CHEMICAL METHODS vs PHYSICAL METHODS FOR PDVF MORPHOLOGY STUDIES

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Morphology of poly(vinylidene fluoride) PDVF is of practical concern, this polymer may be processed to give a number of different crystal forms such as α, β, γ and these may exhibit a wide range of different morphologies. Due to the difficulty of the PVDF material presents to be observed by electron microscopy techniques, Vaughan developed a method that implies chemical treatments that allows to reveal the PDVF crystalline structures [1]. On the other hand, plasma etching is a process for removing material from surfaces [2]. The process can be chemically selective, removing one type of material while leaving other materials unaffected, and can be anisotropic, removing material at bottom of a trench while leaving the same material on the sidewalls unaffected [2]. It has been reported that plasma introduces modification at the surface of some polymer, leaving the bulk properties intact, the various reactive species in the plasma (electrons, ions, free radicals and metastable species) interact with the polymer surface and can introduce different modifications, although the exact mechanisms are not well understood [3]. In this work we report the results obtained from the application of etching with chromium trioxide-based reagent and cold plasma etching to PVDF and compared the surface modifications studying by electron microscopy.

Samples studied in this work were PVDF used as piping in the chlorine-alkali plant in El Tablazo Refinery, Venezuela, as well as unused PVDF. Chemical treatment time was varied from 1h to 100 h. For plasma etching we have exposured the PVDF to a cold plasma. Treatment time was varied from 20 to 45 minutes. The electric current was set at 20 mA and the power was around 30 W. Ar, air and oxygen plasma, were used. The PVDF samples were set at the end of the plasma.

Figure 1 shows a micrograph of a sample of unused PVDF etching with the chromium trioxide-based reagent during 96 h[4]. The SEM micrograph shown in the figure 1b corresponds to the tube failed in service treated during 24 h with the chromium reagent, it can be noticed clearly the lamellar structure, with a central sheaf-like structure surrounded by radially grown lamellae. The time necessary to reveal the lamellae in the used PVDF is shorter than that for unused PVDF, this can be attributed to the products that flow through the pipe together with the high temperatures of the environment have an effect of pre-treatment that weakens PVDF structure during service.

For air plasma, it was used 20, 25 and 30 minutes of treatment, at 20 minutes it is possible see some spherulites, figure 2, time longer than 25 minutes it was not found crystalline structures. Figure 3 corresponds to 25 minutes oxygen plasma treatment, spherulites can be seen. Results from Ar plasma treatment allowed to see a few spherulites with a marked deterioration. It should be pointed out that is possible to appreciate the PVDF degradation under argon plasma which is noticed by the change of color from transparent to yellow and brown. It is possible that conditions used in this work were too strong so it is necessary to used shorter treatment time. The use of air or oxygen cold plasma as preparation method for the PVDF for electron microscopy studies give satisfactory results since it was possible to reveal the crystalline structure of the material on shorter time to ones for chemical attacks, besides not requiring the employment of toxic substances. The oxygen plasma causes the smallest damage to the surface of the PVDF.

It seems that surface modifications depend on the nature of the gases present in the plasma. A clean way by using a low-pressure plasma, of either inert or reactive gases, that processes usually requires short treatment times.

References

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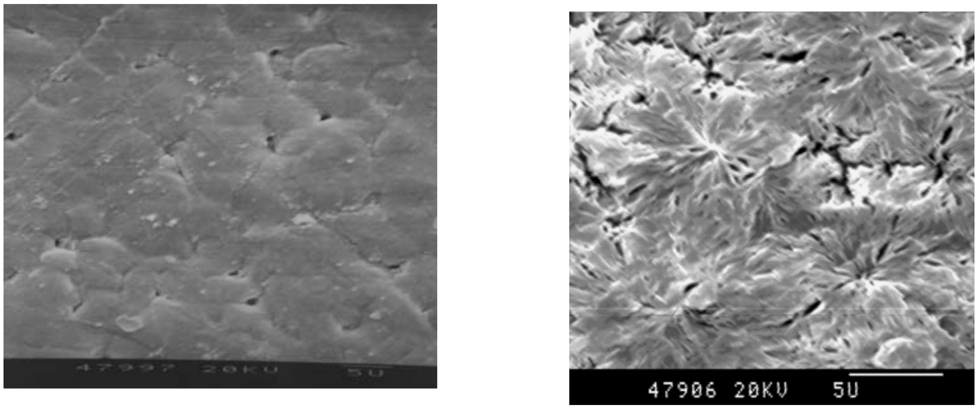
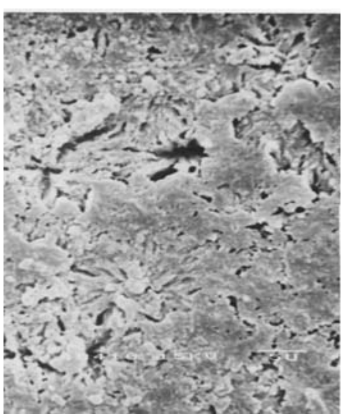


a) PVDF unused, 96 h.

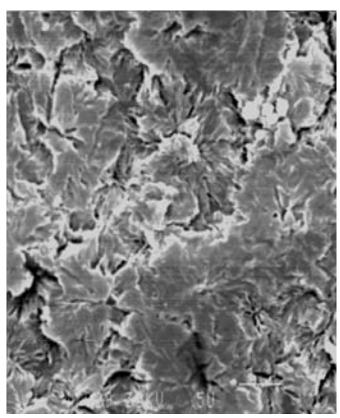
b) PVDF used, 24h.

Figure 1



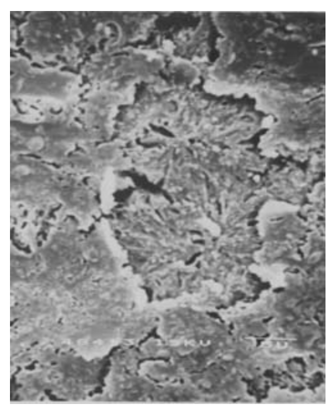
Air plasma, 20 min

Figure 2



O_2 plasma, 25 min

Figure 3



Ar plasma, 45 min

Figure 4