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THERMOMECHANICAL AND RHEOLOGICAL ANALYSIS OF POLYAMIDE 11 UNDER AGEING CONDITIONS IN OFFSHORE FIELDS

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Abstract. *Thermoplastics parts are historically used in the oil and gas industry in a large range of successful applications, such as offshore flexible pipes as pressure barrier and outer sheath layers (API17J) for oil and gas production and water and/or gas injection. In onshore application, thermoplastic self-supported pipes are currently used, for instance, in natural gas supply chain. Polyamide 11 or PA-11 is a thermoplastic polymer largely used in the oil and gas industry given its good overall thermomechanical performance. In offshore fields, as pressure barrier layer in flexible pipes, PA-11 can be exposed to different scenarios, leading to different ageing levels within lifespan (API17TR2). The work presented herein investigated PA-11 molecular weight changes considering different ageing levels (corrected inherent viscosity - CIV), based on the correlation between rheological and thermal properties of PA-11. Rheological tests were performed in a Haake rotational rheometer using plate-plate geometry. Frequency sweep tests were performed at temperature of 190°C, for the different levels of ageing evaluated, in order to determine storage (G') and loss (G'') modulus. A Shimadzu DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric analysis) were used to determine thermal performance of PA-11 under inert media, more specifically crystallinity and mass loss/thermal endurance of PA-11, respectively. Preliminary results shows that there is a relationship between molecular weight obtained in rheological tests and those calculated by correlated inherent viscosity using API 17TR2. Thus, rheological and thermal tests can possibly be used as alternative experiment routes to measure molecular weight for polymer 11 in the absence of correlated inherent viscosity.*

Keywords: *polyamide 11, corrected inherent viscosity, DSC, rheological properties, TGA*

1. INTRODUCTION

Offshore oil exploration demands using the technology of flexible pipelines and risers to connect the seafloor to platforms or among several platforms (Bispo, 2008). Thermoplastics are used in the oil gas industry from upstream offshore production to transportation and as a barrier layer in flexible pipes or umbilicals, as external sheath of flexibles or as external anticorrosion coating for rigid steel pipe (Dang, Marchioni, Mason, & Werth, 2004). Flexible pipelines are multilayer structures composed basically of metallic and/or polymeric material, being constituted by several concentric layers overlapped (Da Costa, 2006). These pipelines are built following a standard order: stainless steel carcass layer, which is in contact with fluid and prevents collapse; inner thermoplastic sheath, known as pressure barrier, which works as sealing; pressure armor made from carbon steel profiles that supports the internal pressure;

tensile armors that mainly resist to tension and torque; and external thermoplastic sheath, which prevents water ingress in the structure (API RP 17B, 2014) (API Technical Bulletin, 2003) (Witz, 1996) (De Lima, Vaz, Da Costa, Gomez, & De Oliveira, 2020). The internal layer seals the line, avoiding the contact between fluid and steel layer (Domingos, et al., 2012).

Polyamide 11 (PA-11) is a bio-based commercial aliphatic polymer produced from castor (Scott & Buchard, 2019) (Martino, et al., 2014) (Patel, Ruehle, Dorgan, Halley, & Martin, 2014) (Di Lorenzo, Longo, & Androsch, 2019) PA-11 is a specialty nylon extensively used for the internal insulation layers in flexible pipelines due its excellent mechanical properties as high creep and fatigue resistance, low frictional coefficient excellent creep resistance) and good chemical resistance (Merdas, ThomINETTE, & Verdu, 2003) (API Technical Bulletin, 2003) (Dang, Marchioni, Mason, & Werth, 2004). It also has lower water absorption properties which results in excellent ageing and chemical resistance (Dang, Marchioni, Mason, & Werth, 2004). PA-11 is a semi-crystalline polymer, rigid at room temperature (Olufsen, et al., 2021) (Di Lorenzo, Longo, & Androsch, 2019). It exhibits a rigid amorphous fraction (RAF) that devitrifies at higher temperatures (Xenopoulos & Wunderlich, 1990). It also shows crystal polymorphism that depends on thermo-mechanical history (Mathias, Powell, Autran, & Porter, 1990) (Zhang, Li, & Yan, 2004) (Nair, Ramesh, & Tashiro, 2006) (Rhoades, Wonderling, Schick, & Androsch, 2016). The amide (—CONH—) linkages in the chain provides a strong interaction between the hydrogen bonds, which explains the outstanding mechanical properties of PA-11 (Domingos, et al., 2012) (Dang, Marchioni, Mason, & Werth, 2004). Plasticizers are used to improve flexibility and to reduce the hardness. Generally, the plasticizer N-butyl-benzenesulfonamide in 12 % concentration is used for PA-11 (Merdas, ThomINETTE, & Verdu, 2003) (Apgar, 1998) (Romão, et al., 2009) (Jolly, Tidu, Heizmann, & Bolle, 2002) (Domingos, et al., 2012).

The degradation process of PA-11 is correlated by some factors as: water contained in fluids, temperature, acidity, composition of the oil, and the presence of other chemical products used for oil treatment. These elements are capable to affect properties as elasticity and reducing the molar mass. The first is affected by loss of plasticizer, which leads on changing in morphology. The second is affected due its hydrolysis. Among all the factors, the main damage mechanism of PA-11 degradation is hydroslyis (Jacques, Werth, Merdas, ThomINETTE, & Verdu, 2002) (Merdas, ThomINETTE, & Verdu, 2003) (De Paoli, 2008), which can be defined as the breaking of the amide connections of the backbone during the deformation, specially on the amorphous phase, causing a decrease of the molecular weight (Romão, et al., 2009) (Domingos, et al., 2012).

The Corrected Inherent Viscosity (CIV) is a parameter used by the oil & gas industry to estimate the level of integrity of PA-11 (API Technical Bulletin, 2003). The model proposes a quantification of the accumulated damaged in terms of CIV in polyamide layers of flexible pipe and lifetime acceptance criterion, depending on the temperature, water presence, and pH (De Lima, Vaz, Da Costa, Gomez, & De Oliveira, 2020). This phenomenon is reversible and is exponentially dependent on temperature. Some studies (Jacques, Werth, Merdas, ThomINETTE, & Verdu, 2002) affirm that the inherent viscosity (IV) decreases in function of hydrolysis, reaching a plateau on the range from 90°C- 140°C, which means that the system is in a state of equilibrium. In addition, IV values or the molar mass in the equilibrium state is slightly dependent on temperature (Jacques, Werth, Merdas, ThomINETTE, & Verdu, 2002) (Meyer, Jones, Lin, & Kranbuehl, 2002) (Chaupt, Serpe, & Verdu, 1998) (Romão, et al., 2009).

2. METHODOLOGY

Rheological oscillatory tests were performed using parallel plate rheometer assembly of Mars III rheometer (Haake). Samples were formed in a plate - plate geometry, circular shape of 20 mm diameter. The gap between the plates was set to be 1 mm. Oscillation time tests were performed at 210 °C for 15 minutes The frequency was set to 1 Hz, with stress of 500 Pa before the frequency tests to ensure that the samples were dry. The frequency range was from 0,01 – 600 rad/s, with 500 Pa. The tests were performed within the linear viscoelastic region. The tests were conducted at 190°C temperature measuring storage and loss modulus. A Shimatzu Differential Scanning Calorimeter (DSC) was used to measure the crystalline content of PA-11. A ramp rate of 3 °C/min was used to heat the samples of 10 mg under nitrogen from 40 to 220 °C with peak integration limits of 140– 200 °C. A Shimatzu Thermal Gravimetric Analysis (TGA) was used to measure the mass loss of PA-11 under nitrogen. First, a ramp rate of 20°C/min was used to heat the samples of 10 mg from 30 to 100°C. Then, an isotherm was kept for 30 minutes at 100°C. After the isotherm, the sample is heated from 100 to 230 °C with a ramp rate of 20°C. Finally, the sample an isotherm is established at 230°C for 70 minutes.

All the tests were performed using the outer parts of aged pipes used in offshore applications. The values of CIV were established by the methodology of (API Technical Bulletin, 2003). Thus, the values used are 1,49 dL/g and 1,92 dL/g.

The corrected inherent viscosity values of PA-11 (API Technical Bulletin, 2003) were measured through Mark – Houwink correlation displayed at Eq.(1):

$$\eta = KM_n^\alpha \quad (1)$$

where: $K = 7,42 \times 10^{-4}$; $\alpha = 0,743$; M_n = Molecular Weight; $[\eta]$ being expressed in dL/g

The rheological parameters obtained in oscillatory tests are defined as Eq. (2), Eq. (3), Eq. (4) and Eq. (5):

$$G' = \frac{G \omega^2 \lambda_{rel}^2}{1 + \omega^2 \lambda_{rel}^2} \quad (2)$$

$$G'' = \frac{G \omega \lambda_{rel}}{1 + \omega^2 \lambda_{rel}^2} \quad (3)$$

$$|G^*| = \sqrt{(G')^2 + (G'')^2} \quad (4)$$

$$|\eta^*| = \frac{|G^*|}{\omega} \quad (5)$$

Where λ_{rel} is the relaxation time of a Maxwell fluid, is equal do μ/G ; ω is the angular frequency.

G' is called storage modulus [Pa]; G'' is the loss modulus [Pa], $|G^*|$ is the complex modulus [Pa] and $|\eta^*|$ is the complex viscosity [Pa.s].

3. RESULTS

3.1 Rheological results

Oscillatory tests are shown on Fig. 1 (a), (b) and Fig. 2 (a), (b). For both scenarios, time sweep is exhibit on left side (a) and frequency sweep on the right side (b).

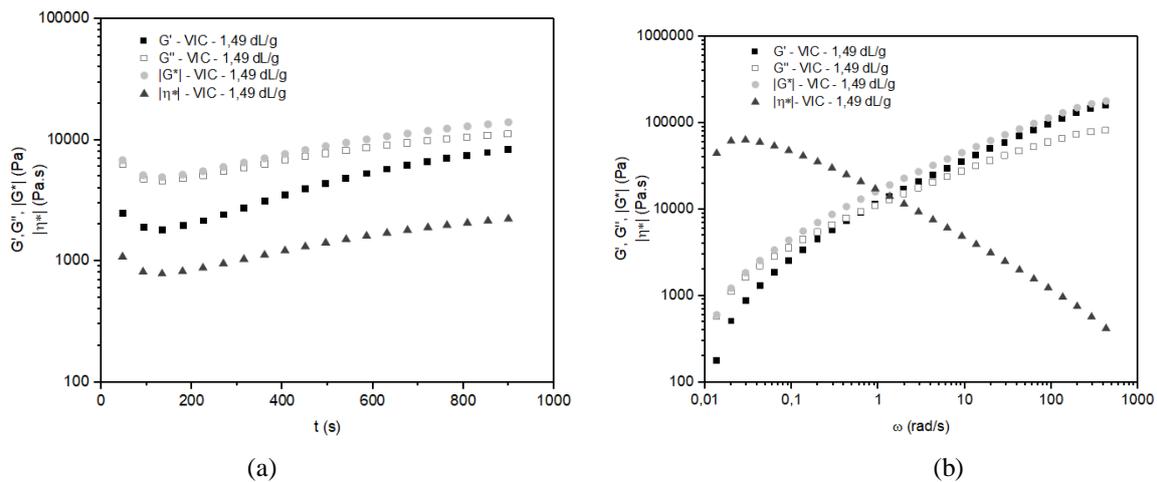


Figure 1. PA-11 with CIV 1,42 dL/g. (a) Time Sweep ; (b) Frequency Sweep

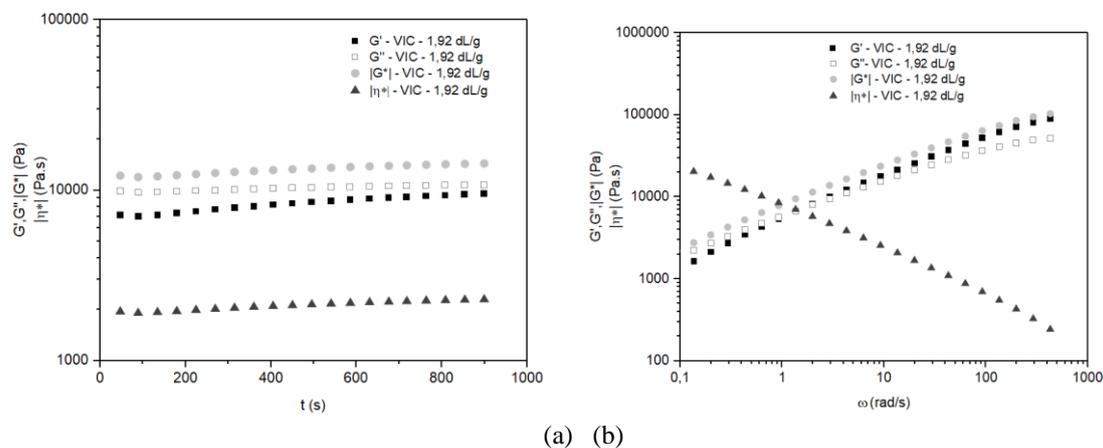


Figure 2. PA-11 with CIV 1,92 dL/g. (a) Time Sweep ; (b) Frequency Sweep

For both conditions of CIV, PA-11 exhibits shear thinning behavior (Patankar, Ginzburg, & Billovits, 2019) for all the investigated range (Huang, et al., 2009) (Walha, Lamnawar, Maazouz, & Jaziri, 2016). Dynamic moduli, complex modulus and complex viscosity show a constant behavior for time sweep test, as reported by (He, et al., 2006). The shear thinning is evidenced by the decrease of complex viscosity in the investigated frequency range.

The relationship between complex viscosity and apparent viscosity is called Cox – Merz rule, that is defined by the Eq. (6):

$$|\eta^*(\omega) = \eta(\dot{\gamma})|_{\omega=\dot{\gamma}} \quad (6)$$

The Cox – Merz rule proposes that the viscosity (η) should be the same function of shear rate ($\dot{\gamma}$) as the modulus of complex viscosity $|\eta^*|$ is of angular velocity (ω) (Barnes, Hutton, & Walters, 1989). This correlation is the most accurate empirical method to estimate the relation between viscosity in stationary and oscillatory tests. As Cox – Merz rule establishes a correlation between complex viscosity and apparent viscosity, it can be inferred that both samples exhibit pseudoplastic behavior according to Eq.6.

Storage modulus (G'), loss modulus (G'') and complex viscosity (G^*) increase for the frequency range investigated. For both cases, it occurs an intersection of G' and G'' . The crossover generally indicates a transition from the plateau zone to terminal region of the polymers., changing the rheological behavior from viscoelastic liquid ($G'' > G'$) to viscoelastic solid ($G' > G''$) (He, et al., 2006)

3.2 DSC/TGA Results

Enthaphy was measured by the area under the curve , as shown on Fig. 3(a) and (b). DSC tests are the responsible by giving information about enthalpy, as exhibit in Fig. 4 (a) and (b). The y axis filled by the division of power to mass for both figures. The area of DSC tests provides the enthalpy in [J/s].

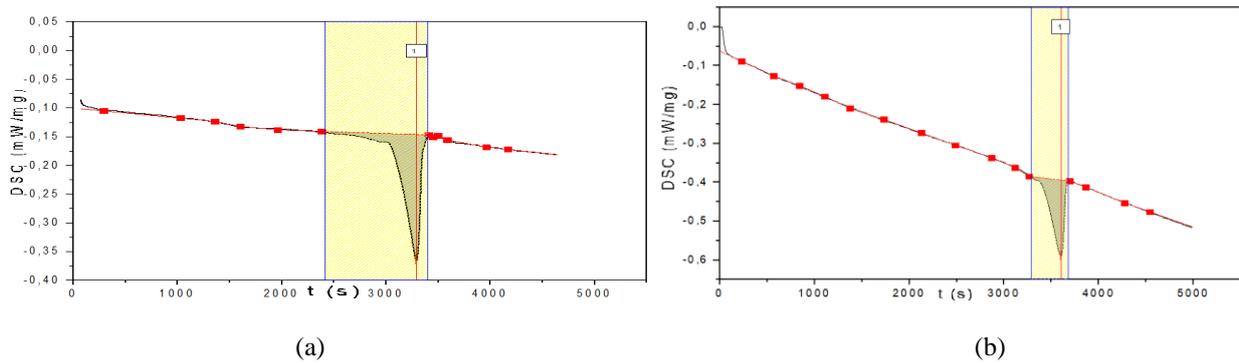


Figure 3. Enthalpy measures (a) CIV - 1,49 dL/g; (b) CIV – 1,92 dL/g

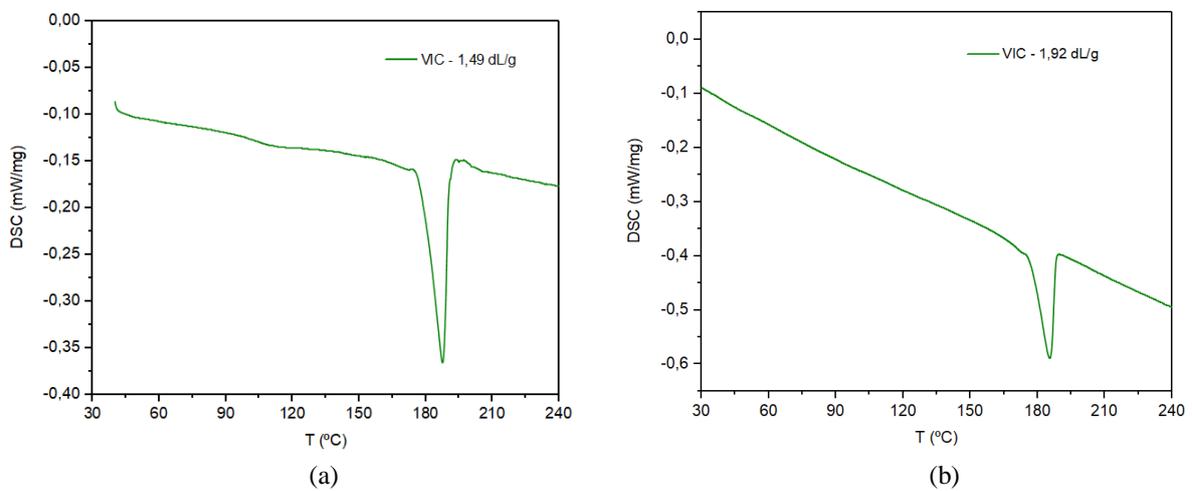


Figure 4. DSC (a) CIV - 1,49 dL/g; (b) CIV – 1,92 dL/g

The corresponding enthalpy values determined on DSC testes are established on Tab. 1:

Table 1. Enthalpy values

CIV (dL/g)	ΔH (J/g)
1,49	40,81
1,92	28,78

The results of Tab. 1 point a relation between the enthalpy value and inherent correlated viscosity (CIV). It can be inferred that increasing values of CIV, it occurs a decrease of enthalpy values.

Figure 4 (a) and (b) shows TGA tests for PA-11. It exhibits hydrolytic degradation process caused by the presence of water, being accelerated under high temperatures (> 90 °C) (Jolly, Tidu, Heizmann, & Bolle, 2002) (Romão, et al., 2009) (Bernstein, Derzon, & Gillen, 2005) (Gonçalves, Poulsen, & Ogilby, 2007) (Merdas, Thominette, & Verdu, 2003). This degradation causes decrease in weight average molar mass (Mw) and loss of plasticizer, also shown at Fig. 1 (Romão, et al., 2009) (Domingos, et al., 2012).

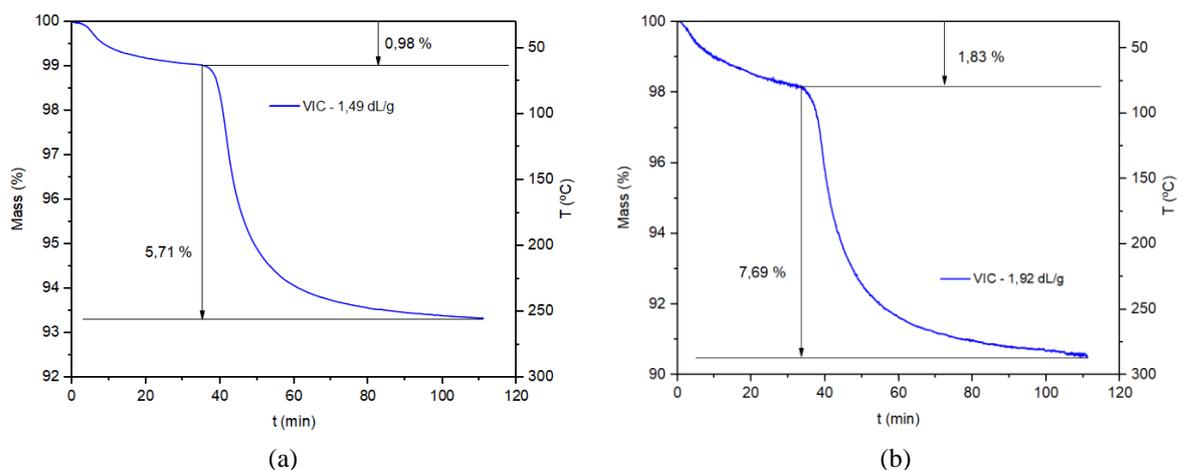


Figure 4. TGA (a) CIV - 1,49 dL/g; (b) CIV – 1,92 dL/g

The degradation process interferes on the microstructure of the material as well as some mechanical characteristics, including the elastic properties, rate-sensitivity, hardening and locking behavior, and thereby the ductility in general, due the amorphous phase where the chain scission process is anticipated to be most prominent (Rozanski & Galeski, 2013) (Walczak, 2013) (Olufsen, et al., 2021). On the deformation process of semi – crystalline polymers, an interplay between semicrystalline and amorphous phase is detected (Van Dommelen, Poluektov, Sedighiamiri, & Govaert, 2017) (Bartczak, Deformation of semicrystalline polymers – the contribution of crystalline and amorphous phases, 2017) (Bartczak & Galeski, Plasticity of Semicrystalline Polymers, 2010).

The reduction of molecular weight occurs during the degradation, meantime the degree of crystallinity increases in deformation, causing a reduction of ductility (Olufsen, et al., 2021).

Table 2 indicates the summatory of extractable content of PA-11 for CIV 1,49 and 1,92 dL/g.

Table 2. Extractable contents and weight polymer

CIV (dL/g)	Extractable (%)		Polymer (%)
	Water	Plasticizer	1- Extractables (%)
1,49	0,98	5,71	93,31
1,92	1,83	7,69	90,48

Table 2 gives information about the degree of crystallinity, that is measured according to Eq. (7) and indicated on Tab. 3:

$$X_c = \frac{\Delta H_M / \Delta H_M^0}{1 - \text{extractables}} \quad (7)$$

Where ΔH_M is the measured enthalpy of the melting and $\Delta H_M^0 = 226,4 \text{ J/g}$ (Inoue, 1963) is the melting enthalpy for the PA-11 pure crystalline phase (De Lima, Vaz, Da Costa, Gomez, & De Oliveira, 2020)

Table 3. Degree of crystallinity

CIV (dL/g)	X_c (%)
1,49	19,32
1,92	14,05

The results of Tab. 3 point out that an increase of CIV values provides a decrease in degree of crystallinity. These results converge with the studies of (De Lima, Vaz, Da Costa, Gomez, & De Oliveira, 2020). This decrease of CIV demonstrate an occurrence of random chain scission due the hydrolysis process (De Lima, Vaz, Da Costa, Gomez, & De Oliveira, 2020) (Jacques, Werth, Merdas, Thominette, & Verdu, 2002) (Romão, et al., 2009) (Mazan, Berggren, Jorgensen, & Echtermeyer, 2015). Therefore, the reduced size of the chains increases their mobility and the local higher temperature provides an increase on crystallinity

4. CONCLUSION

Finally, the study presented an overview of PA-11 rheological properties. Polyamide 11 displayed shear thinning behavior, marked by the decrease of viscosity in the specific frequency range, according to Cox-Merz rule. It also presented viscoelastic solid properties, evidenced by the crossover of dynamic moduli. The storage modulus turns higher than loss modulus when the frequency values increase.

DSC/TGA tests indicated enthalpy values and mass loss of PA-11, respectively. Enthalpy is linked to the degree of crystallinity. An increase of CIV values indicated a decrease of crystallinity. Then, DSC tests can be used to estimate difference on CIV values through measured enthalpy and further degree of crystallinity.

5. ACKNOWLEDGEMENTS

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