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VISCOELASTIC PROPERTIES OF PVDF INVESTIGATED BY DYNAMIC MECHANICAL ANALYSIS

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Abstract. *Polymers are viscoelastic materials and the use of polymeric materials has grown on the world stage due to its good mechanical properties. In the oil area, the polymeric materials are often used in the manufacture of some of the layers that make up the flexible tubes. Dynamic Mechanical Analysis is an excellent method to obtain information about viscoelasticity since it measures the stiffness and damping of polymers as a function of temperature and frequency. The present work is concerned with the mechanical behavior of a polyvinylidene fluoride (PVDF) in tension. The polymer was tested on dynamic mechanical analysis (DMA). Analyzes were performed in two different manners. In the first, five different frequencies were set and the temperature was ranged from -20°C to 40° . Finally, four isothermal temperature steps were set and the frequency was ranged from 0.01Hz to 100Hz.*

Keywords: *PVDF, DMA, Temperature, Frequency.*

1. INTRODUCTION

The use of polymeric materials has grown on the world stage due to its good mechanical properties, as well as their use in replacing to metals. The oil industry has made use of this material in their risers. Risers are flexible lines that are used for the transportation of various fluids in the oil industry, especially for oil extraction on the high seas.

The combination of the high temperature in the operation of the transported fluids and the low temperature of the sea water in relevant depth, arises the temperature gradients on the risers. Such thermal loading can modify the mechanical properties and structural behavior of the risers.

Another problem also related to the great depths and temperature is the loss of heat along the flow of the fluid in the line. Because in the case of production in deep waters, the fluid produced leaves the well at an elevated temperature, much higher than the water sea, being conducted from the well to the floating production system by submerged ducts. An important temperature gradient arises in the radial direction of the line and the fluid starts to lose heat, which consequently decrease the temperature. This temperature reduction can cause problems in the flow of this fluid.

The inner layer known as internal pressure barrier is responsible for the internal integrity of the tube, not allowing the transported fluid contact with the other layers of the tube. Aimed at the characterization of the mechanical behavior of this layer, this work presents a study of behavior in tension of PVDF (polyvinylidene fluoride), material used to manufacture this layer, under different frequency and temperature. Through traction tests are provided quantitative data of the mechanical characteristics of the material. Considering the variation of the frequency and the temperature of the trials was assessed if the mechanical properties of the polymer are affected. The PVDF has mechanical behavior with non-linear deformation when prompted and the elasticity module shows significant changes in the tests.

2. EXPERIMENTAL PROCEDURE

The PVDF specimens used in the experiments were drawn from an inner pressure barrier sample of an actual flexible tube.

First the samples were placed in the DMA and the heater was programmed to reach the desired temperature. Once such temperature was reached and stabilized, the experiment started. Were also programmed the static constant of 2,0N, dynamic force of 4N, factor of 1,1 and amplitude of 200Mn.

A dynamic mechanical analyzer (DMA 242D, NETZSCH, Germany) was used for measuring the temperature dependent elastic modulus of the material. Fourteen samples with mean dimensions of 20 x 4 x 3 mm were tested in tension mode, according to ASTM D7028 (ASTM D7028, 2007). Two different analyzes were done. On the first type, the material was tested from -20°C to 40°C in five frequencies (0.01, 0.1, 1, 10 and 100Hz) that show the temperature for the different relaxations at each frequency. For the second type, isothermal temperatures were set (-20, 0, 20 and 40°C) while the samples oscillated in the 0.01, 0.1, 1, 10 and 100Hz that is useful to obtain the viscoelastic functions for the polymeric materials.

The modulus coming from the stress in phase to the strain is called the modulus of storage (E'), while the module coming from the viscous component is called the modulus of loss (E''). Mathematically its sum is given by $E^* = E' + E''$, and the tangent of E'' / E' is called the loss or damping tangent.

The information obtained were analyzed through the program NETZSCH Proteus Thermal Analysis, where the curves of the storage modulus, loss modulus and loss tangent were presented, showing the conditions under which the material was studied and analyzed.

3. RESULTS AND DISCUSSION

The DMA allows performing tests with a very high temperature variation, from extremely low temperatures, achieved through the use of liquid nitrogen, to very high temperatures that simulate approximately the temperature of the oil when extracted from the well.

In addition, the DMA also allows variation of the charging frequency along with this temperature variation. It is possible to determine a time interval which a specific load is desired to be made on that specimen while the temperature is changing. With this combination, results can be obtained to indicate the mechanical strength of this material at a given temperature.

The intent of the tests was to reproduce conditions to which this material is subjected in the pipelines and to confirm if the results obtained in previous work would be confirmed, but at this time the in a micro specimen. It was expected, according with others work, that this polymer presented a superplastic behavior that accentuates at higher temperatures, reducing its mechanical resistance. Changes in temperature also cause changes in the material flow stress. Therefore, the dependence of the PVDF with the temperature variation is significant, causing changes in the stiffness, the yield limit and the plastic behavior of the material. It was also expected that the polymer would exhibit a more rigid behavior with a cooling temperature. These results were confirmed.

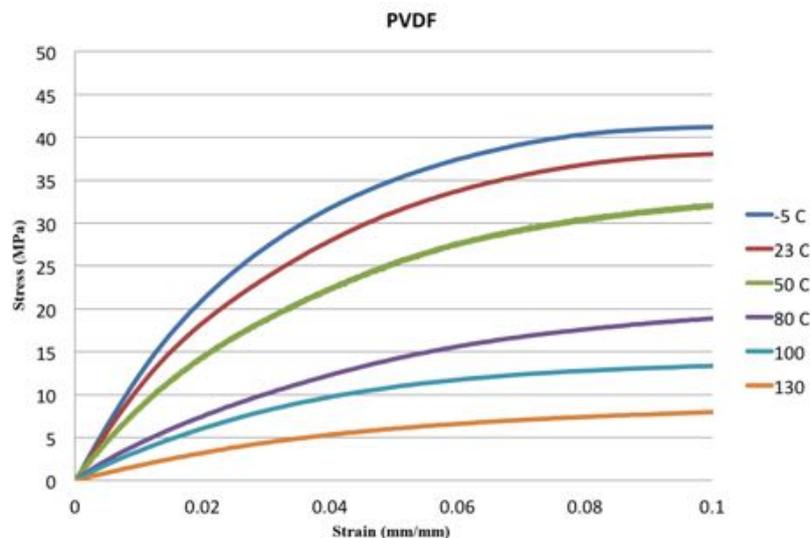


Figure 1: Superplastic behavior of PVDF. (Soares, 2015)

The results showed the major dependence of the temperature for the storage modulus of the PVDF. Figures 2 and 3 shows the viscoelastic behavior of PVDF. At high frequencies or low temperatures, the polymer presents a vitreous

behavior, presenting higher storage modulus. For higher temperatures and lower frequencies, the polymeric chains of PVDF present a viscoelastic behavior to the tension applied, showing lower or a decrease of storage modulus.

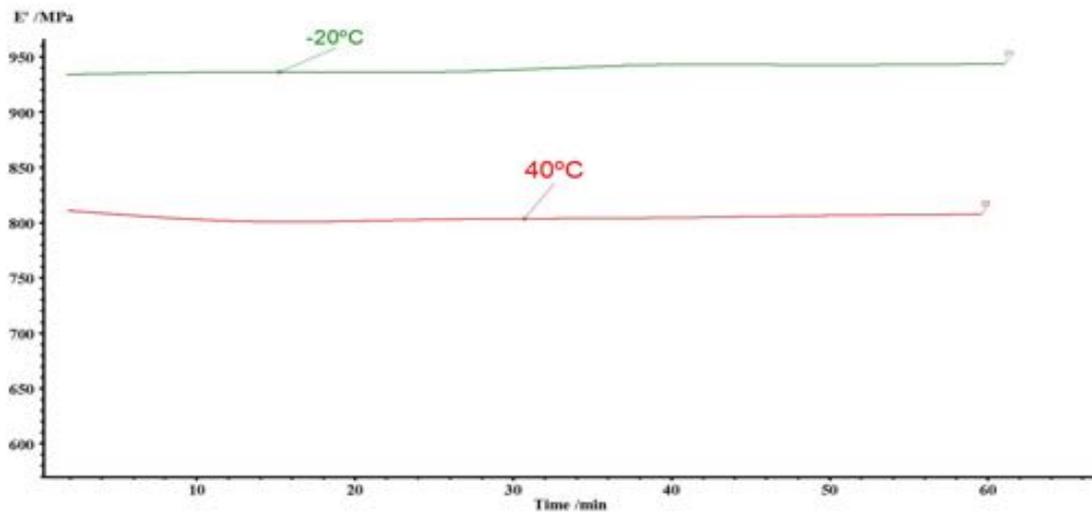


Figure 2. Isothermal lines, -20°C and 40°C , at 100.00Hz.

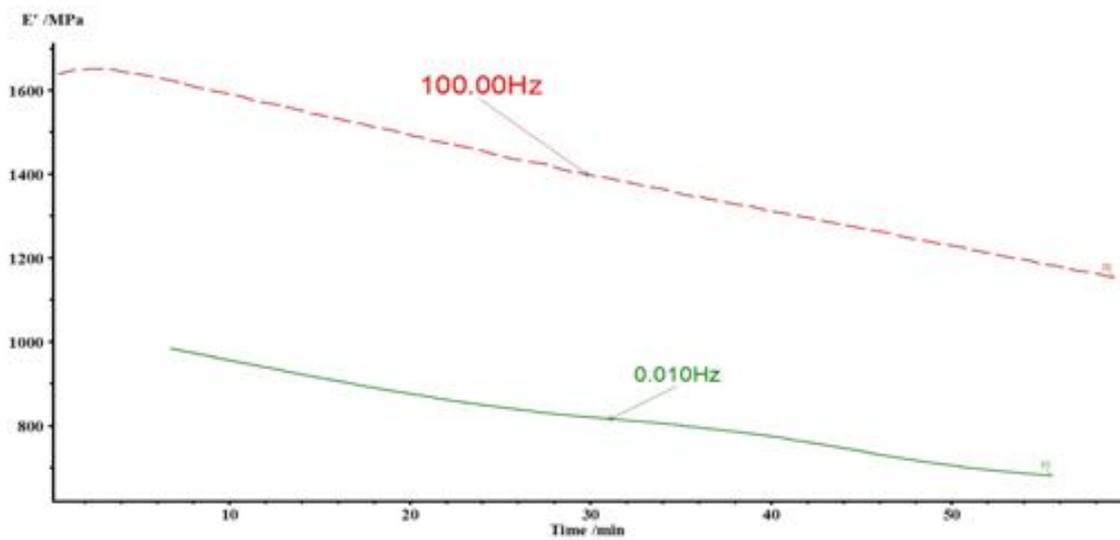


Figure 3. Frequency fixed in 100Hz and 0.010Hz and temperature ranged.

Figures 4 to 8 show the curves for different fixed frequencies, varying the temperature, and the curves of the isothermal tests with a frequency ranged.

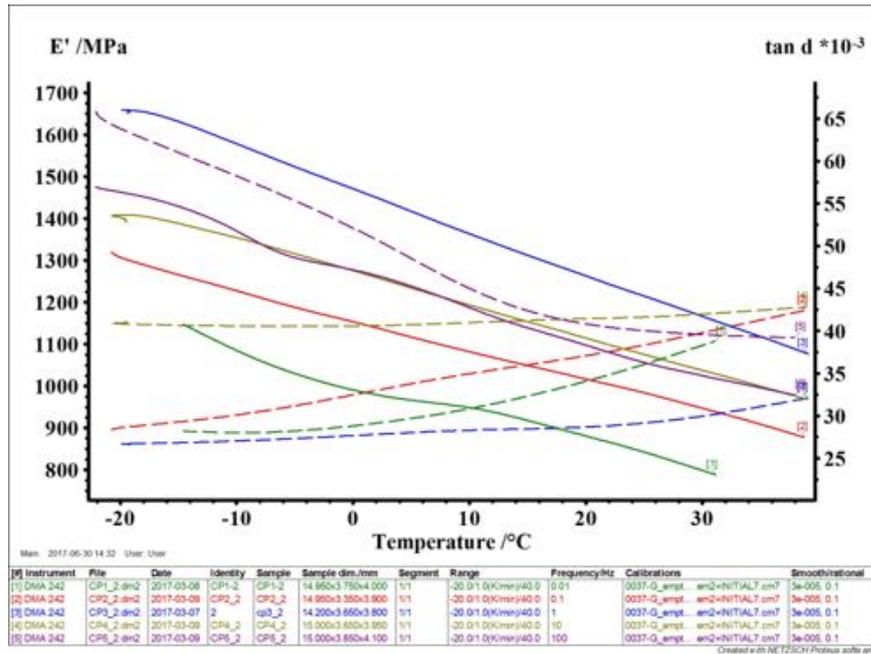


Figure 4: Curves of the storage modulus and tangent of loss.

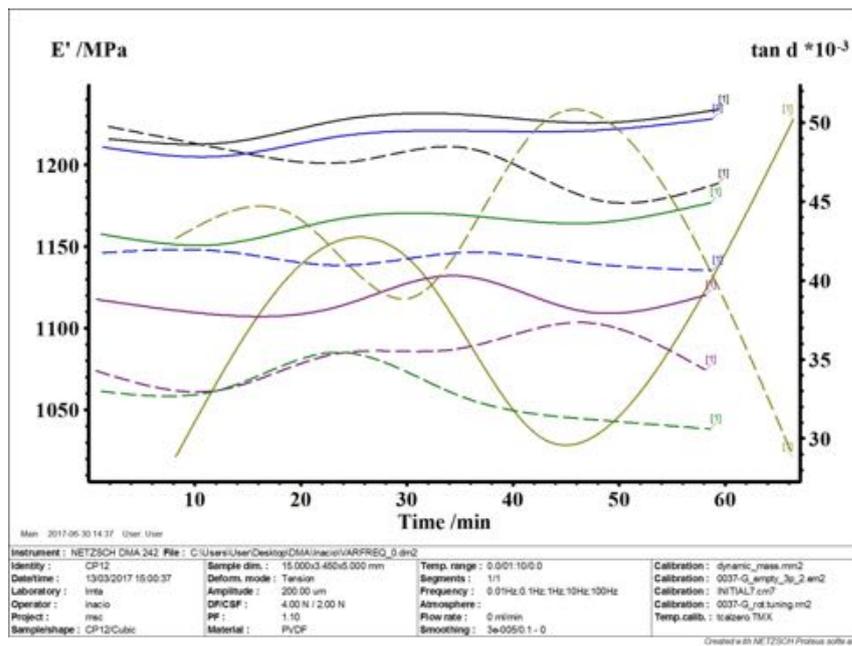


Figure 5. Storage modulus and tangent of loss from isothermal test at 0°C of PVDF.

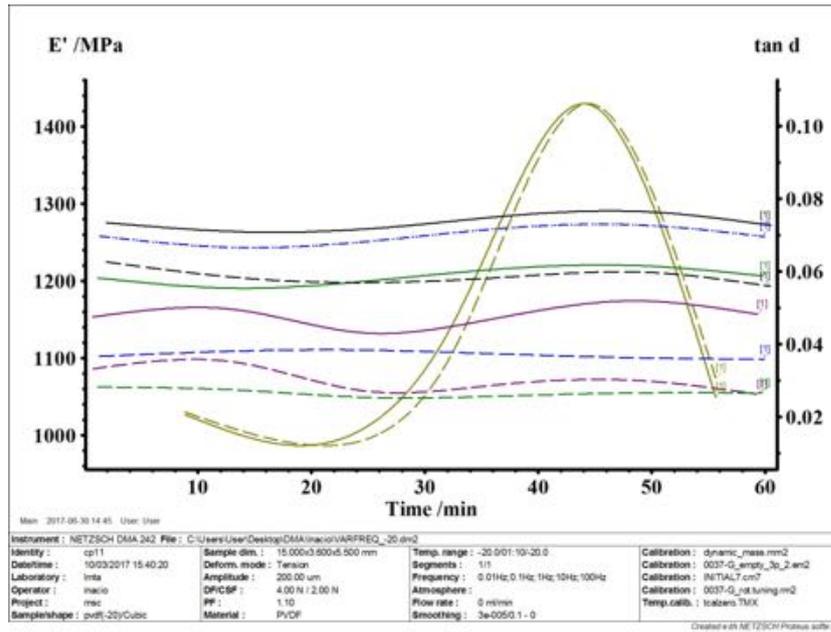


Figure 6. Storage modulus and tangent of loss from isothermal test at -20°C of PVDF.

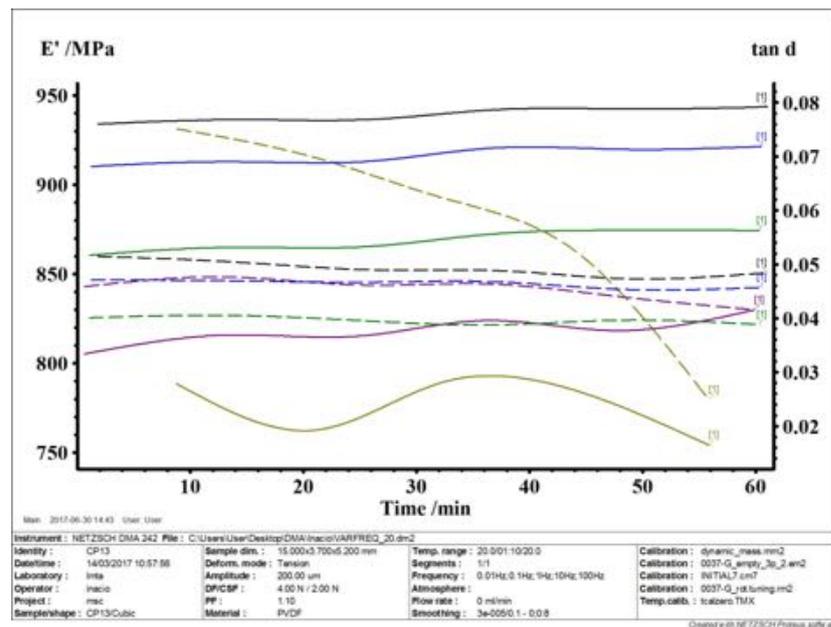


Figure 7. Storage modulus and tangent of loss from isothermal test at 20°C of PVDF.

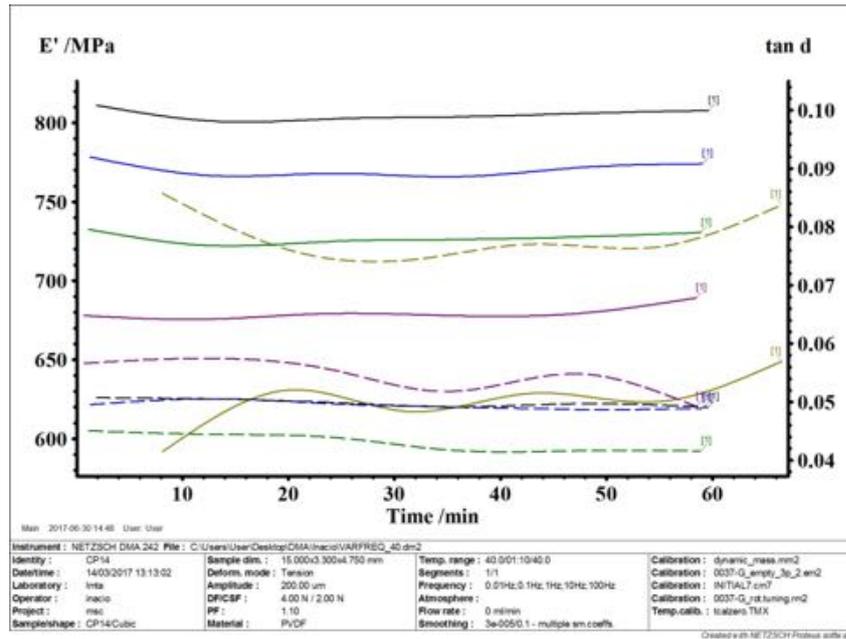


Figure 8. Storage modulus and tangent of loss from isothermal test at 40°C of PVDF.

It was observed that at high frequencies the elasticity modulus remains practically constant. This is due to the fact that a high loading speed in a micro sample, the variation of the storage module is difficult to note in the graph. And at low frequency the oscillation of the module becomes quite noticeable.

It was also noted that PVDF exhibits viscoelastic behavior when tests were performing on micro-specimens in DMA. And observing previous works, this hypothesis was confirmed.

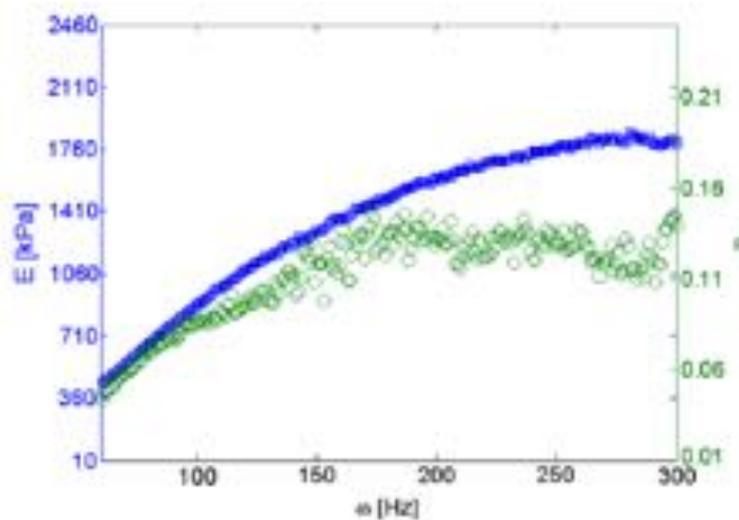


Figure 9. Viscoelastic behavior of PVDF (Frioui et al. 2009)

4. CONCLUSIONS

This work has demonstrated the mechanical behavior of PVDF under different conditions. With the lower temperature, the storage module presents higher values, the opposite happens when the temperature increases: the storage modulus decrease. Then can be conclude that this material presents higher rigidity at low temperatures. Vitreous behavior of the material at high frequencies and a decrease in the storage modulus at lower frequencies were also noted.

The study, besides having satisfactory results, also showed that at a higher temperature the polymer presents viscoelastic behavior.

The viscoelastic behavior in this material is important for increasing damping rate and significant reductions in system vibrations. These characteristics are important for their use in oil exploration.

The study also aimed to collect information on the microscopic properties of PVDF through laboratory tests in DMA in order to compare them with previous tests and studies on macroscopic specimens.

5. ACKNOWLEDGEMENTS

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7. RESPONSIBILITY NOTICE

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