

PVDF의 polymorphism에 따른 기체 전달현상 특성

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Effet of polymorphism of PVDF to the gas transport

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Poly(vinylidene fluoride) (PVDF) is a semi-crystalline polymer which has drawn both scientific and technological attention because of the useful pyroelectric and piezoelectric properties it presents. It is also one of the rare polymers that exhibit diverse crystalline forms, having at least four phases known as α , β , γ and δ . The apolar α phase is the most common, normally being obtained by crystallization from the melt at moderate or high supercooling ($<160^{\circ}\text{C}$). The polar phase β is technologically the most interesting because of its better pyroelectric and piezoelectric properties. However, crystallization of PVDF from the melt takes place predominantly in the α phase, and the β phase is normally obtained by drawing of α phase films. It was recently demonstrated that it is possible to obtain β phase PVDF films by solution crystallization with dimethylacetamide(DMA) at adequate temperature conditions[1]. The γ phase, also polar, was obtained by solution crystallization in dimethylformamide(DMF), DMA, and dimethylsulphoxied(DMSO). In all of them, the chains are packed in the unit cell in such a way that the dipoles associated with individual molecules are parallel one to the other, leading to the non-zero dipole moment of the crystal. Both the molecular and crystal dipoles are perpendicular to the chain axis. In α phase, the chains are packed in the unit cell in such a way that the molecular dipoles are antiparallel and there is no net (crystal) dipole. Polar crystals in PVDF can be obtained from non-polar α modification by various processes such as

mechanical deformation(β form)[2,3], poling under large electric fields(δ and β forms)[4], annealing or crystallization at high temperatures(γ form)[5].

In this work it is suggested that the polymorphism of PVDF will have an influence on the behavior of the gas transport, particularly, permanent gases such as He, H₂, O₂, and N₂.

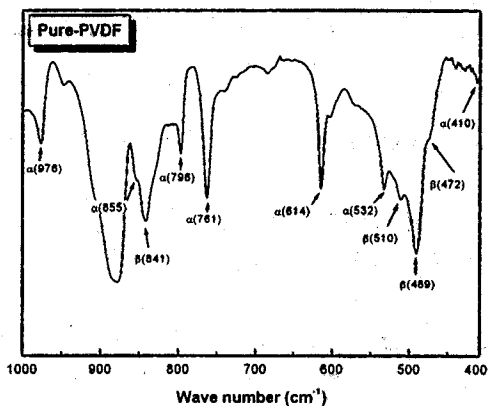


Figure 1. FT-IR spectrum of original PVDF

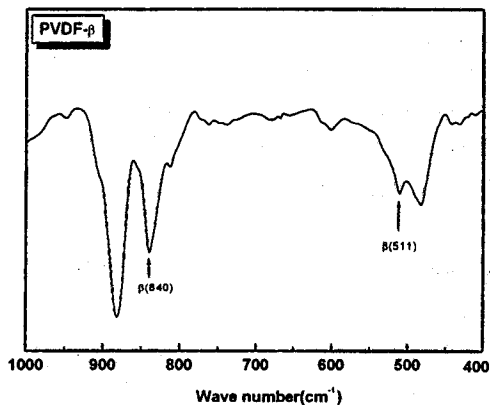


Figure 2. FT-IR spectrum of PVDF(20wt% DMF solution at 60°C)

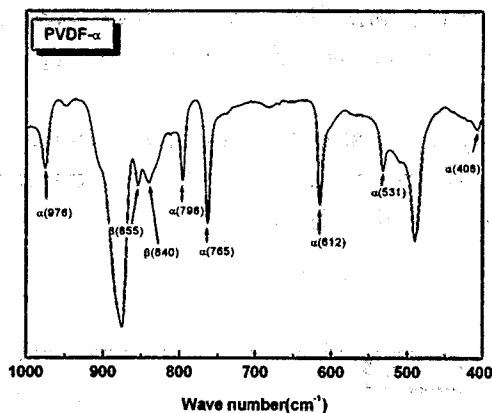


Figure 3. FT-IR spectrum of PVDF(20wt% DMF solution at 120°C)

Figs. 1 and 3 show FT-IR spectrum of original and modified PVDF, respectively. PVDF films(PVDF-I) prepared in 20 wt% DMF solution at 60°C showed predominantly β phase, on the other hand, PVDF films (PVDF-II) prepared in 20wt% DMF solution at 120°C showed predominantly α phase. In the case of PVDF-I, the permeability of He gas was 33 barrer ($1 \text{ barrer} = 10^{-10} \times \text{cm}^3(\text{STP})\text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$), and in the case of PVDF-II was 15 barrer at 30°C.

References

- [1] R.J. Gregorio and M.J. Cestari, J. Polym. Sci., B32, 859, 1994.
- [2] J.B. Lando, H.G. Olf, A. Peterlin, J. Polym. Sci, A1, 941, 1966.
- [3] J.C. McGrath, I.M. Ward, Polymer, 21, 855, 1980.
- [4] D. Naegle, D.Y. Yoon, M.G. Broadhurst, Macromolecules, 31, 585, 1977.
- [5] S. Weinhold, M.H. Litt, J.B. Lando, Macromolecules, 13, 1178, 1980.