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Aging of poly(vinylidene fluoride) hollow fibers in light hydrocarbon environments

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ABSTRACT

In this work, PVDF hollow fibers were aged in different light hydrocarbon solvents (e.g. paraffins, olefins, and aromatics with carbon number <9) and the thermal, mechanical, morphological, and structural properties of the resulting fibers were determined. While TGA, DSC, and DMA are used to probe the thermal and mechanical stability for the bulk samples, XRD and FTIR are used to probe the polymorphic crystalline phases on the sub-nanometer length scale. Combined with BET and SEM results on pore structure, the changes in polymorphic crystalline phases together with the changes in the morphology provide scientific insights on the interactions that the hydrocarbon solvents and aging have on the properties of the PVDF micro-porous hollow fibers. The results suggest that after a long-term exposure at $\leq 50\,^{\circ}$C, the chemical and morphological structures of PVDF change more noticeably in solvents with the carbon number ≥ 6 than those with a lower carbon number. Furthermore, aromatic solvents produce greater changes than the paraffins of the same carbon number do. However, aging studies show that the PVDF hollow fibers preserve the thermal and mechanical properties in light hydrocarbon solvents for more than two years at the elevated temperature.

1. Introduction

Poly(vinylidene fluoride) (PVDF) is used for many unique applications because it has high thermal, chemical, aging, and weather resistance. PVDF has excellent inertness to solvents and biocompatibility, to hydrocarbons, to acids, and to alkalis because of its low surface energy (oil and water repellency), low flammability, and low moisture absorption [1,2]. With easy processability and stable chemical/thermal stability in many organic solvents, PVDF is commonly fabricated into high performance membranes, and is regarded as one of the most attractive polymers in the micro-porous membrane industry. PVDF membranes find a wide variety of applications – gas separation, water treatment, medical applications, fuel cell membranes, etc. [2–8].

The utilization of hollow fibers as structured packings in olefin/paraffin distillation is a newly developed membrane application that can substantially reduce energy consumption for petroleum and chemical industries. Recently, we have explored the use of the PVDF micro-porous hollow fibers as structured packings in the light hydrocarbon distillation (e.g. propane/propylene, iso-/n-butane, etc.) and demonstrated that high separation efficiency and high capacity can be achieved [9–11]. In this application, the hollow fibers are assembled into a heat-exchanger configuration [11–13]. While liquid flows inside the tube side of the hollow fibers, vapor counter-currently flows in the shell side of the columns. Ideally, the two phases flow in their own channels and intimately contact along the porous wall of the fibers, which requires that the fiber wall can hold the liquid inside well. If the liquid phase largely leaks into the shell side, it will interrupt the vapor flow, result in poor stability, and thus reduce the separation efficiency [9]. Therefore, there are some specific requirements for the morphological properties (e.g. pore size, porosity, wall thickness, polymer compatibility, and dimension) of the hollow fibers [10]. On the other hand, since the hollow fibers are constantly exposed to the organic fluids at elevated temperatures for an extensive period of time, the membrane lifetime stability (morphological, thermal, mechanical, and structural properties) is also critical for the applications. In the last few decades, extensive investigations have been conducted to understand the effect of the membrane processes on the types of crystalline phases because PVDF with different crystalline phases possess different properties [1,14–17]. Some studies on the thermal stability of the PVDF membranes after the exposure to organic solvents have been reported in the literature, but most of them focus on the solvent effect on the PVDF membrane formation processes [1,4,16,18–21]. Systematic studies on the morphological and the polymorphic crystalline phases of the PVDF hollow fibers after the long time exposure to light hydrocarbon solvents are limited. To fully understand the solvent interactions and

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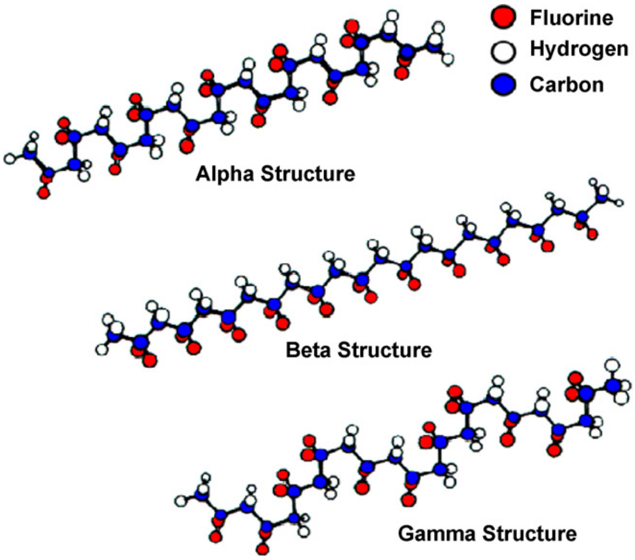

Fig. 1. The three primary polymorphic crystalline phases of PVDF [1].

the aging of the PVDF membranes, multiple characterizations are essential to determine the morphological and structural changes at the different length scales. In this work, we study the thermal, mechanical, morphological and structural properties of the PVDF hollow fibers exposed to light hydrocarbon environments using Brunauer, Emmett and Teller (BET) surface area analysis, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). We found that solvent exposure changes the morphological and structural properties of PVDF at different length scales. Some of them can be detected by BET, XRD, and FTIR, but are not manifested in SEM, TGA, DSC, or DMA. The detailed results are discussed. For the clarity of discussion, we would like to provide some background information before we discuss the experimental results.

2. Background

2.1. Polymorphic crystalline phases of PVDF

PVDF typically exhibits between 50 and 70% crystallinity and has five distinct crystalline polymorphs (α, β, γ, δ and ε) [15,17,22]. The different crystalline phases can alter the physical and electrical properties of PVDF polymer [1,16,23]. The α, β, and γ polymorphic crystalline phases are the three commonly observed. Their molecular structures are shown in Fig. 1.

To characterize different polymorphic crystalline phases, XRD is frequently used to probe the structural information on the sub-nanometer length scale. The literature values of diffraction angle (2-theta) and unit cell structure for the α, β, and γ polymorphs of PVDF are summarized in Table 1 [17]. The α phase is a non-polar phase and is more easily obtained during processing because it is formed from the melt crystallization at temperatures above 110 °C [17]. At temperatures between 70 and 110 °C, a mixture of the α–β phase is known to co-exist [17]. The β phase is known to form at temperatures below 70 °C and usually when there is a solvent present during processing [17]. The γ phase is obtained by crystallizing near the melt temperature of the α phase, or by annealing the material near the T_m of the α phase [17]. Benz et al. also report that a high humidity environment promotes a higher fraction of γ phase, apparently due to the electro-static interaction between water and the polar γ phase [16].

Table 1
Literature values for the 2-theta values and the particular diffraction direction for each crystalline phase observed in the XRD of PVDF [17].

Phase	2-Theta (°)	Direction
α and γ	17.66	(1 0 0)
	18.30	(0 2 0)
	19.90	(1 1 0)
	26.56	(0 2 1)
β	20.26	(1 1 0)+(2 0 0)

Table 2
FTIR absorption bands (in unit of cm^{-1}) related to the α, β, and γ crystalline phases in PVDF (* the bands will be discussed in our results).

α phase	*	*	*	*	*	*	*
Reference	[17,24]	[24]	[24]	[17,24]	[23]	[23]	[23]
Wavenumber	762–764	795–796	854–855	976	1210	1383	1423
β phase	*		*	*			*
References	[20,23]		[26]	[14,22,23]			[23]
Wavenumber	839–840		1074	1275, 1276, 1286			1431
γ phase	*	*			*	*	*
References	[17,20]	[20,21,23]	[17,20]	[20,23]	[17]	[20–22]	[20,22]
Wavenumber	776	812	833	840, 882	1117	1233–1234	1250

However, Gregorio pointed out that it is difficult to distinguish the difference between α and γ crystalline phases using XRD because the values for 2-theta and diffraction directions are identical [15,17]. Gregorio hypothesizes that since the γ-phase is formed from an α → γ transition at elevated temperatures near the T_m of the α-phase, a majority of α-phase remains in the material and contributes to the diffraction [15]. In addition, the breadth of the (1 0 0) diffraction peak may overlap the (1 1 0) + (2 0 0) diffraction peaks associated with the β crystalline phase and small quantities of the β crystalline form could only be manifested as a weak shoulder to the (1 0 0) peak. An alternate method of determining those crystalline phases is FTIR. The FTIR absorption bands for each crystalline phase present in PVDF have been well established and are shown in Table 2 [15,16,23–26]. By combining the XRD and FTIR techniques, the different crystalline phases in PVDF can be identified.

2.2. Compatibility between solvents and polymers

When a polymer is exposed to organic solvents, its properties may change. For example, if a polymer is plasticized by the solvent, its T_g will decrease. For semi-crystalline polymers, a reduction in the T_g will increase molecular mobility, which can cause an increase in crystallinity. The strongest interactions occur when the chemical structure of the polymer is similar to that of the solvent. The adage of like-dissolves-like is important for polymers. The concept of a solubility parameter is one method of quantifying these interactions. Higher solubility parameters usually indicate greater polarity of the solvent. Typical values for the solubility parameter range from 11.8 (MPa)$^{1/2}$ for non-polar molecules to 48.1 (MPa)$^{1/2}$ for water. As the solubility parameter approaches that of the polymer, generally more solvent is retained. For uncross-linked polymers, when the solubility parameter of the solvent is similar to that of the polymer, the polymer dissolves. For chemically and physically cross-linked polymers, the maximum swelling occurs when the solubility parameters of polymer and solvent are the same. For the semi-crystalline polymers, the crystallites act as physical cross-links that can inhibit its dissolution [1,27,28]. For PVDF, its solubility parameter was reported as 23.2 (MPa)$^{1/2}$ [20,29], and its Hansen solubility parameters are 17.2, 12.5, and 9.2 (MPa)$^{1/2}$ for the contributions of dispersion forces, polar forces, and hydrogen-bonding, respectively [29].