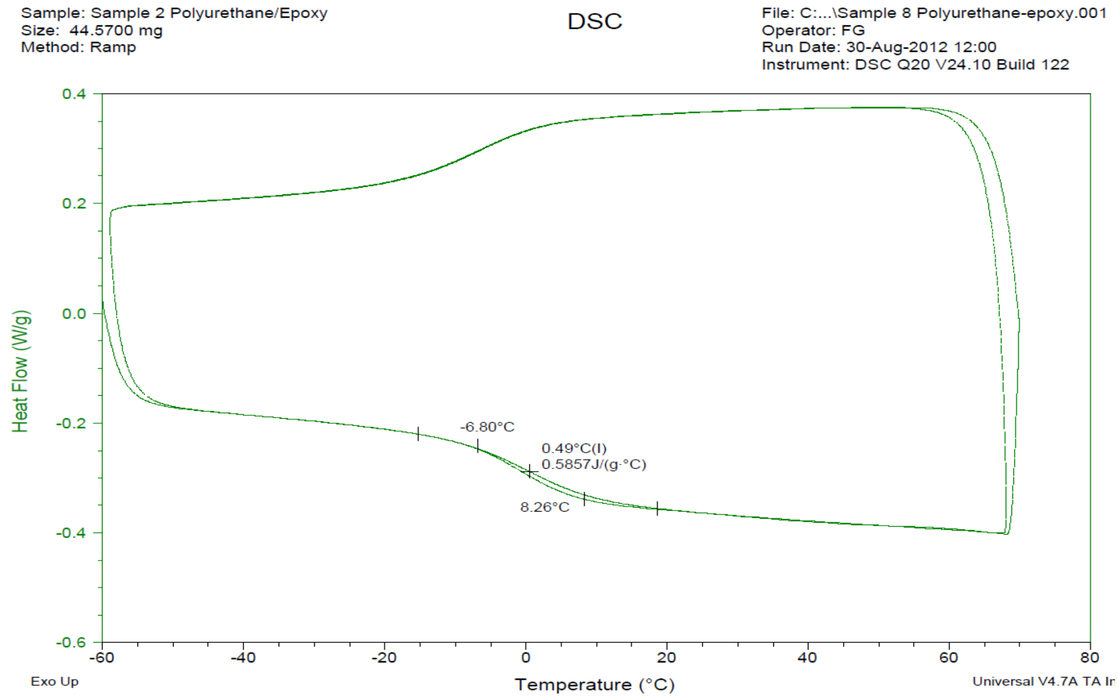


Figure 3-7 epoxy sample, thermodynamic cycle with glass transition temperatures

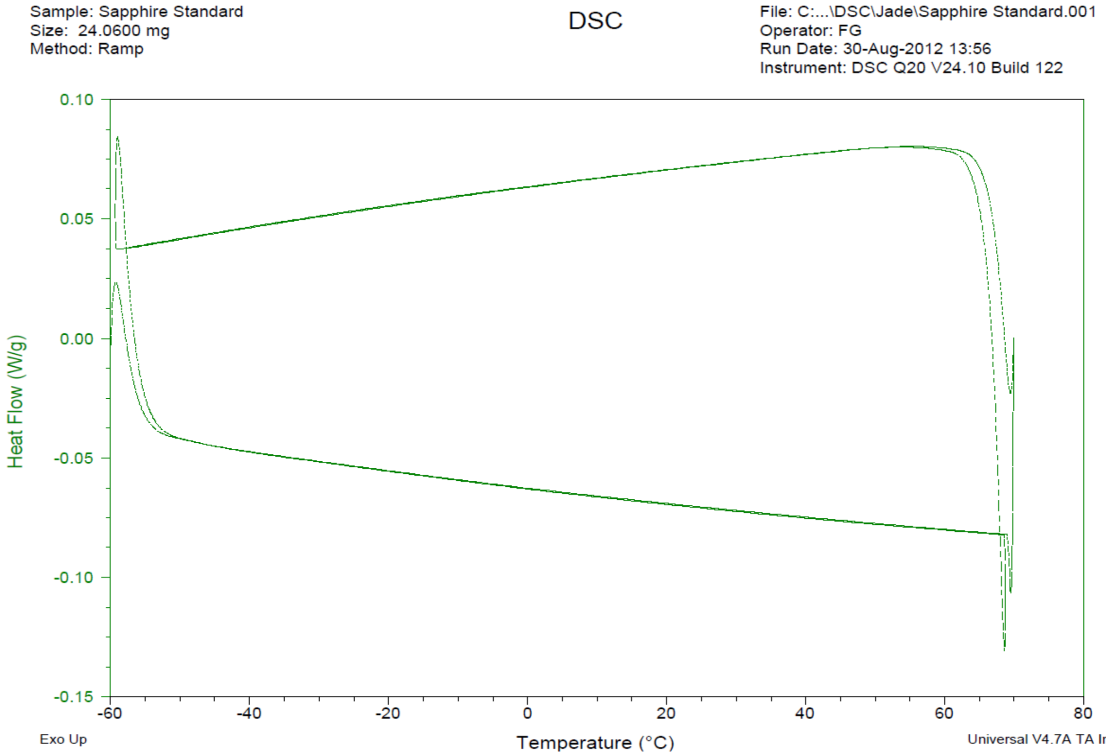


Figure 3-8sapphire reference sample, thermodynamic cycle with glass transition temperatures

3.4.4 Heat capacity definition and calculations

The heat capacity Cp is normally calculated by the following equation. (American society for testing and material, Scanning test method for determining specific heat capacity by differential scanning calorimetry, 2012)

$$C_p = \frac{m_{sapphire}}{m_{sample}} \times \left(\frac{h_{m\,sample} - h_{ref}}{h_{m\,sapphire} - h_{ref}}\right) \times C_{p\,standard}$$

$C_p = specific\ heat\ of\ the\ sample$

$m_{sapphire} = mass\ of\ the\ sapphire\ sample$

$m_{sample} = mass\ of\ the\ sample$

$h_{m\,sample} = heat\ flow\ measured\ for\ the\ sample$

$h_{m\,sapphire} = heat\ flow\ measured\ of\ the\ sapphire\ sample$

$h_{ref} = heat\ flow\ of\ the\ empty\ pan\ used\ as\ reference$

$C_{p\,standard} = specific\ heat\ of\ the\ sapphire\ sample$

However, the differential scanning calorimetric machine and software we used already subtracted the heat flow of the empty pan reference and, therefore, provided the complete heat flow values and graphs for each sample so that the heat capacity equation could be simplified. The equation used to determine the specific heat capacity of the sample is the following one. (American society for testing and material, Scanning test method for determining specific heat capacity by differential scanning calorimetry, 2012)

$$C_p = \frac{m_{sapphire}}{m_{sample}} \times \left(\frac{h_{sample}}{h_{sapphire}}\right) \times C_{p\,standard}$$

3.4.5 Results in terms of heat capacity with diagrams for each cycle

The most important result for the purpose of this study is the differential scanning calorimetric results in terms of specific heat capacity. The unit of the heat capacity is the Joule per Kelvin. However, the temperature is expressed in degrees Celsius instead of degrees Kelvin, in order to show the temperature of the tests and the practical range of temperatures of the samples.

For each sample, the specific heat has been calculated for a large range of temperatures for each of the four cycles. Also, a graph represents these values. For most of the graph, it is possible to notice that the values of cycle 1 and cycle 3 are similar, and the values of cycle 2 and cycle 4 are also similar. This could be explained by the fact that cycle 1 and cycle 3 started at -60 degrees Celsius and finished at +70 degrees Celsius, and cycle 2 and cycle 4 started at +70 degrees Celsius and finished at -60 degrees Celsius. The results represent only a reduced number of temperatures, as the calculation of the specific heat for the sample requires the specific heat of the sapphire sample. And the specific heat of the sapphire provided by the American Society for Testing and Materials is given with an increment of 10 degrees only. Therefore, only thirteen specific heats can be calculated between -60 degrees Celsius and +70 degrees Celsius.

	Specific heat			
temperature C	cycle 1	cycle 2	cycle 3	cycle 4
-53.15	0.316148048	0.12702761	0.337889213	0.129001613
-43.15	0.309413578	0.170893823	0.310301593	0.172287987
-33.15	0.325330736	0.224872016	0.325537925	0.225809239
-23.15	0.358654676	0.296574629	0.361538815	0.297305802
-13.15	0.422849987	0.377099167	0.427645607	0.377571182
-3.15	0.477234092	0.437641171	0.477533892	0.437036699
6.85	0.500939277	0.505178955	0.500411561	0.505691226
16.85	0.569678763	0.617125068	0.584923212	0.618833796
26.85	0.660406967	0.676724996	0.664025707	0.67910627
36.85	0.677944603	0.697661971	0.672736935	0.703180819
46.85	0.680282443	0.715886309	0.672328264	0.724452001
56.85	0.682393924	0.739697121	0.671261621	0.751672205
66.85	0.690766686	0.8034658	0.670252944	error

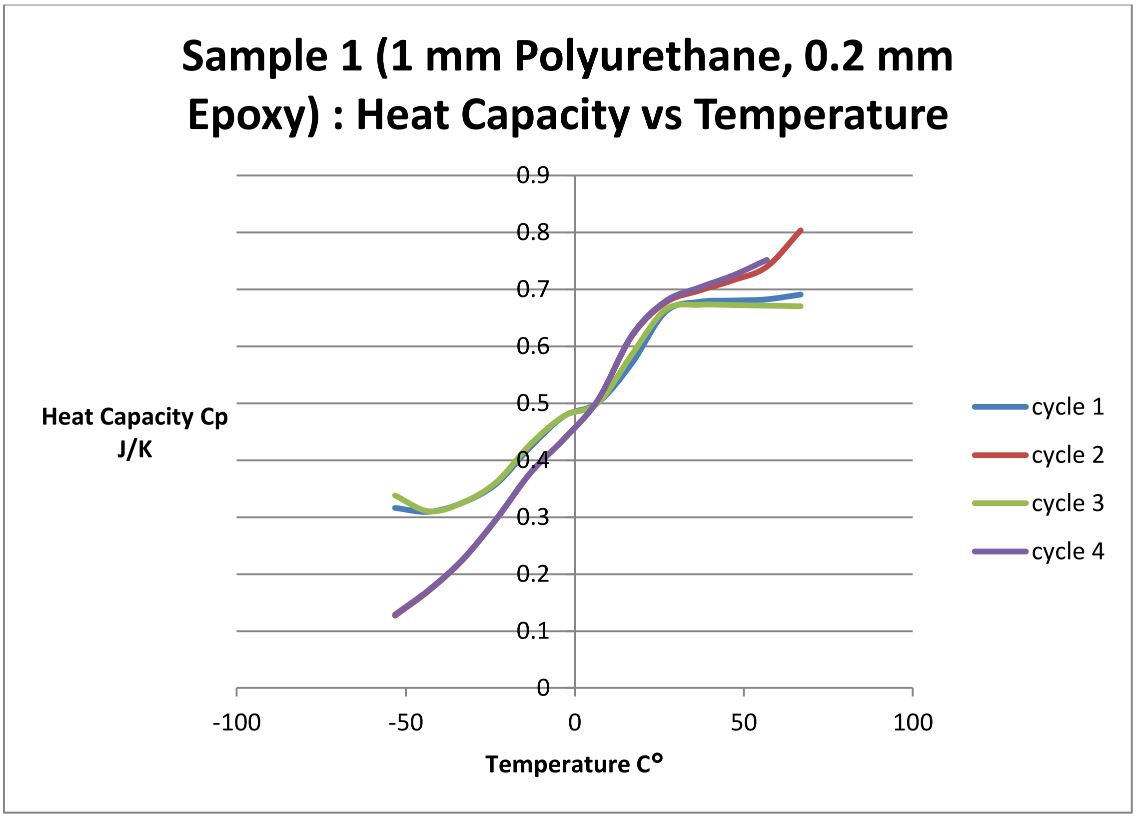


Figure 3-9Heat capacity for a polyurethane-epoxy sample 1

The figure 3-9 represents the evolution of the heat capacity of a sample made of 1 mm of polyurethane and 0.2 mm of epoxy. The heat capacity constantly remains below 1 J/K.

	Specific heat			
temperature C	cycle 1	cycle 2	cycle 3	cycle 4
-53.15	0.547594131	0.234922828	0.562863914	0.242127087
-43.15	0.602760535	0.365269475	0.613829094	0.36938343
-33.15	0.66978721	0.522891468	0.679853593	0.524402875
-23.15	0.782640632	0.72862918	0.794091161	0.732277692
-13.15	0.982804979	0.951663688	0.998330438	0.957815098
-3.15	1.159514423	1.105791456	1.165634456	1.129753329
6.85	1.257706874	1.310443983	1.249561536	1.322821414
16.85	1.499842764	1.615219071	1.523556875	1.627377629
26.85	1.741096237	1.74796608	1.755249717	1.771920084
36.85	1.807445838	1.7963225	1.790754173	1.825909899
46.85	1.848298963	1.837682357	1.802116788	1.870389556
56.85	1.903840246	1.871578017	1.81887215	1.915022058
66.85	1.998924273	1.659207964	1.846218554	error

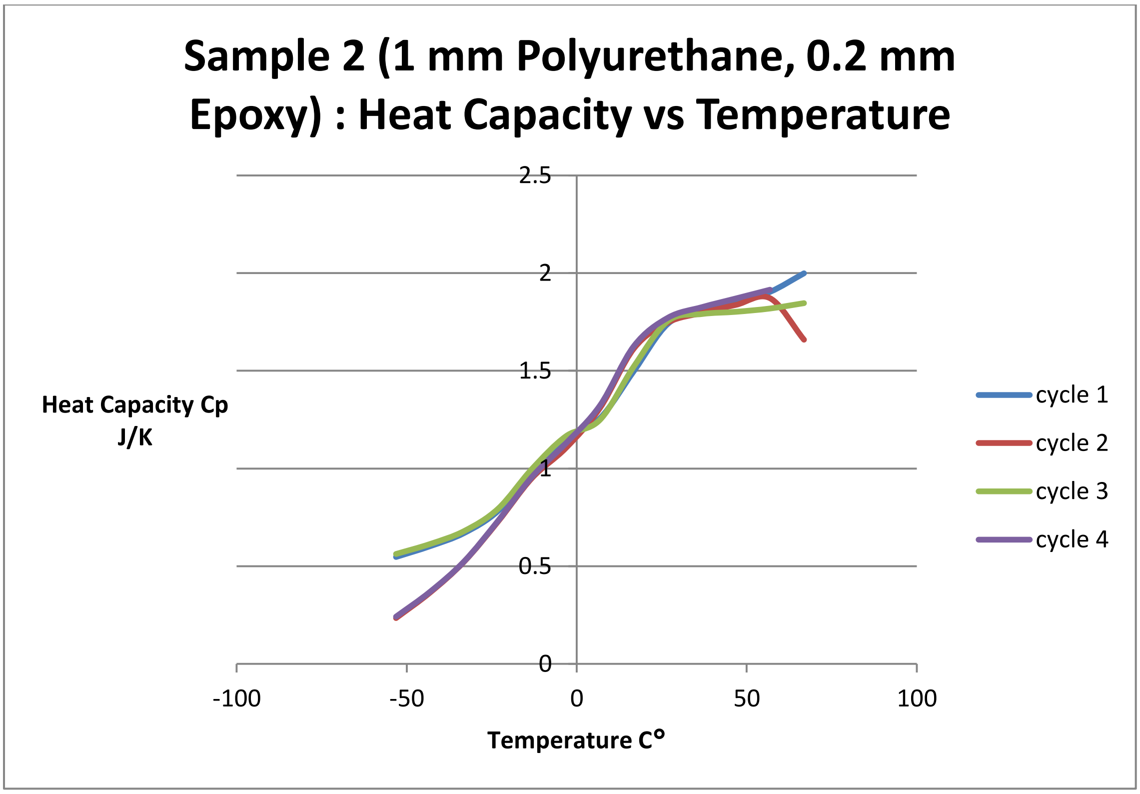


Figure 3-10 Heat capacity for a polyurethane-epoxy sample 2

The figure 3-10 represents the evolution of the heat capacity of a sample made of 1 mm of polyurethane and 0.2 mm of epoxy. The heat capacity constantly remains below 2 J/K.

	Specific heat			
temperature C	cycle 1	cycle 2	cycle 3	cycle 4
-53.15	-0.570532961	-0.321002116	-0.900355798	-0.304162254
-43.15	-0.244359327	-0.198200475	-0.278568459	-0.199746071
-33.15	-0.158700632	-0.081150755	-0.180222653	-0.084693686
-23.15	-0.071592952	0.056051344	-0.084906295	0.052505998
-13.15	0.067909178	0.209357072	0.067181306	0.200198007
-3.15	0.220332714	0.312261583	0.220143617	0.304353577
6.85	0.307186987	0.437956593	0.301310674	0.428933477
16.85	0.425970939	0.589912783	0.437668764	0.582962602
26.85	0.613255855	0.628559908	0.615220515	0.622271008
36.85	0.683065827	0.632782417	0.665510108	0.629357289
46.85	0.717611511	0.618899143	0.684285715	0.612366503
56.85	0.758317714	0.562739183	0.701899624	0.511152611
66.85	0.808531028	error	0.721891713	error

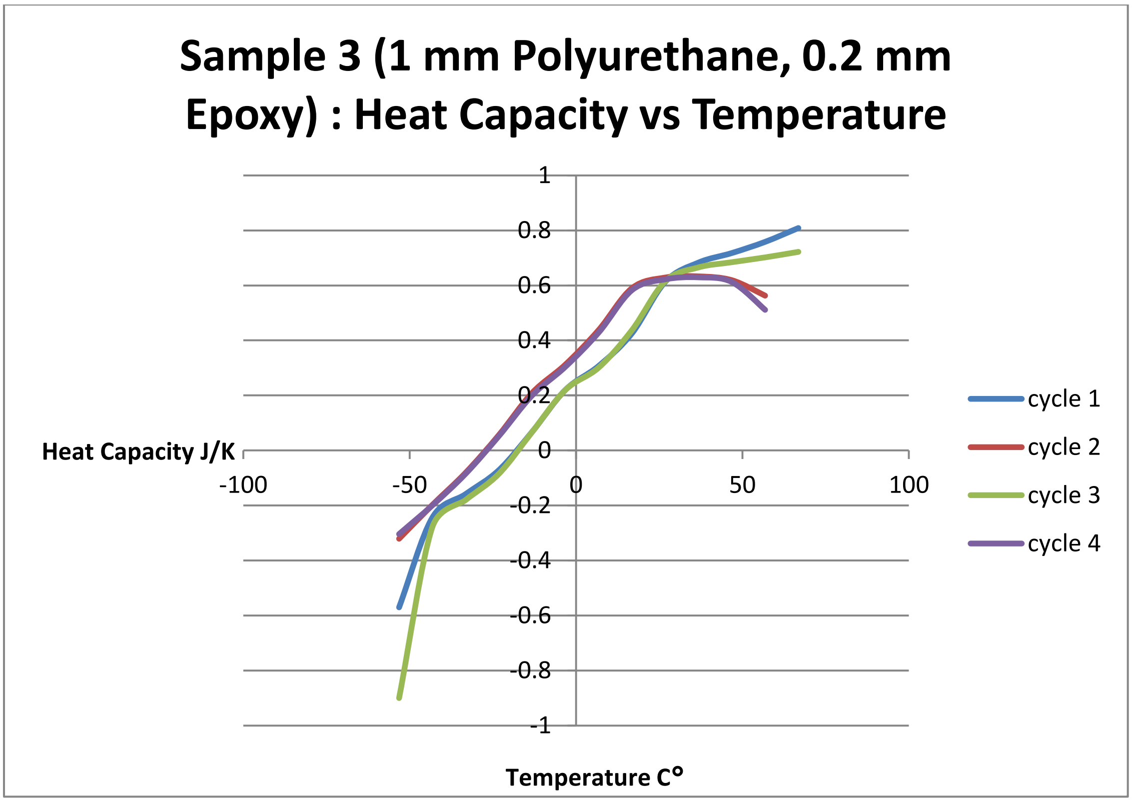


Figure 3-11 Heat capacity for a polyurethane-epoxy sample 3

The figure 3-11 represents the evolution of the heat capacity of a sample made of 1 mm of polyurethane and 0.2 mm of epoxy. The heat capacity constantly remains below 0.8 J/K.

	Specific Heat			
temperature C	cycle 1	cycle 2	cycle 3	cycle 4
-53.15	0.629816376	0.57326579	0.612934503	0.562596571
-43.15	0.672329923	0.622566747	0.667145179	0.607536877
-33.15	0.723480118	0.715959719	0.714707396	0.705528033
-23.15	0.838844311	0.918897221	0.816583843	0.90071937
-13.15	1.100240851	1.147246938	1.064070671	1.133457173
-3.15	1.253106237	1.220677966	1.24245579	1.213444419
6.85	1.276281186	1.254341936	1.257025907	1.251426133
16.85	1.31012433	1.296160437	1.285075633	1.292582082
26.85	1.350789611	1.31395898	1.320821542	1.311706256
36.85	1.376630914	1.319977898	1.333303244	1.32504928
46.85	1.405254778	1.324618288	1.343433205	1.33302099
56.85	1.439254914	1.324501689	1.358633418	1.340001563
66.85	1.472349304	1.123831396	1.377493204	error

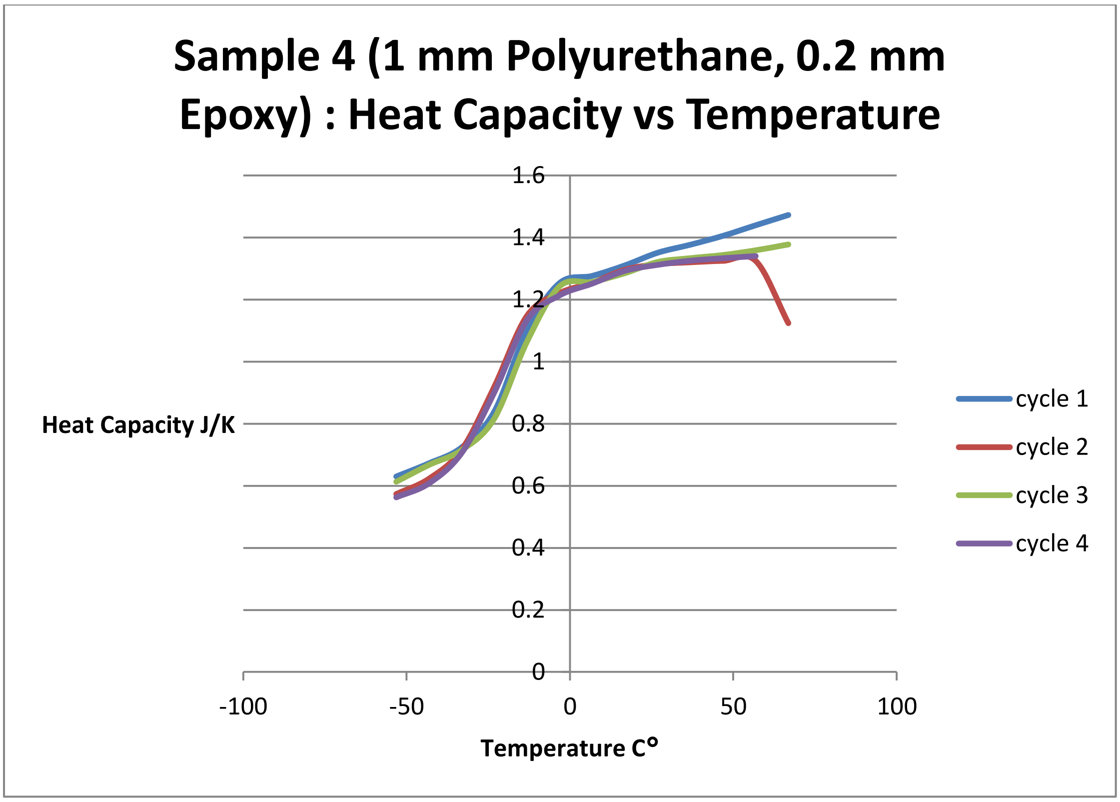


Figure 3-12 Heat capacity for a polyurethane-epoxy sample 4

The figure 3-12 represents the evolution of the heat capacity of a sample made of 1 mm of polyurethane and 0.2 mm of epoxy. The heat capacity constantly remains below 1.5 J/K.

	Specific Heat			
temperature C	cycle 1	cycle 2	cycle 3	cycle 4
-53.15	0.944451695	0.6561128	1.043408694	0.650498451
-43.15	0.914901154	0.70675522	0.954541448	0.748325421
-33.15	0.960531872	0.826756246	0.997644425	0.829117723
-23.15	1.102237293	1.07055922	1.125334436	1.067695811
-13.15	1.426766741	1.425674135	1.44068112	1.411170002
-3.15	1.636989435	1.563916176	1.669039878	1.560624767
6.85	1.643729476	1.592253492	1.666985776	1.589293463
16.85	1.639144999	1.615684228	1.652888399	1.615328461
26.85	1.635813388	1.64368926	1.642611486	1.645981502
36.85	1.638563637	1.669652621	1.635256475	1.676466975
46.85	1.652795806	1.70040894	1.632404933	1.710759298
56.85	1.709756653	1.741985774	1.635231586	1.76387368
66.85	1.721260882	1.968584611	1.639693078	error

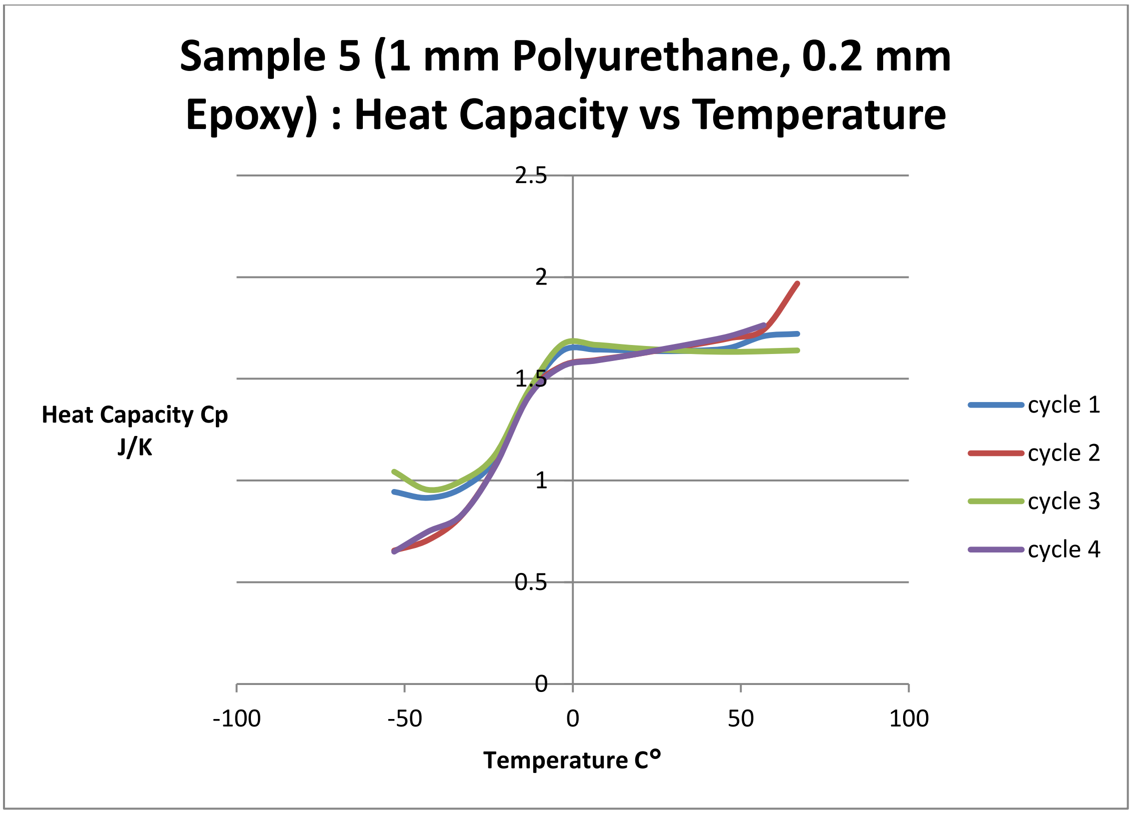


Figure 3-13 Heat capacity for a polyurethane-epoxy sample 5

The figure 3-13 represents the evolution of the heat capacity of a sample made of 1 mm of polyurethane and 0.2 mm of epoxy. The heat capacity constantly remains below 2 J/K.

	Specific Heat			
temperature C	cycle 1	cycle 2	cycle 3	cycle 4
-53.15	0.910728147	0.821701701	0.909288482	0.816063793
-43.15	0.962423886	0.922692402	0.95366083	0.917318808
-33.15	1.044113993	1.064720188	1.039104428	1.058131267
-23.15	1.184129267	1.271190416	1.187965514	1.262421563
-13.15	1.40104743	1.494803303	1.41713853	1.485834191
-3.15	1.625077985	1.633930522	1.629038126	1.626886059
6.85	1.710715108	1.769011476	1.705066446	1.757029832
16.85	1.886209717	1.928543963	1.889613944	1.917621697
26.85	1.999558853	1.984450829	1.990904653	1.976245359
36.85	2.043336326	2.008354651	2.022425682	2.007950124
46.85	2.080473446	2.027531569	2.047725421	2.031394443
56.85	2.138829982	2.039128629	2.079647462	2.054690231
66.85	2.222360717	1.947699673	2.121193206	2.610940557

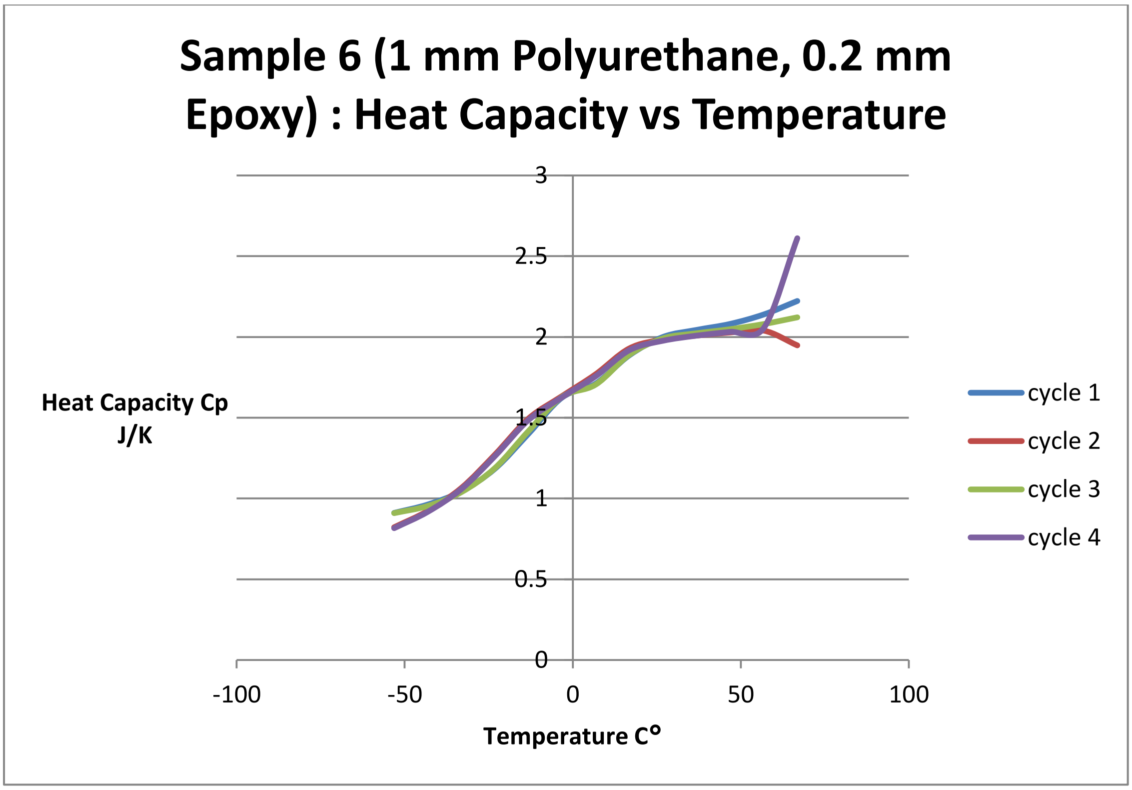


Figure 3-14 Heat capacity for a polyurethane-epoxy sample 6

The figure 3-14 represents the evolution of the heat capacity of a sample made of 1 mm of polyurethane and 0.2 mm of epoxy. The heat capacity constantly remains below 2.5 J/K.

	Specific heat			
temperature C	cycle 1	cycle 2	cycle 3	cycle 4
-53.15	0.785238423	1.260295795	0.746154735	1.251716596
-43.15	0.84608006	1.240039604	0.819317137	1.23344463
-33.15	0.914008439	1.251484432	0.891222151	1.243474176
-23.15	1.006851762	1.300244833	0.988593557	1.290994566
-13.15	1.136184398	1.364199559	1.119644434	1.354657959
-3.15	1.252819374	1.362361566	1.235775489	1.355939388
6.85	1.289210343	1.336320695	1.269547406	1.328538641
16.85	1.320426842	1.31002398	1.298872864	1.302090984
26.85	1.352633497	1.285877706	1.33038271	1.276490523
36.85	1.387138679	1.256601137	1.36394746	1.250004873
46.85	1.425969102	1.229320232	1.400868805	1.219814469
56.85	1.468764602	1.209411176	1.44198558	1.202001253
66.85	1.514709165	1.211889343	1.48529418	error

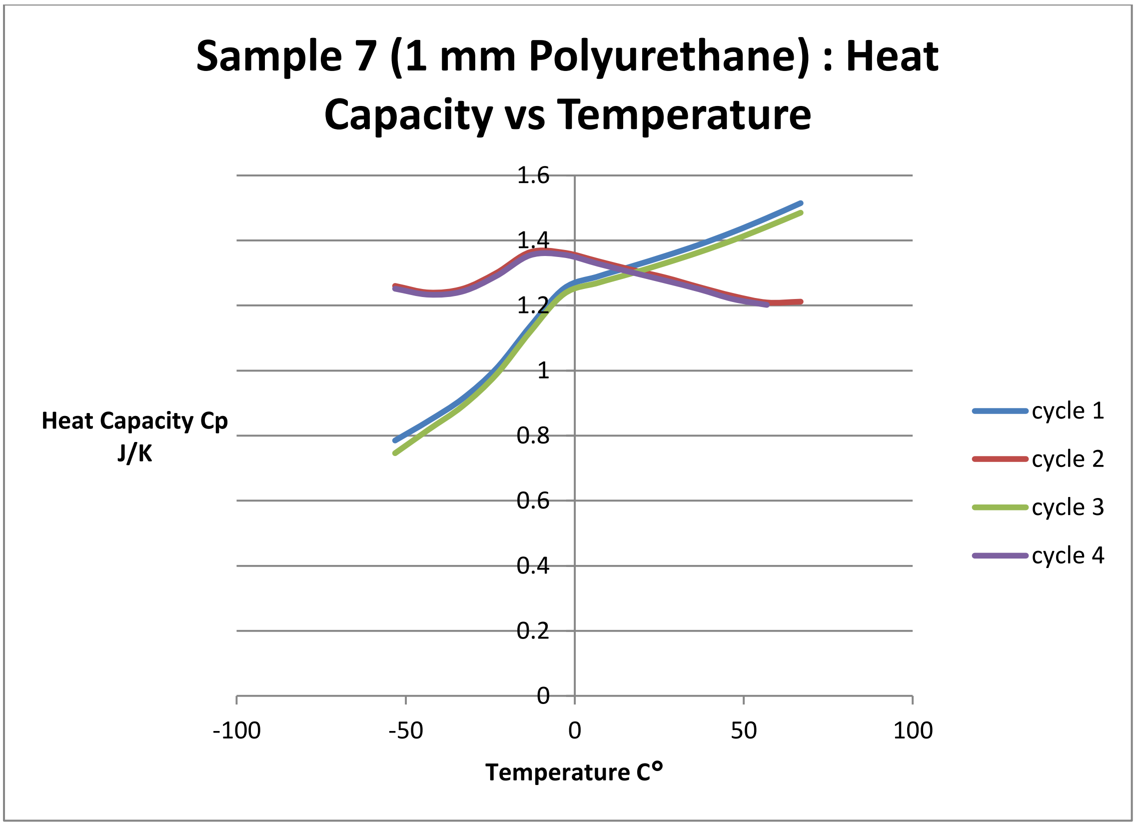


Figure 3-15 Heat capacity for a polyurethane sample

The figure 3-15 represents the evolution of the heat capacity of a sample made of 1 mm of polyurethane only. The heat capacity constantly remains below 1.5 J/K.

	Specific heat			
temperature C	cycle 1	cycle 2	cycle 3	cycle 4
-53.15	0.348838249	0.559880115	0.331475516	0.556068849
-43.15	0.376011723	0.550881404	0.363977548	0.547951619
-33.15	0.406043686	0.555965711	0.395920992	0.552407195
-23.15	0.447288869	0.577627276	0.438983403	0.573517891
-13.15	0.504744247	0.606038844	0.49711859	0.601800036
-3.15	0.556558753	0.605222324	0.548987092	0.602369304
6.85	0.572725259	0.593653798	0.563990097	0.590196659
16.85	0.586593033	0.581971613	0.577017785	0.57844742
26.85	0.600900679	0.571244752	0.591015877	0.567074543
36.85	0.616229433	0.558238782	0.60592685	0.555308424
46.85	0.633557442	0.546119376	0.622328973	0.541896488
56.85	0.652491342	0.537274877	0.640594895	0.533983056
66.85	0.672901985	0.538375791	0.659834525	error

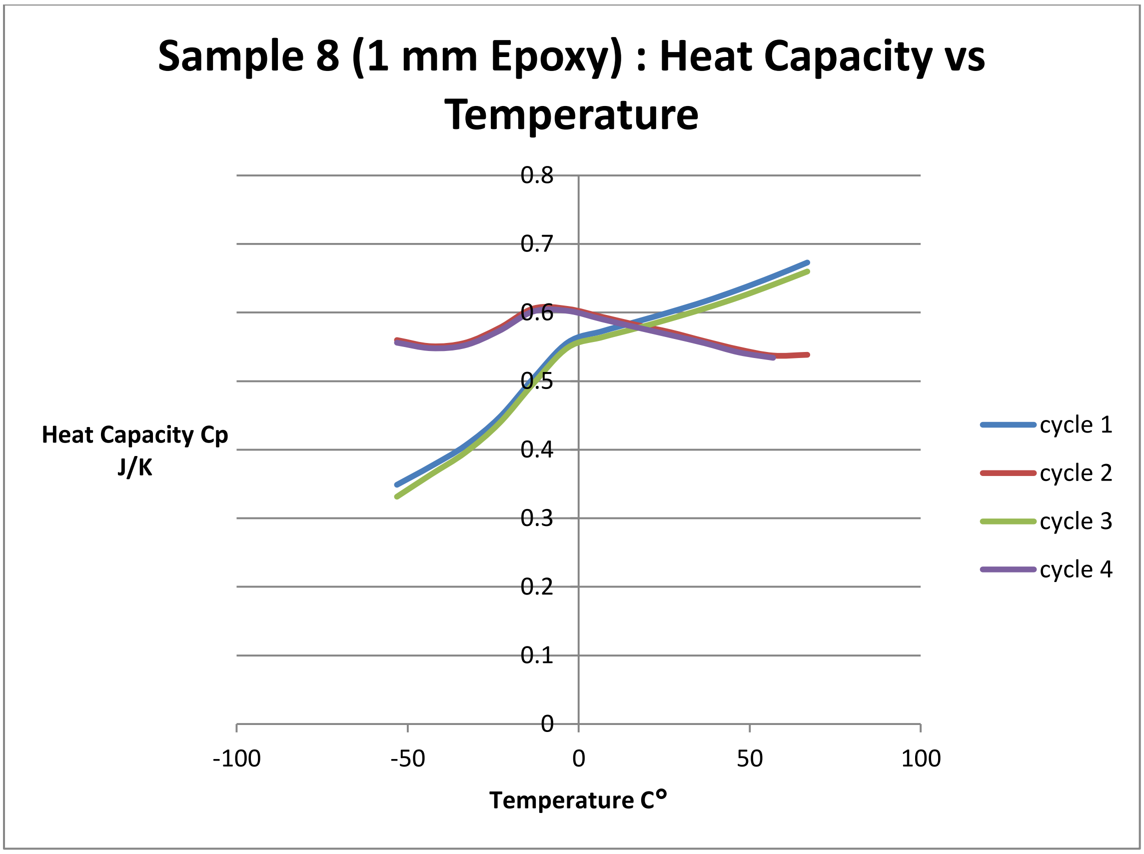


Figure 3-16 Heat capacity for an epoxy sample

The figure 3-16 represents the evolution of the heat capacity of a sample made of 0.2 mm of epoxy only. The heat capacity constantly remains below 0.7 J/K.

3.5 Differential Scanning Calorimetric observations

For all the samples, it was observed that the heat capacity of the material remained reduced for a large range of temperatures. The heat capacity was always below 3 j/g/K during the experiment.

The glass transition temperature of the polyurethane based material was -20 °C. The glass transition temperature for the epoxy was around 10 °C. The differential scanning calorimetric tests presented the same type of results for the double layer sample. The four curves obtained for each cycle had almost the same results. However, the sample made with only the polyurethane based material and only the epoxy presented the same particular characteristic: the four curves did not have the same values. Between -60 °C and 10 °C, the heat capacities obtained during the cycles of increased temperatures (cycle 2 and cycle 4) presented higher results than the heat capacities obtained by cycles of decreased temperatures (cycle 1 and 3). Then, between 10 °C and 70 °C, the heat capacity obtained during the decreased cycles (cycle 1 and cycle 3) was higher than the high capacity obtained during the increased temperatures cycles (cycle 2 and cycle 4). It can be observed on the Figure 3-17 that the layer of epoxy does not decrease the thermal properties of the polyurethane. The heat capacity of a dual layer sample is similar to the heat capacity of a sample made of polyurethane only. The epoxy does not affect the thermal properties of the polyurethane layer and can be used as an external protective material. The protective material can maintain an appropriate thermal protection, even after corrosion of the epoxy.

	Composition of the sample	Cp at -40°C	Cp at 0°C	Cp at 30°C	Cp at 60°C
Sample 1	1 mm polyurethane and 0.2 mm of epoxy	0.3	0.4	0.7	0.7
Sample 2	1 mm polyurethane and 0.2 mm of epoxy	0.5	1.2	1.7	1.8
Sample 3	1 mm polyurethane and 0.2 mm of epoxy	-0.2	0.3	0.6	0.8
Sample 4	1 mm polyurethane and 0.2 mm of epoxy	0.6	1.2	1.3	1.4
Sample 5	1 mm polyurethane and 0.2 mm of epoxy	0.9	1.5	1.6	1.6
Sample 6	1 mm polyurethane and 0.2 mm of epoxy	1.0	1.6	2.0	2.2
Sample 7	1 mm polyurethane	0.8	1.3	1.3	1.5
Sample 8	1 mm epoxy	0.4	0.5	0.6	0.7

Figure 3-17 Table summarize of the DSC results

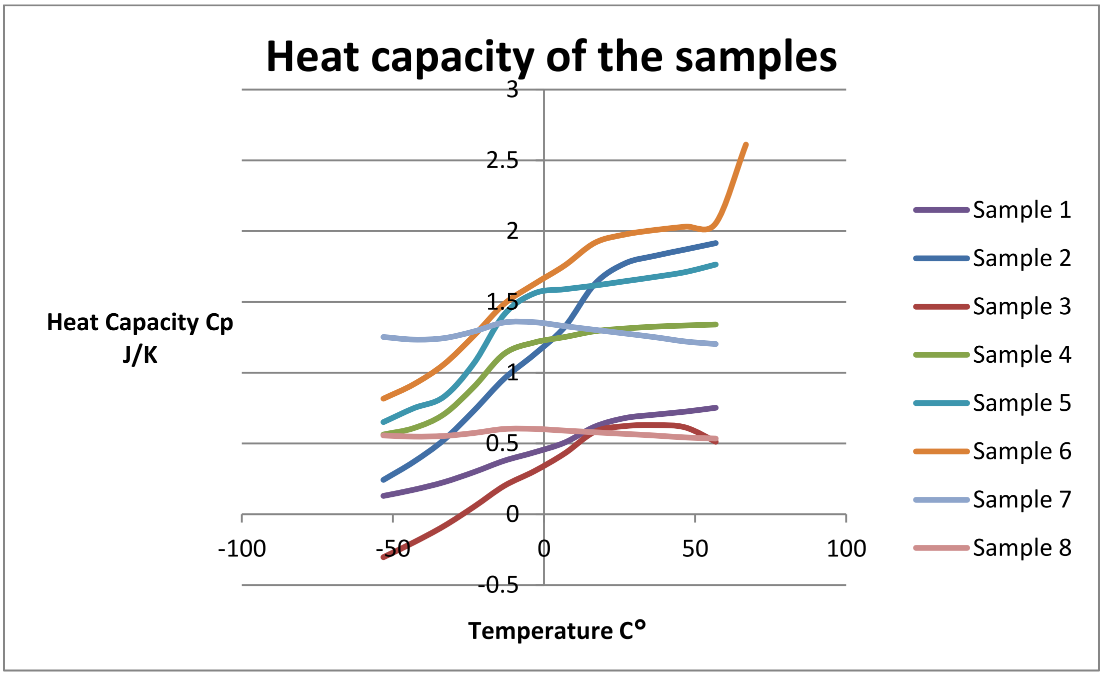


Figure 3-18 Comparison of the Heat capacity vs Temperature of the different samples

3.6 Dynamic mechanical analysis

3.6.1 Purpose of the DMA

During a dynamic mechanical analysis, a small sinusoidal stress is imparted to a polymer sample. The sinusoidal stress could be a torque push-pull, or a flexing mode of angular frequency ω.

The energy loss in the system during each thermodynamic cycle can be calculated from the “loss tangent” tan delta. “tan δ” represents the internal friction inside the system during a thermodynamic cycle. It can be calculated by dividing the loss modulus E’’(ω) by the storage modulus E’(ω). “tan δ” represents how the material can absorb or lose energy (Cowie, 1991).

$$\tan \delta = \frac{E''(\omega)}{E'(\omega)}$$

3.6.2 Protocol

The protocol for the dynamic mechanical analysis is quite simple. The sample must be at least 60 mm long. The thickness and the width must be known and written into the software. Then, the sample is positioned in the dynamic mechanical analysis machine between the fixed part and the cantilever. The position is maintained using two screws, each of them pressing each side of the sample. Then the dynamic mechanical analysis machine is closed. The analysis could then be run. In order to analyse the behaviour of the material for a large range of temperatures, two thermodynamic cycles are run. One cycle is normally made of maintaining the room temperature for a few minutes, then reducing the temperature to reach -70 °C, and increasing the temperature to reach +70 °C.

The difficulty of the dynamic mechanical analysis is to determine which type of test would be the most suitable for the material. As there is only a reduced literature about the behaviour of polymers for a large range of temperatures, it was not possible to know what type of effort and what intensity of stress the material was able to sustain. Therefore, few preliminary tests were realised in order to determine the most appropriate test for the material.

A multifrequency experiment with constant strain was realised first in order to determine the appropriate frequency. This experiment was not conclusive as some fractures appeared on the samples.

Another method was used. A multi stress cycle with non-constant force was applied to the sample, from 5N to 20N. The results given by the machine were extremely inaccurate (noise on the curves), so the testing method was not conclusive.

A third testing method was tried: a multi strain cycle with constant frequency (1Hz) and constant effort (5N). This method was tried on another sample of the same dimension. The loss modulus curve and the storage modulus curve were accurate, and presented a relatively low level of noise. The amplitude of the noise had a value below 5% of the maximum value. Consequently, this method was kept to determine the average loss modulus, storage modulus and tan δ of the material, and to describe the global mechanical behaviour of the material for a large range of temperatures.

3.6.3 Organisation of samples

Samples were organised in three categories. The first category is made of two samples. Each sample has one layer of polyurethane based material of 3 mm and one layer of epoxy of 1 mm. The second category is also made of two samples with one layer of polyurethane based material of 3 mm and one layer of epoxy of 1 mm. The sample of the first and second category does not come from the same polyurethane and epoxy sample. In order to prevent any error, two different polyurethane based material and epoxy were prepared in the same condition. The third category is only made of polyurethane based material to determine the difference between a single layer material and double layer material. It is assumed that the single layer material made only with polyurethane should have almost the same behaviour as the double layer material made with polyurethane and epoxy. The epoxy should not have a significant consequence on the stiffness of the material. The storage and loss modulus should not be affected by the presence of a 1 mm epoxy layer.

3.6.4 Results for storage modulus and loss modulus

The result for the storage modulus and loss modulus are given in a graph, representing both moduli against the temperature.

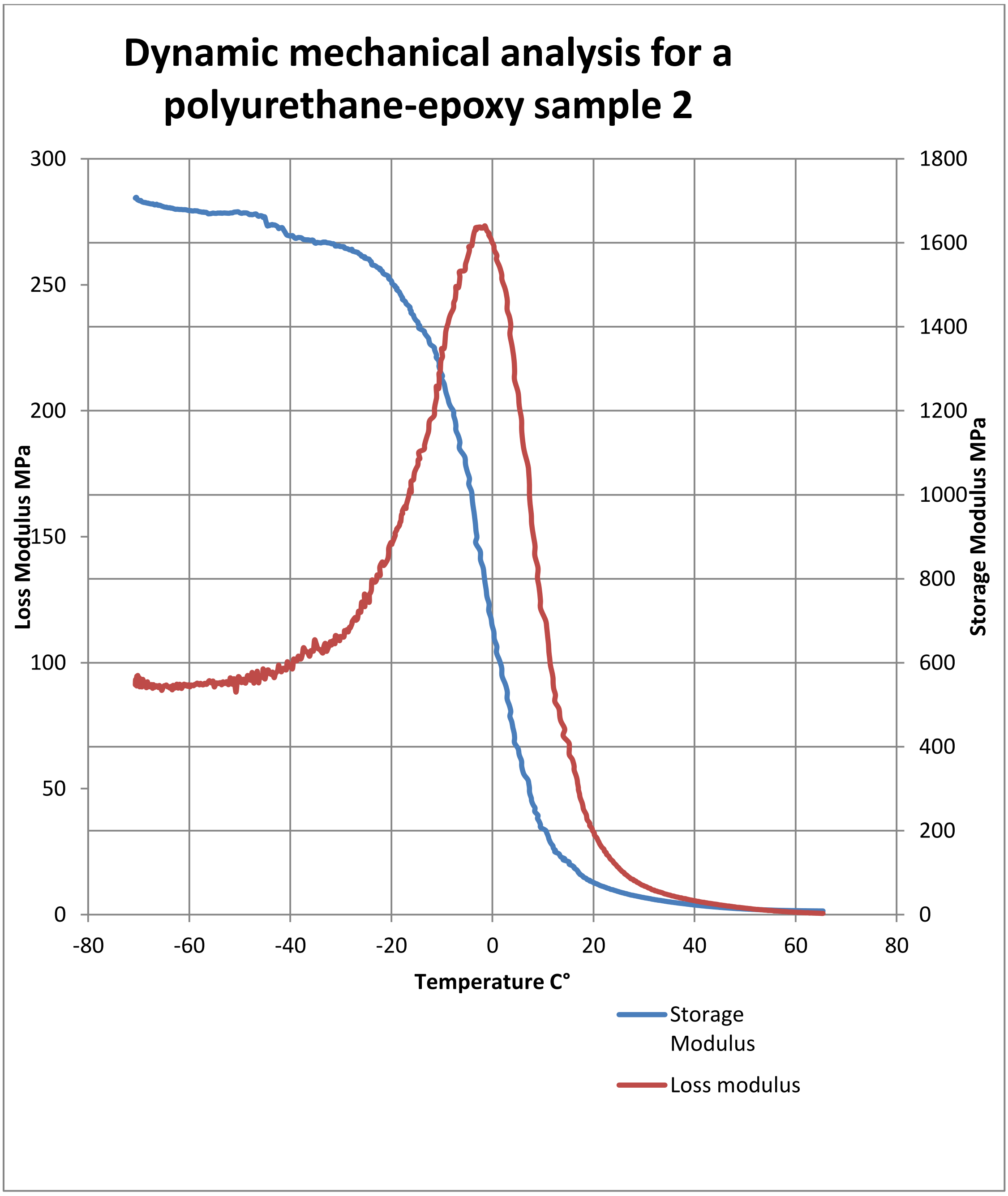


Figure 3-19 storage and loss modulus for a polyurethane-epoxy sample 2

This graph presents the storage modulus and loss modulus for a sample made of polyurethane based material and epoxy. The loss modulus has an average value of 90 MPa between -70 °C and -40 °C. It increases rapidly to reach a maximum of 260 MPa for a temperature of -5 °C and decreases rapidly to reach a value of 40 MPa at 20 °C. It slowly diminishes to reach a zero value at 60 °C. The storage modulus has a value up to 1700 MPa at -70 °C and decreases to reach a zero value at 60 °C.

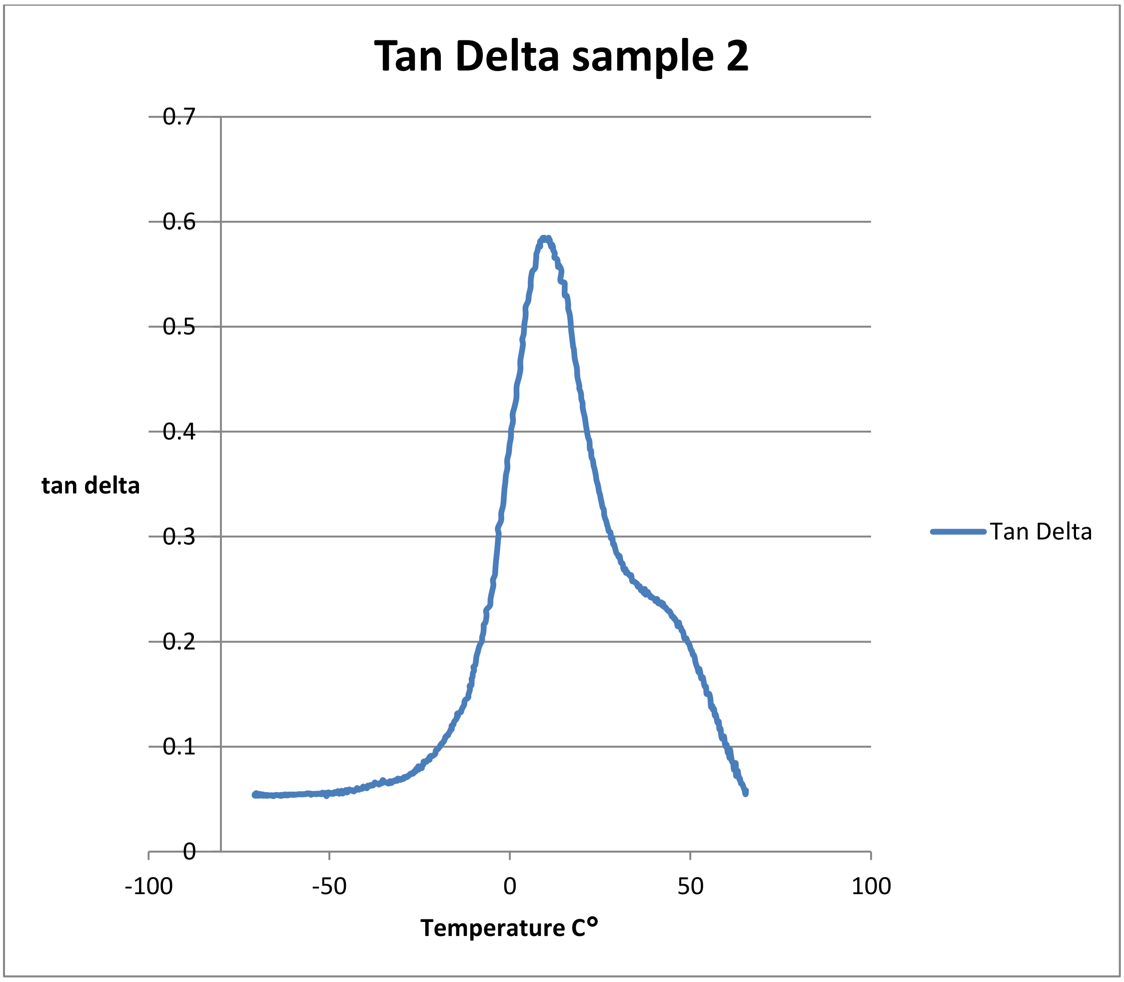


Figure 3-20 Tan delta for a polyurethane-epoxy sample 2

For this sample, tan δ is below 0.1 for a range of temperature from -70 °C to -20 °C. tan δ rapidly increases to reach a maximum of 0.6 at 10 °C and decreases below 0.1 after 60 °C. The sample loses a lot of energy for temperature between -20 °C and 60 °C. Below -20 °C, the material does not lose a lot of energy.

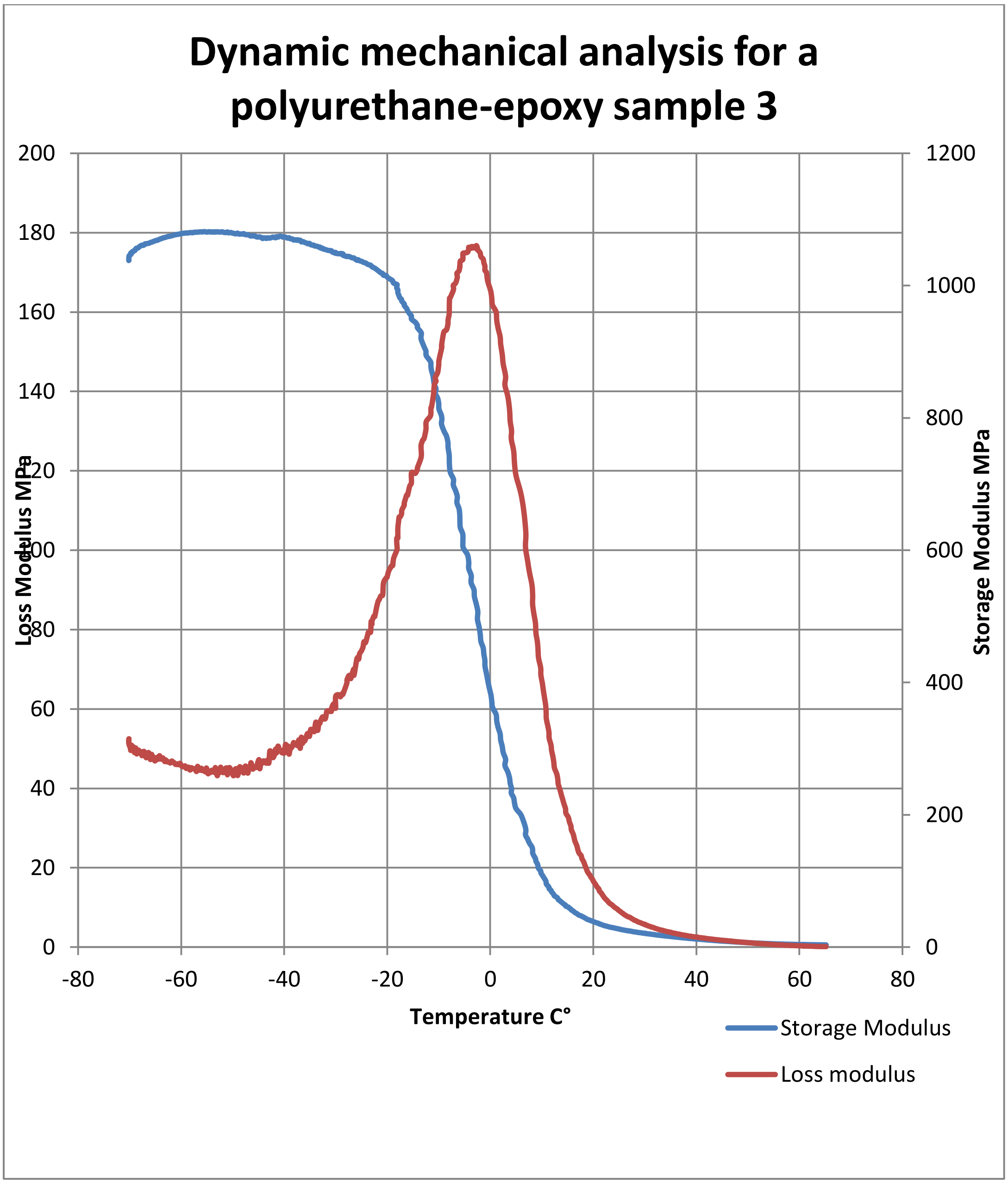


Figure 3-21 storage and loss modulus for a polyurethane-epoxy sample 3

This graph also presents the storage modulus and loss modulus for a sample made of polyurethane based material and epoxy. The loss modulus has an average value of 50 MPa between -70 °C and -40 °C. It increases rapidly to reach of maximum of 180 MPa for a temperature of -5 °C and decreases rapidly to reach a value of 20 MPa at 20 °C. It slowly reduced to reach a zero value at 60 °C. The storage modulus has a value up to 1100 MPa at -70 °C and decreases to reach a zero value at 60 °C.

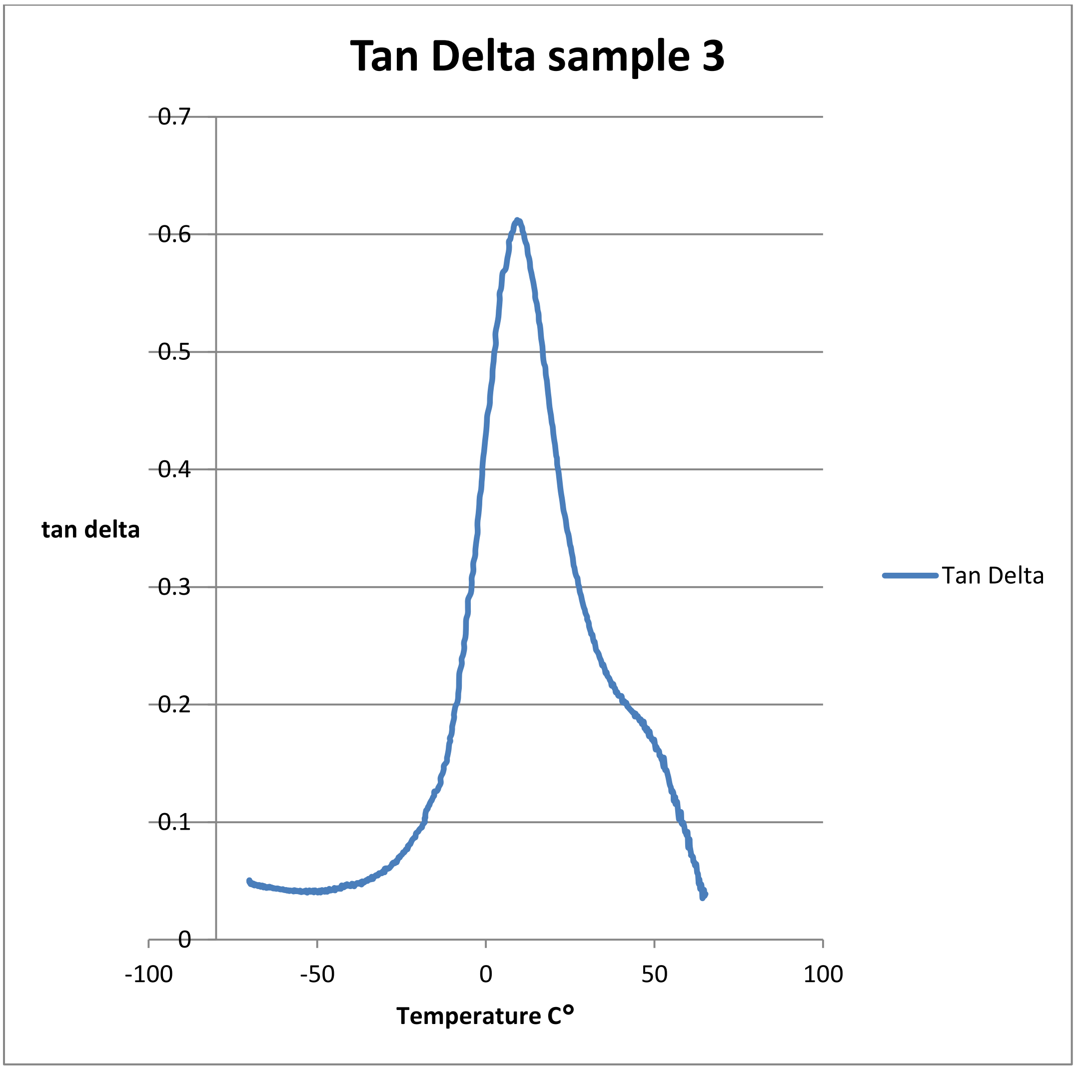


Figure 3-22 Tan delta for a polyurethane-epoxy sample 3

For sample 3, tan δ is below 0.1 for a range of temperature from -70 °C to -20 °C. tan δ rapidly increases to reach a maximum of 0.62 at 10 °C. tan δ decreases below 0.1 after 60 °C. The sample loses a lot of energy for temperatures between -20 °C and 60 °C. Below -20 °C, the material does not lose a lot of energy.

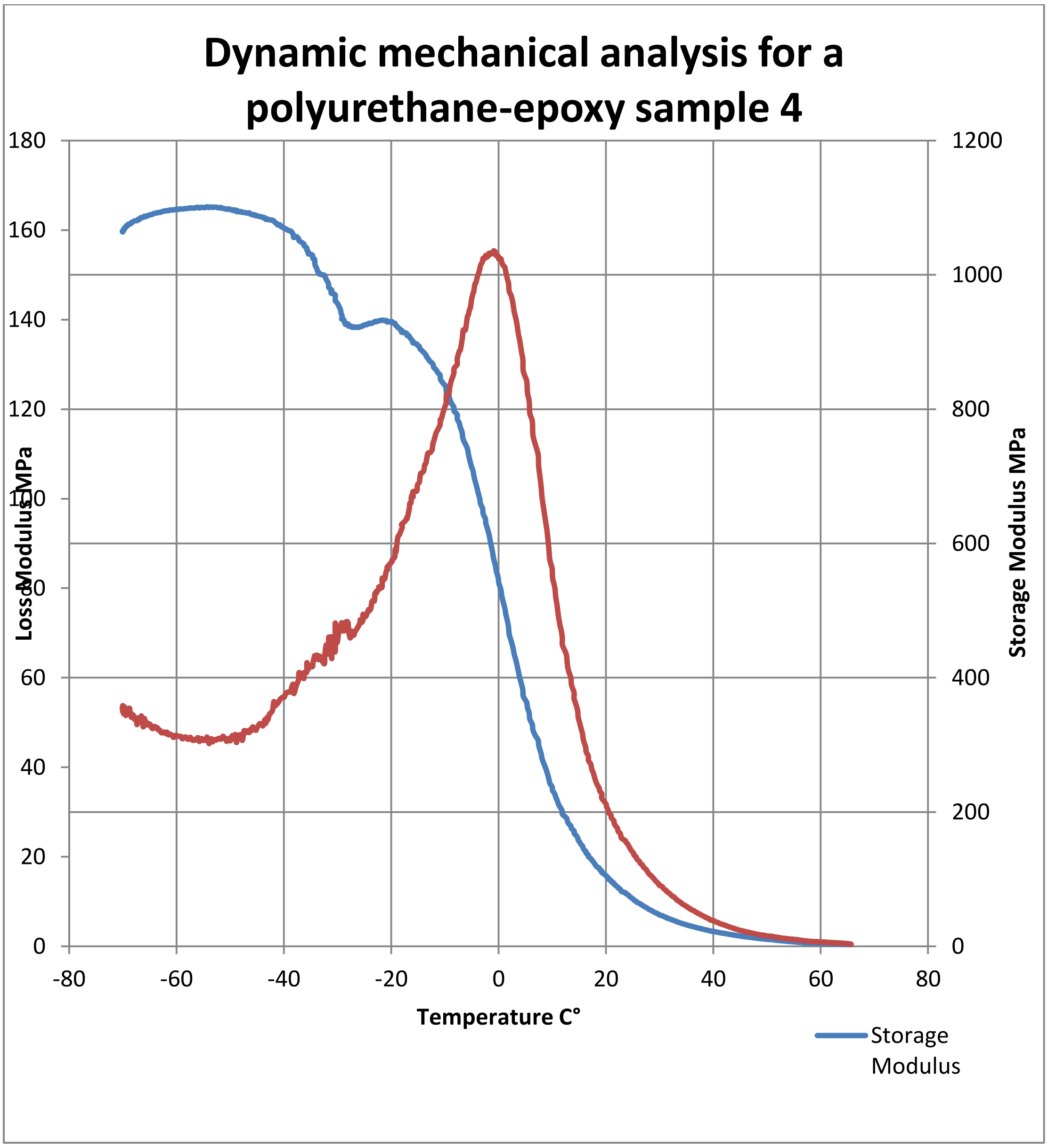


Figure 3-23 storage and loss modulus for a polyurethane-epoxy sample 4

This graph also presents the storage modulus and loss modulus for a sample made of polyurethane based material and epoxy. However, a lot of noise and possibly a measured error can be noticed between -40 °C and -20 °C. The loss modulus has an average value of 50 MPa between -70 °C and -50 °C. Then it increases rapidly to reach of maximum of 160 MPa for a temperature of 0 °C. It decreases rapidly to reach a value of 20 MPa at 20 °C. It slowly reduces to reach a zero value at 60 °C. The storage modulus has a value up to 1100 MPa at -70 °C and decreases to reach a zero value at 60 °C.

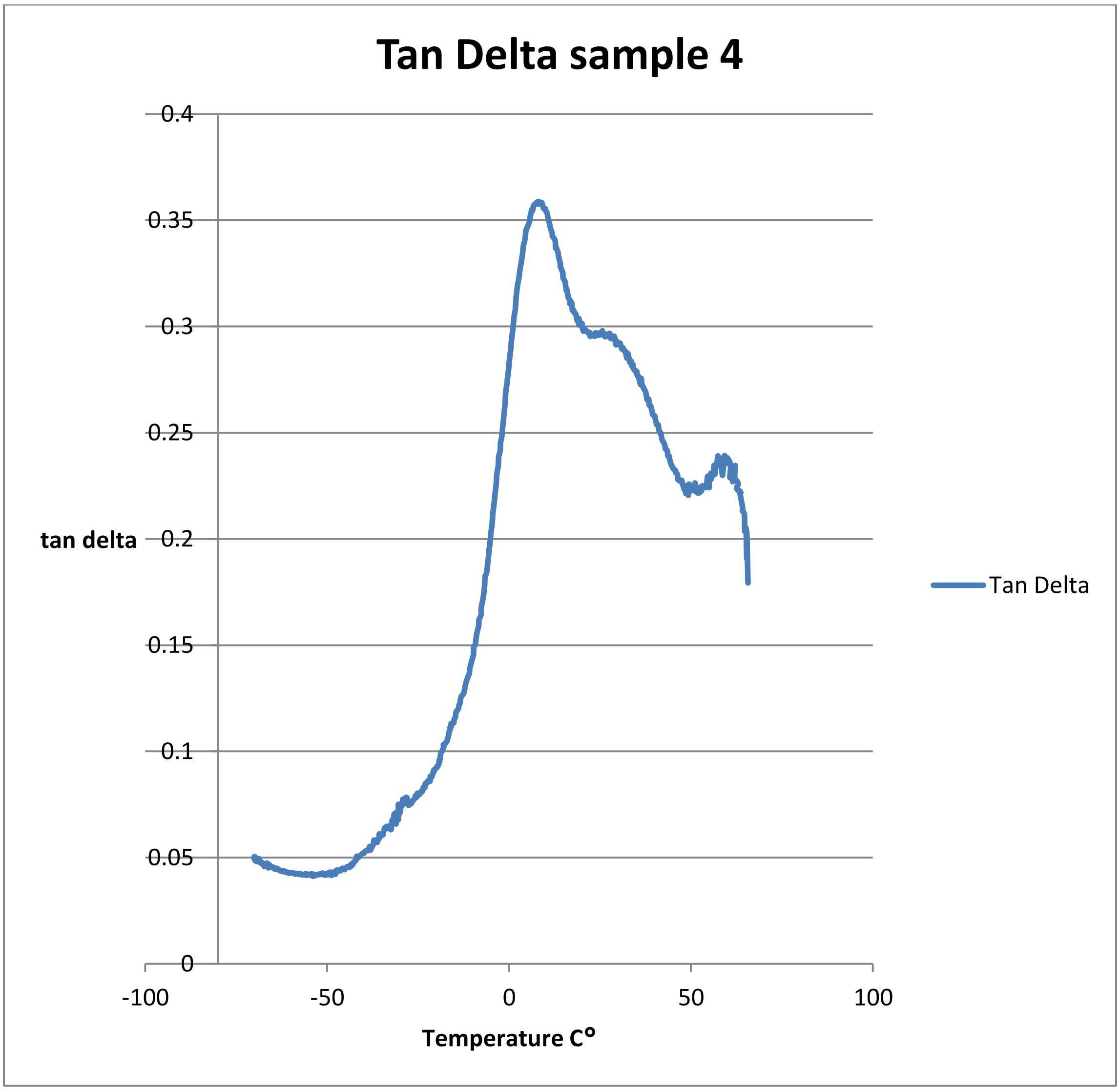


Figure 3-24 Tan delta for a polyurethane-epoxy sample 4

For sample 4, tan δ is below 0.1 for a range of temperature from -70 °C to -20 °C. tan δ rapidly increases to reach a maximum of 0.35 at 10 °C. This value is relatively low compared to the previous values obtained for sample 2 and 3. Also, the curve obtained for the positive does not present the required accuracy. There are at least two "drops" (at 20 °C and 50 °C) even though the curve should decrease regularly. Therefore, this sample cannot be considered conclusive.

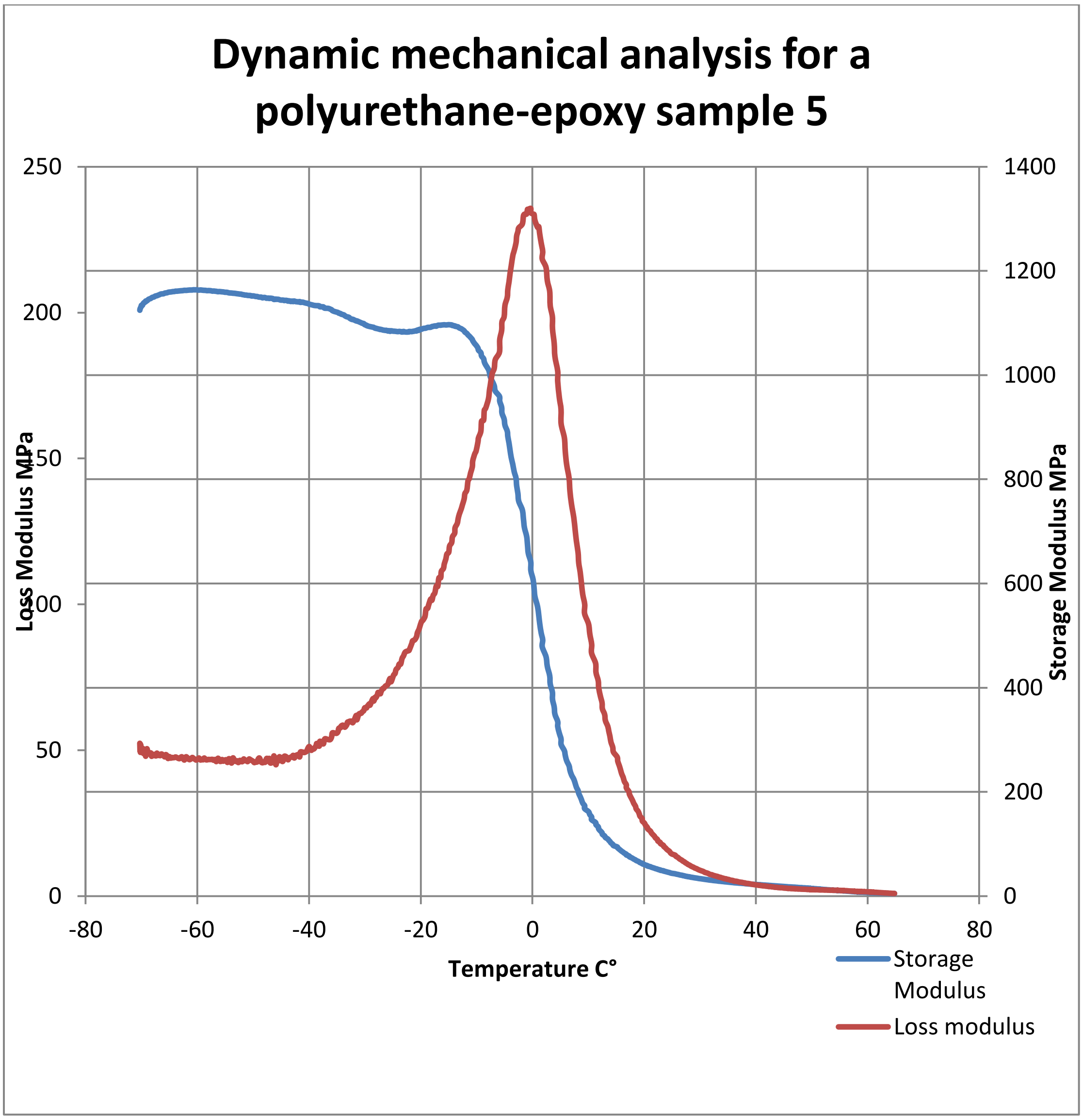


Figure 3-25 storage and loss modulus for a polyurethane-epoxy sample 5

This graph presents the storage modulus and loss modulus for a sample made of polyurethane based material and epoxy. The quality of this analysis is much better than the previous one because there is almost no noise on the curves. The loss modulus has an average value of 50 MPa between -70 °C and -40 °C. It increases rapidly to reach of maximum of 240 MPa for a temperature of 0 °C. It also decreases rapidly to reach a value of 20 MPa at 20 °C. It slowly reduced to reach a zero value at 60 °C. The storage modulus has a value up to 1150 MPa at -70 °C and decreases to reach a zero value at 60 °C.

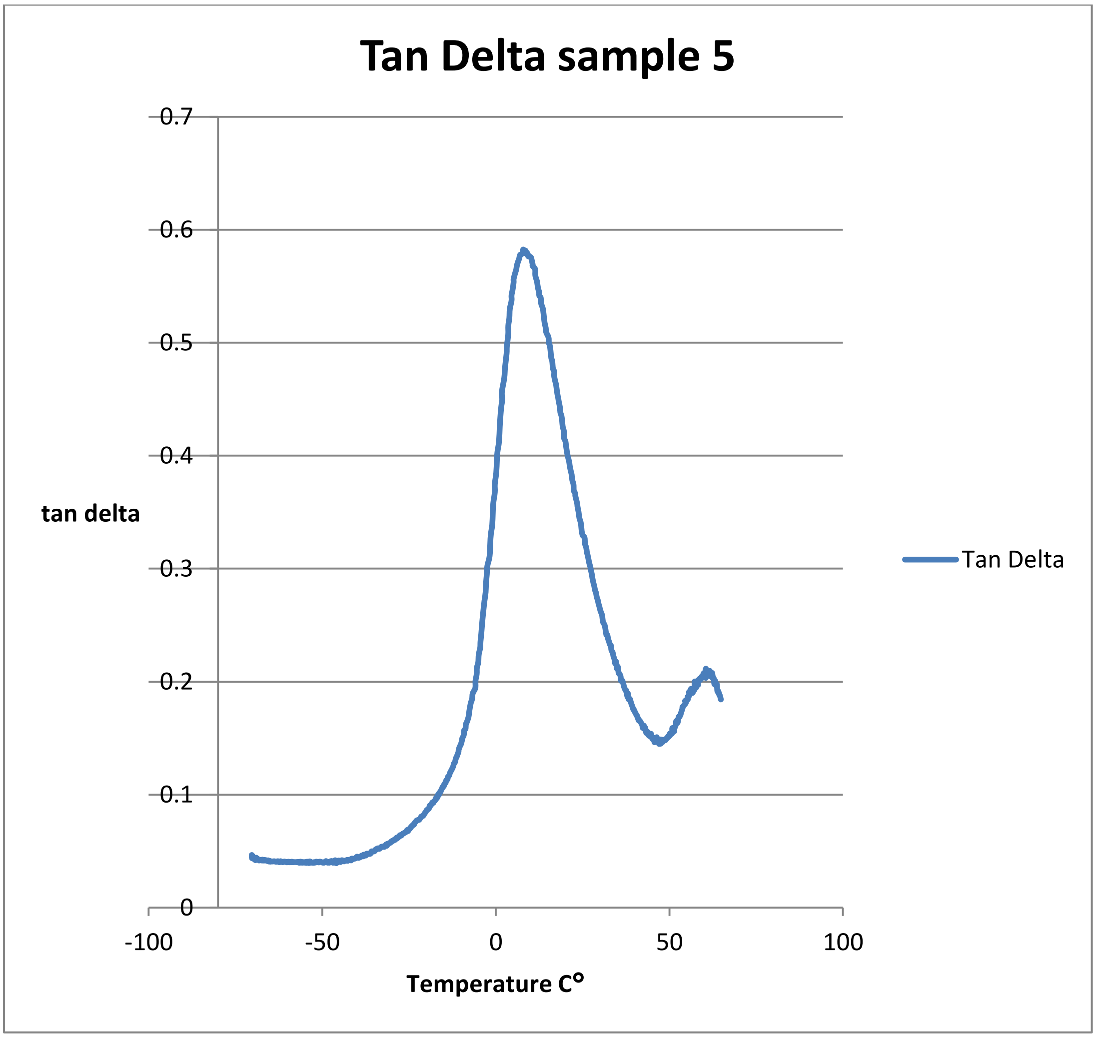


Figure 3-26 Tan delta for a polyurethane-epoxy sample 5

For sample 5, tan δ is below 0.1 for a range of temperature from -70 °C to -20 °C. tan δ rapidly increases to reach a maximum of 0.62 at 10 °C. Then, the tan δ decreases. After 50 °C, the curve starts increasing again, but this is not expected. Therefore, only the curve between -70 °C and 50 °C can be considered conclusive. For this range of temperature, the sample does not lose a large amount of energy in heat before reaching -20 °C.

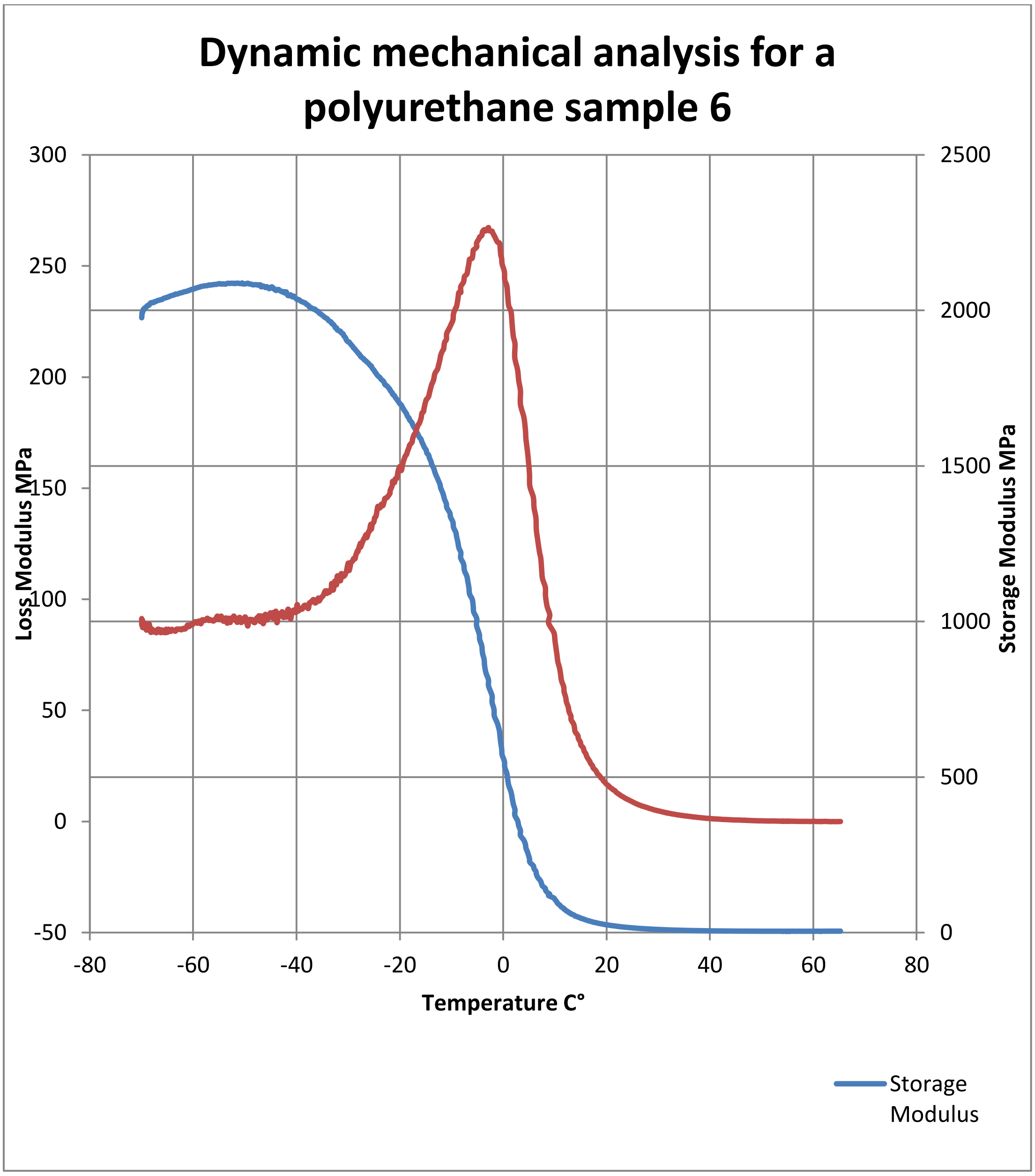


Figure 3-27 storage and loss modulus for a polyurethane sample 6

This graph also presents the storage modulus and loss modulus for a sample made of polyurethane based material without epoxy. The loss modulus has an average value of 90 MPa between -70 °C and -40 °C. It increases rapidly to reach a maximum of 260 MPa for a temperature of -5 °C. At 20 °C, the loss modulus is almost equal to zero. The storage modulus cannot be analysed because all the values higher than 0 °C are below zero MPa. It is possible to notice that in the absence of an epoxy layer the storage modulus is larger (2300 MPa) than the other samples made of polyurethane and epoxy.

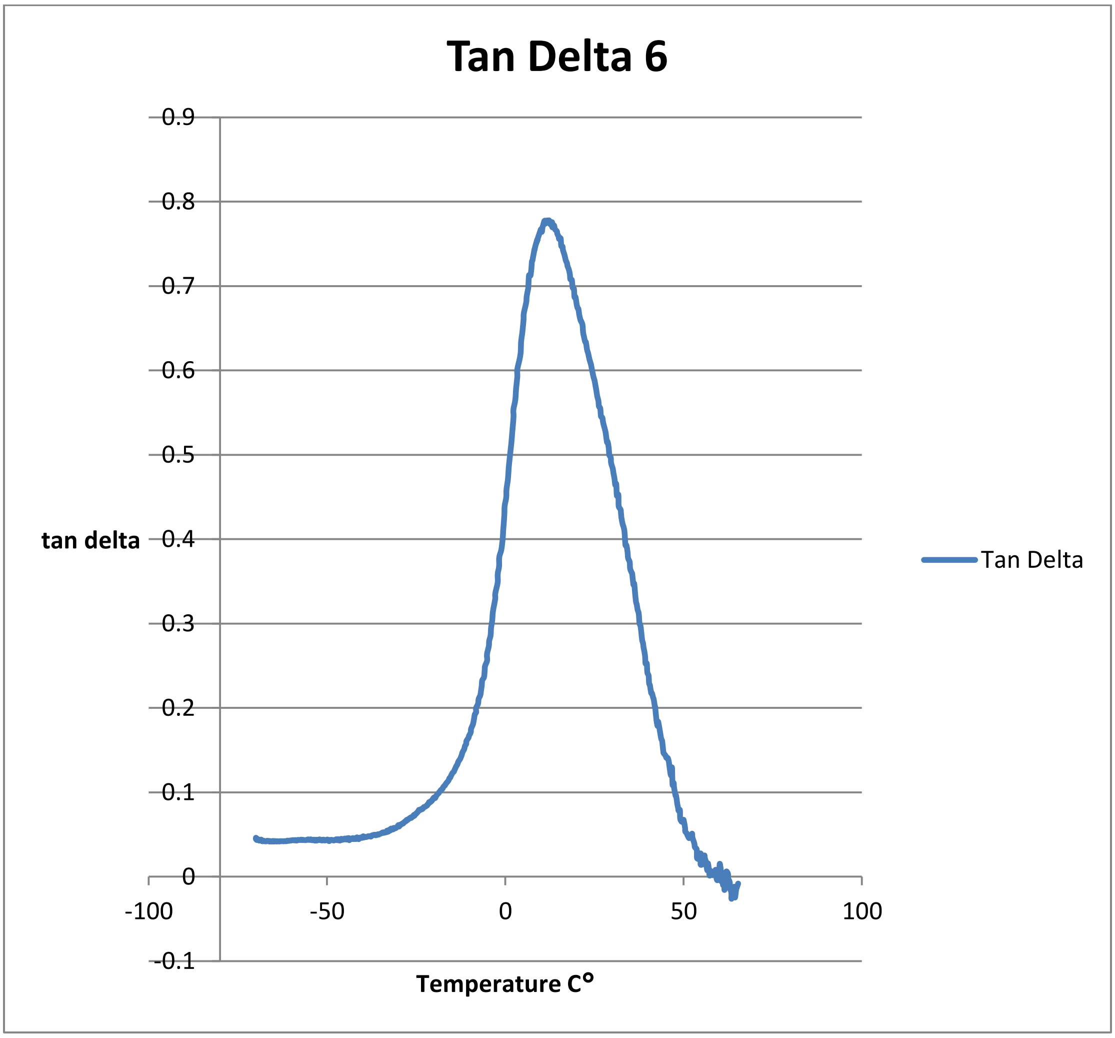


Figure 3-28 Tan delta for a polyurethane sample 6

For sample 6, which is only made of a polyurethane based material without epoxy, tan δ is below 0.1 for a range of temperature from -70 °C to -20 °C. tan δ rapidly increases to reach a maximum of 0.8 at 10 °C. Then tan δ decreases. After 50 °C, the curve drops below zero. This was not expected. Therefore, only the curve between 70 °C and 50 °C can be considered conclusive. For this range of temperature, the sample does not lose a large amount of energy in heat before reaching -20 °C. But it does lose a large amount of energy at 10 °C.

3.6.5 Summary of the results

Except the first sample, all the samples made of 1 mm of polyurethane and 0.2 mm of epoxy present the same storage modulus, the same loss modulus and the same type of curve for the tan delta. It seems that the second sample presents a different behaviour from the other sample made of polyurethane and epoxy. But it present the same type of behaviour as the last sample, made exclusively from polyurethane.

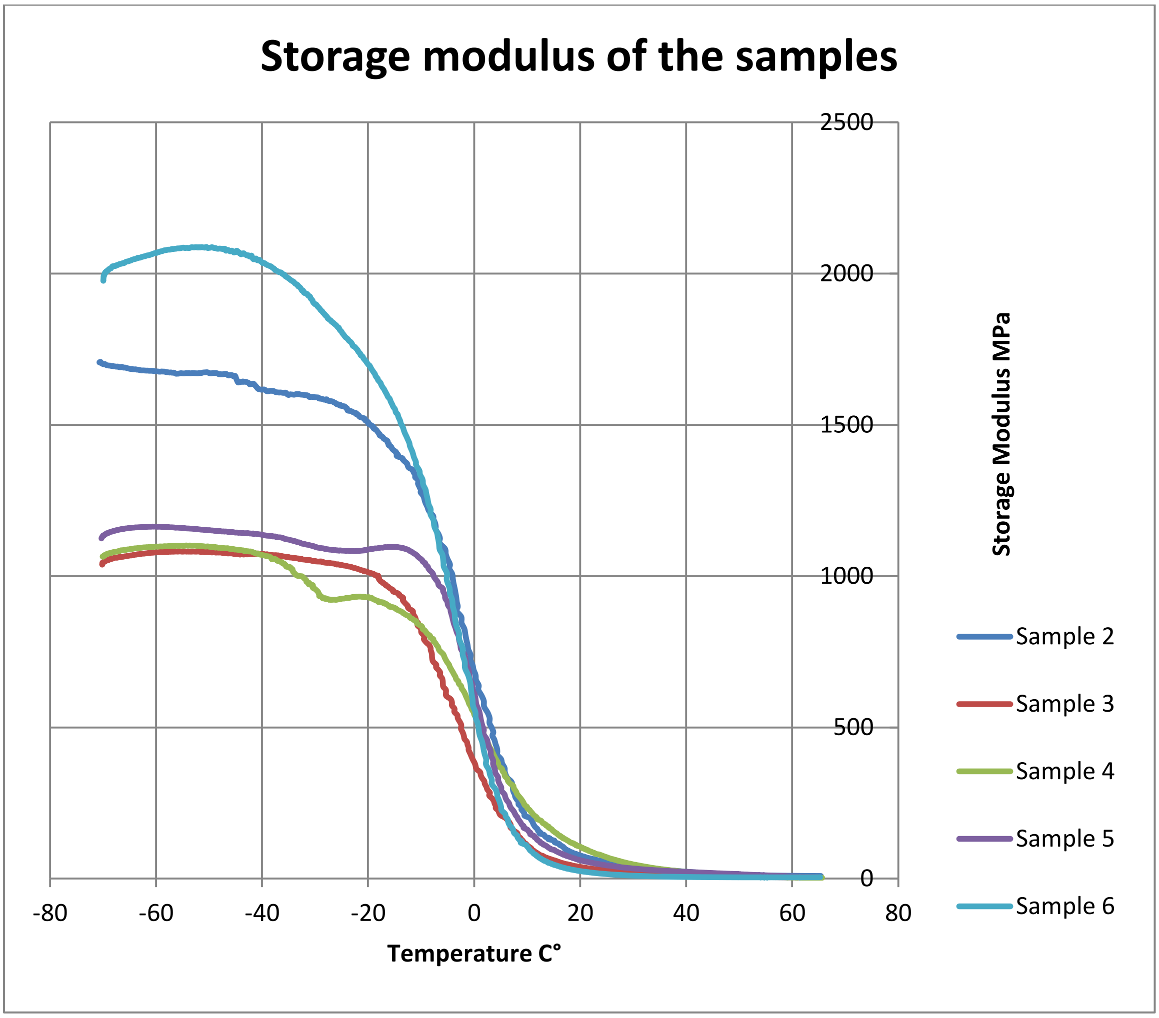


Figure 3-29 Comparison of the storage modulus of the different samples

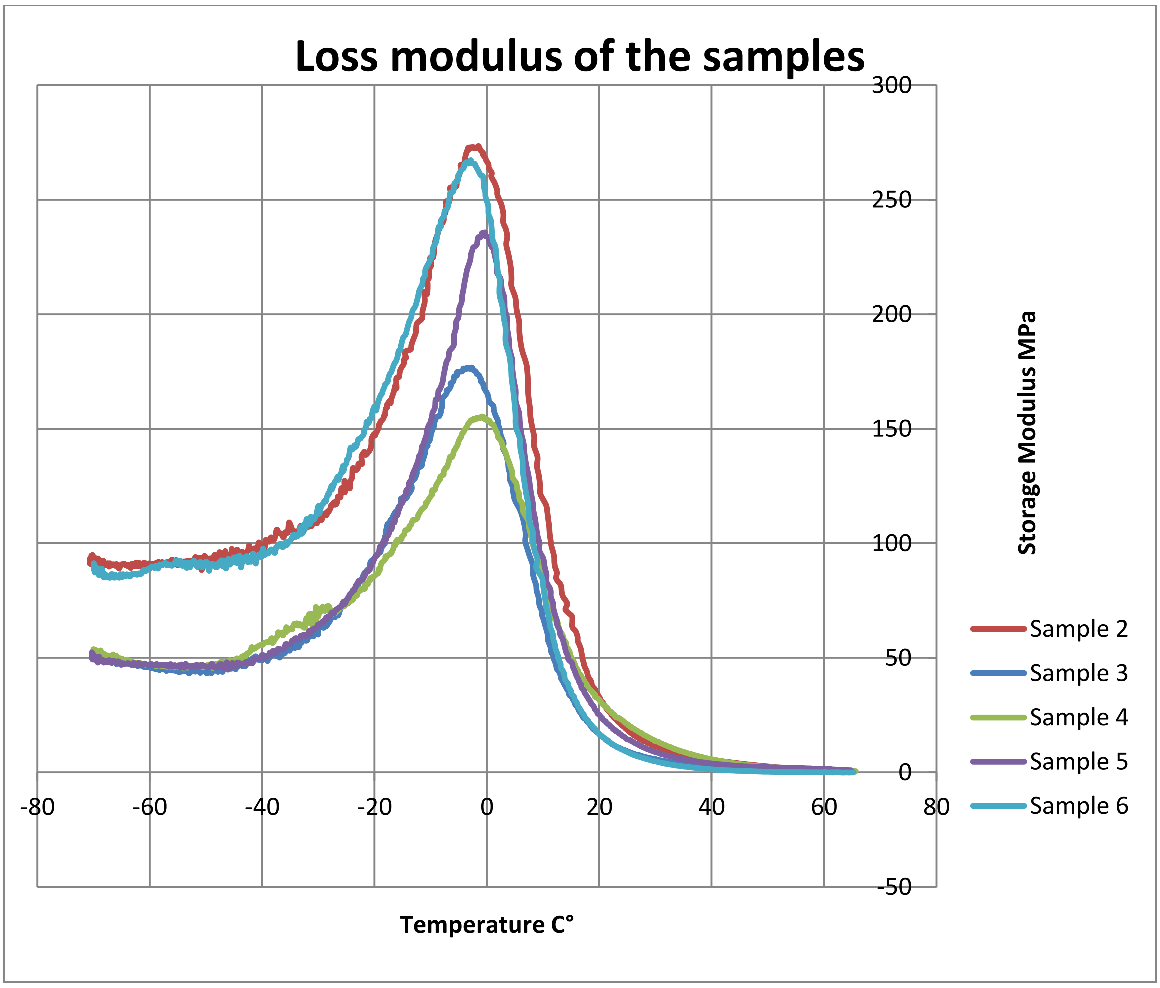
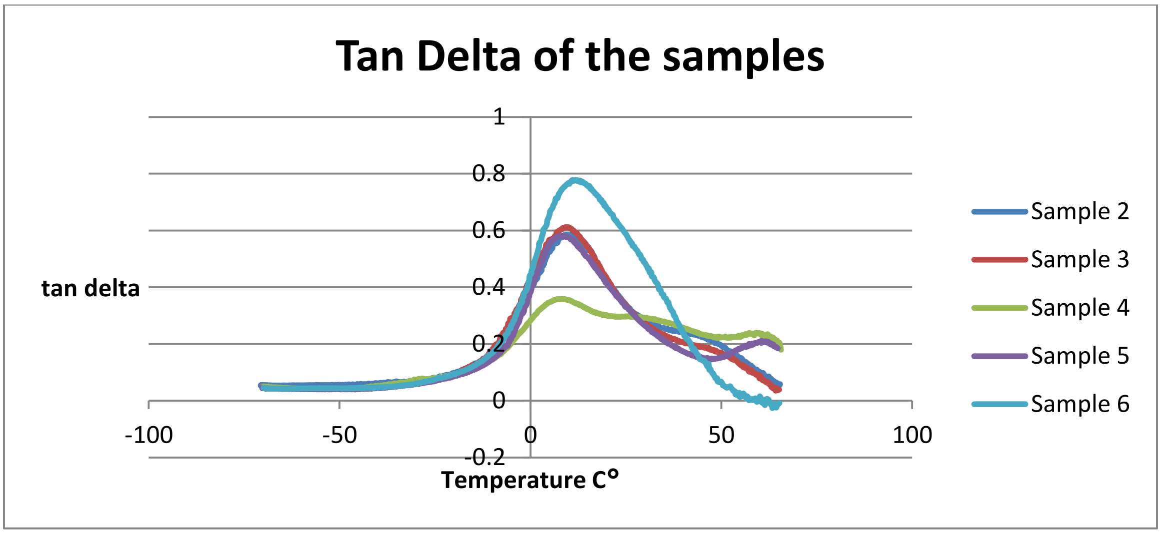


Figure 3-30 Comparison of the loss modulus of the different samples



4. Figure 3-31 Comparison of the Tan Delta of the different samples

3.7 Comparison and analysis of the results

3.7.1 Differential scanning calorimetric tests

The differential scanning calorimetric tests were used to determine the glass transition temperatures and the heat capacity of the samples. It has been observed that the glass transition temperature of the samples were directly related to the materials of each layer. It was noticed that the two layer samples present two different glass transition temperatures. The glass transition temperature of the polyurethane based material was around -20 °C, and the glass transition temperature of the epoxy was around 10 °C. These values are relatively low. However, in the present case, a low glass transition temperature is an advantage: the material becomes plastic at a low temperature. The protective coating will maintain a relative elasticity at extreme cold temperatures, which may reduce the risk of plastic fractures and the infiltration of water.

The heat capacities of the samples were also studied for high temperatures. As expected, the heat capacity increases with the temperature. Two complete thermodynamic cycles were realised by the machine. For each temperature, the heat capacity is verified four times. Most of the solid material has a heat capacity below 0.9. Thus, they can be heated rapidly, but they also can transmit the heat rapidly. Therefore, they are not suitable for reducing the heat transfer of a system, nor insulating against the cold. The polyurethane based material associated with the epoxy presents a heat capacity up to 3 for high temperatures, which means they are difficult to heat, and they restore the heat very slowly. They are therefore suitable for insulating the topside against the cold. An additional layer of polyethylene might help to reduce the heat transfer, which may be particularly interesting for a high temperature processing unit.

3.7.2 Dynamic mechanical analysis

The storage modulus represents the stored energy, representing the elasticity of the material. And the loss modulus represents the energy dissipated as heat, which is the viscous portion. It has been observed that the storage modulus of each sample is at least one hundred times bigger than the loss modulus, which indicates the material does not lose a lot of energy as a heat and can maintain a good elasticity without having a viscous behaviour. However, through the different processes of the dynamic mechanical analysis experiment, it has been observed that the polyurethane based material recovered with an epoxy layer cannot sustain large forces or different types of vibrations. The experiment was made possible only by maintaining a steady frequency of 1 Hz with a constant force of 20N. Therefore, this material presents a relatively good potential for coating application but cannot be used as a protection against any type of mechanical constraints.

A complete study of the results required the storage modulus and the loss modulus to be analysed with the tan δ. It has been noticed that the dynamic mechanical analysis machine was not able to provide accurate values after 50 °C. Generally, after this temperature, the curve has a non-expected behaviour (tan delta below zero, noise…). The storage modulus of a sample made with polyurethane based material and epoxy has generally a maximum value of 1200 MPa at -70 °C. The loss modulus always reaches its maximum value of around 250 MPa for a temperature of 0 °C.

A sample made only with the polyurethane based material presents some differences. The value of the storage modulus is higher and reaches a maximum of 2200 MPa at 60 °C. The absence of epoxy might explain this higher storage modulus for extreme cold temperatures. The samples made with polyurethane based material and epoxy generally do not lose a large amount of energy by cold temperature. This loss is maximised for temperatures between 0 °C and 20 °C.

3.7.3 Comparison with existing results

The use of polymers for offshore structures protection is relatively new, and not many studies have been conducted on the behaviour of multilayers of polymer material exposed to cold temperature. However, the behaviour of polyurethane for LNG tanks protection is well documented, and it is possible to compare the results of our studies with those studies.

The mechanical properties of sandwich foam have been recently studied (Yu, Cryogenic reliability of the sandwich insulation board of LNG ship, 2012). This study focused mostly on the tensile failure strength of an insulation board,made of

0.3mm polyurethane for cold temperature. The main results were an increase of mechanical reliability and thermal performance of the insulation board protected with polyurethane foam. It has been proven that increasing the polyurethane foam thickness by 1 mm will increase the safety factor by 42%. Our study demonstrated that a protection made of polyurethane can effectively increase the thermal properties of the protected material. This thermal protection is greatly increased when the polyurethane layer is protected by a thin layer of epoxy.

The protection of polyurethane by a cost efficient material in order to face the Arctic environment had been required because the polyurethane was principally used for inside LNG insulation (Demharter, 1997). The epoxy did not only increase the thermal properties of the protective layer, it also increased its durability, particularly for outside use (main deck, drill floor).

The icing represents one of the main issues for structures operating in the Arctic environments and can be effectively reduced by using hydrophobic materials (Kraj, 2009).

4 Conclusion

4.1 Summary of key finding

The protection of a structure against the arctic environment can be achieved by using appropriate materials associated with the appropriate maintenance. Different solutions could be used, depending on the type of structure and the possibility to operate a maintenance operation on it. The arctic environment reduces the possibility of doing regular preventive and curative maintenance. Due to the snow and the ice, it may be difficult to perform efficient inspections. The main issues due to the Arctic environment are the ice, the cold temperature, and the green waters.

After a review and study of different materials, it was noticed that only the polymer material was able to protect the topside efficiently. Using one material directly exposed to the outside environment presents low maintainability.

In order to maintain the efficiency of the coating protection, the concept of multi-layer protection was studied: each layer should face a reduced number of issues so that in case of an incident, the others layers can still perform their tasks. The inside layer, which is not in direct contact with the cold temperature and water, is made of polyurethane. This polymer presents one of the lowest heat conductivity for a solid. Also, it presents an excellent hydrophobicity. This inside layer can insulate the system and avoid infiltration of water. The polyurethane also presents an excellent elasticity for a large range of temperatures, which reduces the risk of plastic fractures. The outside layer is made of epoxy. The epoxy is a well-known polymer, easy to install and replace, totally hydrophobic, with excellent anti-icing properties. Also, the epoxy can easily be coated onto any type of polyurethane based material.

This dual layer coating protection theoretically represents an appropriate solution against the Arctic environment by reducing the heat transfer, and avoiding the icing, the infiltration of water and the permeation of fluid. The fast and simple maintenance of the outside layer makes this protection efficient. However, the epoxy presents rapidly a relatively high plasticity, which might lead to the defection and infiltration of water between the two layers.

Most of the flat structures of a rig (main deck, second deck) could be chemically treated against ice. A curative mechanical ice removal could also be applied to these structures.

However, it is not possible to apply a chemical or a mechanical treatment to active units, as it will require shutting down the unit to carry out the maintenance operation, which might not always be possible. The dual layer coating could be applied to these units, and specifically to the power generator (which must remain in working condition to power the whole rig), the mud unit (which provides the drilling mud), the processing unit (used on the production rig to process the extracted oil and must not stop working) and the whole drill-floor and drilling topdrive.

These units can be coated previous to starting their mission and should not require any maintenance during the first few months. The mitigation of ice should therefore be achieved without any extra maintenance operation.

In terms of cost, the cost of producing a dual layer material made of polyurethane and epoxy could not be estimated unless applied on a real scale structure. This cost should be compared with the cost of offshore maintenance operations required to remove the ice and non-producing time due to these operations. There is no doubt that for a long term operation a preliminary coating in a shipyard would certainly reduce the maintenance and operation cost of a rig.

4.2 Future possible research

Further studies and works could develop the work already conducted. These works should focus on the replication of DSC results in order to determine an accurate behaviour of a dual layer material and potentially investigate the range of incertainty expected of heat capacity for each temperature. It could be interesting to vary the thickness of the layers to determine the effect on the heat capacity and the materials used, in order to determine the most appropriate material to effectively protect a system operating in an arctic environment.

As for the DMA, it could be interesting to focus on the long term mechanical behaviour of a dual material subject to long cold cycles and vibration. Fracture inspection could also be integrated to the research to analyse the life time of the external layer.

Finally, potential researchs could include a real scale pipeline, covered with a multi layer material, exposed to long cycles of cold temperature and to regular flow of water.

There are a lot of future possible research studies related to the production of oil and gas in the Arctic environment. The issues faced during the production of oil and gas are often related to the characteristic of the oil field. Therefore, the external environment should not affect the production. However, most of the future possible research studies should be related to the integrity of the platform, particularly its structure and its topside. As studied during the Hibernia project, a fixed concrete platform can be protected efficiently against floating ice and icebergs. However, there is no efficient solution to protect a floating structure against floating ice and potential icebergs. The company SBM is building a few FPSOs with an external detachable turret in order to disconnect the FPSO to avoid collision with an iceberg. However, this solution cannot be considered as an efficient protection against floating ice. The other level of protection is related to the topside of the platform with the deck and the different units. As the risk of icing can only be reduced but not completely avoided, an efficient curative anti-icing system must be studied. The Sintef project analysed the different anti-icing methods. The mechanical removal of ice is difficult and time consuming. The chemical method requires a large quantity of chemicals, which might not be authorised by the environmental regulation of the country in which the platform operates. The electrical method might represent an option; using an electromagnetic wave to destroy ice has been proved, but more experiments should be realised to determine the feasibility of implementing a series of electromagnetic pulse systems on a large and complex structures.

During this project, it has been shown that a polymer material can be used to efficiently protect a system against cold temperatures, ice and the infiltration of water. The continuity of this project is to look for new polymer materials to be used to reduce heat transfer and the risk of icing. Instead of doing a series of experiments on commercial products, new polymers should be created by modifying their cross-links, their molecular weight and their glass transition temperatures. Another important property to be investigated is the aging. In order to reduce the maintenance of the coating protection, it is necessary to perform a series of aging experiments to determine the capability of the coating to maintain its properties over a long period. All research studies related to the production of oil and gas in the Arctic can be used in others field: material engineering, low maintenance protection, the shipping industry, the insulation of structures and coastal engineering.

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