

15th Brazilian Polymer Conference
October 27-31, 2019

SAXS INVESTIGATION OF THE STRUCTURAL FEATURES OF RELAXED POLY(VINYLDENE FLUORIDE)

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Abstract - Poly(vinylidene fluoride) (PVDF) relaxed samples were analyzed by Small Angle X-ray Scattering (SAXS). The long period (L_p) and several structural parameters were calculated using Bragg's Law and the linear correlation function $\gamma(r)$ methods. By the last method, it was observed that L_p decreases as relaxation temperature rises. The amorphous thickness (L_a) of relaxed samples got lower in comparison with non relaxed sample, even for relaxation at 23°C, suggesting that chain recoil took place in amorphous region. Both lamellar (L_c) and intermediate phase (IT) thicknesses rose as relaxation temperature increased, indicating the occurrence of thermal crystallization and a partial ordering of intrafibrillar amorphous chains.

Keywords: SAXS, PVDF, Relaxation, Linear Correlation Function

Introduction

Poly(vinylidene fluoride) (PVDF) is a high-performance engineering polymer with excellent thermal stability and chemical strength. It makes PVDF a good option for flexible oil pipelines (risers) and others industrial applications in which aggressive fluids resistance is required. Concurrently, the polymorphism and piezoelectric properties arising from specific polymorphs instigate academic attention, becoming PVDF widely investigated. It's generally accepted that PVDF structure is contained inside a spherulite, which is hierarchically composed of fibrils and a free amorphous phase. The fibrils are stacks of crystalline lamellae, grown radially as of a nuclei, an interface and constrained amorphous layers [1]. The exact morphology of the structure is not completely defined yet; however, it is quite possible that the free amorphous phase might be located in between the fibrils. Nevertheless, concerning to the modifications of the structural features of PVDF after relaxation process, there is still a shortcoming in specialized literature

While Wide Angle X-ray Scattering (WAXS) is a technique suitable to determine the crystalline structure in a subnanometer-sized range, Small Angle X-ray Scattering (SAXS) is

applicable in measurements of 1 - 100 nm inhomogeneities, with electron density difference high enough to promote a contrast between the disperse phase and matrix. So, as this requirement is satisfied in the case of crystalline and amorphous phases of PVDF samples, SAXS can be used to investigate the morphological changes arising from thermo-mechanical demands.

Relaxation processes can occur during operation, servicing and fitting of an oil flexible line production, so, the characterization of relaxed PVDF is an important issue regarding to structural integrity. In this context, the present work aims to characterize PVDF thermo-mechanical relaxed samples by Small Angle X-ray Scattering (SAXS), a powerful technique commonly used in semicrystalline structures studies.

As SAXS is a technique appropriated to observe periodic structures of nanometer size, the assumption of a simple stack layer-like morphology is pertinent. More complex structures, as spherulites, can be conceived as overlapping crystalline lamellae and amorphous chains layers and the long period (L_p) comprises one amorphous/crystalline lamella layer, which can be estimated by Bragg's law (Eq.1):

$$L_B = \frac{2\pi}{q_{\max}} \quad (1)$$

Where q_{\max} represents the position of the scattering peak which appears in the $I(q)$ experimental curve, I being the scattered intensity and q the modulus of the scattering vector ($q=4\pi\sin\theta/\lambda$, θ and λ being the scattering angle and X-ray beam wavelength, respectively). On the other hand, the determination of the structural parameters stems from the linear correlation function ($\gamma(r)$) method (Eq.2) provides a higher detail level of structure features, since even the thickness of the intermediate phase, between amorphous and crystalline layers, can be estimated. In fact, the trends observed for L_p variation using both methods must be the same and the values differences are ascribe to heterogeneity of the lamellar distribution in the matrix [2].

$$\gamma(r) = \frac{1}{Q} \int_0^{+\infty} I_1(q) \cos(qr) dq \quad (2)$$

Where Q is so-called second moment or the invariant ($Q = \int_0^{+\infty} I_1(q) dq$), $I_1(q)$ is the one-dimensional intensity (Lorentz corrected), r is the direction perpendicular to the lamellae surfaces and q is the scattering vector. So, in this work, both methods were applied in order to contribute to the understanding of the relationship between structure-property-application of the PVDF material.

Experimental

The samples were machined from a PVDF (plasticized homopolymer) pipe, in accordance with ASTM D 638 Type I specimen dimensions. The stress relaxation was carried out in tension mode, using a Zwick/Roell machine (Kappa Multistation model). The tests were performed at 23, 80 and 120°C, using 3.5, 7 and 10% strains (ϵ_0) and crosshead speed of 5 mm.min⁻¹. The strain and temperature were kept for 24 h, in order to allow stress relaxation process goes on until quasi-stabilized stress level. Three samples were tested for each condition and a good reproducibility was achieved.

SAXS analysis was carried out using a NanoSTAR SAXS system (Bruker AXS), with a Cu K α source Xenocs (Genix 3D Cu ULD) and a Bruker Vantech 2000 detector. The sample-to-detector distance was 66.7 cm, leading to scattering vectors q in an effective range from 0.01 to 0.36 \AA^{-1} . The data processing was performed by the SUPERSAXS software. Two methods were used to calculate the structural parameters: the Bragg's law equation (Eq.1), applied to the Lorentz-corrected SAXS profiles, and the linear correlation function $\gamma(r)$ (Eq.2). Through the second method, it was possible to calculate the long period (L_p), crystalline lamellar thickness (L_c), amorphous phase thickness (L_a) and the interface thickness (IT) between crystalline and amorphous phases. In addition, the deviation from the ideal two-phase model, the non-ideality (NI), and the linear (or local) crystallinity (χ) were also obtained. The detailed description of the calculation of these parameters is shown in literature [3].

Results and Discussion

Representative curves of stress relaxation tests are shown in Figure 1, in which it can be seen the stress decay, characteristic of the relaxation process. Prior to relaxation, higher levels of stress are achieved for higher levels of strain, since the material is tested in elastic limit. The alignment of amorphous chains during stretching, the disentanglement and unfolding/refolding of chains are expected to happen in overall tension/relaxation process. As the strain increases, the disentanglement and unfolding are improved, which lead to stress rises at first step, followed by a drop in steady deformation (relaxation). The chain alignment must be not enough to promote crystallization in the strain range applied, but it is possible that thermal crystallization occurs over 24 hours at higher temperatures used. In the same way, the high temperature promotes crystallization, it also allows the overcoming of energy barriers for conformational changes of chains in the amorphous phase during relaxation. In fact, the rise of temperature contributes to the drop of viscosity, such that lower stress values are observed for relaxation at 120°C showed in Figure 1.

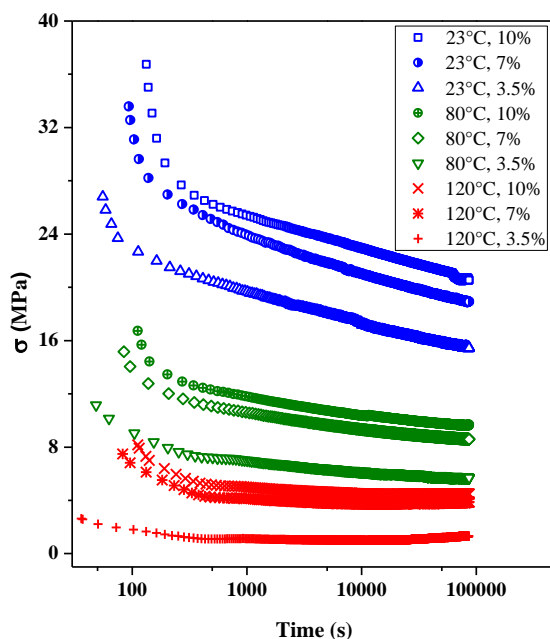


Figure 1. Stress (σ) versus relaxation time curves.

The linear correlation function $\gamma(r)$ curves of samples relaxed at 23 and 120°C are shown in Figure 2 and it is possible to observe greater changes in the curve profile at different temperatures with respect to the applied deformation. The SAXS parameters values are shown in Table 1, where it can be seen a good agreement between L_p calculated by both methods - the Bragg's Law and $\gamma(r)$ - in case of relaxation at lower deformation and temperature, which might lead to a satisfactory homogeneity of the lamellar distribution possibly achieved during the relaxation conditions.

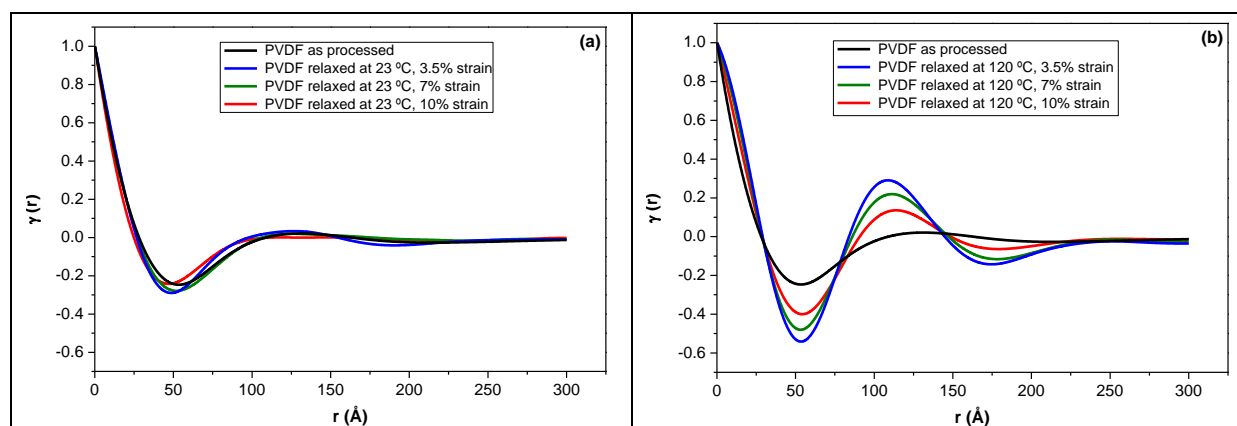


Figure 2. Linear correlation function curves ($\gamma(r)$) of PVDF samples relaxed at 23 (a) and 120°C (b).

As relaxation temperature rises, a reduction of L_p obtained by linear correlation function $\gamma(r)$ (Table 1), can be observed. There is also a decrease in L_a , which suggests that recoil of amorphous chains occurs inside the fibrils. On the other hand, relaxation performed at higher temperatures (80 and 120°C) showed a slight increase of L_c , implying that thermal crystallization might have occurred. The linear crystallinity (χ) was also affected for relaxation at 80°C and 120°C, where the value of 120°C/10% relaxed sample was lower than the 120°C/7% and 120°C/3.5% samples, indicating that higher strains could hinder thermal crystallization. The intermediate phase (IT) thickness rises with relaxation temperature, which leads us to believe that part of amorphous chains undergoes ordering at lamella surface as temperature increases. The NI parameter reflects the quality of the system to be represented by the two-phase model, so as to, the lower NI values the better is the match to the model; and it is observed that samples relaxed at higher temperatures (80 and 120°C) possess its morphology very well represented by two-phase model assumed.

Table 1. Structural parameters of PVDF samples.

Relaxation condition T (°C) ; ε_0 (%)	L_p^B (nm)	L_p^γ (nm)	L_a (nm)	L_c (nm)	IT (nm)	NI	χ (%)
None	13.8	13.1	7.0	3.7	1.3	0.04	35
23 ; 3.5	12.6	12.7	6.3	3.6	1.3	0.05	36
23 ; 7	12.3	12.5	6.7	3.7	1.3	0.03	35
23 ; 10	12.7	11.8	6.1	3.4	1.2	0.04	36
80 ; 7	12.3	10.5	6.2	4.0	1.6	0.001	39
80 ; 10	12.3	10.9	6.6	4.0	1.5	0.001	38
120 ; 3.5	11.9	10.9	6.4	4.3	1.7	0	40
120 ; 7	12.3	11.1	6.5	4.1	1.6	0.002	39
120 ; 10	12.3	11.4	6.9	4.0	1.5	0.002	37

L_p^B and L_p^γ are the long periods obtained by Bragg's law and linear correlation function, respectively.

Conclusions

The structural characterization by SAXS revealed that the stress relaxation process lead to decrease of long period (L_p), determined by linear correlation function, together with the amorphous layer thickness. On the other hand, no tendency was detected to L_p calculated by Bragg's Law method. The relaxation temperature played an important role in crystalline lamellae (L_c) and intermediate phase (IT) thickness, since both parameters rose only when 80 and 120°C were used. The two-phase model represented appropriately all the samples, relaxed or not.

Acknowledgements

The authors acknowledge CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil - Finance Code 001), CNPq, PETROBRAS, PRH-35/ANP and Prof. Cristiano L. P. Oliveira of the Complex Fluids Group, Institute of Physics – USP, for his help in SAXS measurements.

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