Journal of Polymer Science and Technology 5(1) 2020:47-51
ISSN: 2550-1917

EFFECT OF SOLVENT TYPE, CONDITIONS OF DISSOLUTION AND EVAPORATION TEMPERATURE ON CRYSTALLINITY PHASES OF PVDF

F. Z. BENABID[1*], N. KHARCHI [1], F. ZOUAI[2] & D. BENACHOUR[1]
[1]LMPMP, Faculty of Technology, Ferhat ABBAS University Sétif-1, Algeria
[2] Emerging Materials Research Unit, Ferhat ABBAS University Sétif-1, Algeria
**Corresponding author: fzbenabid@yahoo.fr*

ABSTRACT

Poly (vinylidene fluoride) (PVDF) is a semi-crystalline polymer which can form different crystals depending on the condition of the crystallization. These different crystal structures include non-polar α-phase and the polar one (ß-phase). In order to study the effect of the conditions of the crystallization and the evaporation temperature on the crystallinity of the PVDF, we have investigated the solubility of the PVDF using five solvents: dimethylformamide (DMF), tetrahydrofuran (THF), Methyl ethyl ketone (MEK), chloroform and acetone. Three solutions with different conditions of PVDF casted in the DMF were prepared. The two solutions prepared at low temperature and crystallization time showed α crystalline phase, while the third one exhibited the ß-phase form regardless of the high temperature and the long preparation time. The evaporation temperature and time have also influenced the crystalline obtained phase of the PVDF.
Keywords: PVDF; DMF; Crystallinity; α-phase; ß-phase; Preparation conditions

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is a semi-crystalline polymer having wide applications due to its excellent physical and chemical properties i.e. the piezo electric [1-2] and the high abrasion resistance to outdoor exposure and sunlight as well as good thermal stability [3-5]. It is known that samples obtained from the melt and having more than 50 wt% PVDF are partially crystalline [6-7] and those obtained from solution were shown to be semi-crystalline even at smaller PVDF concentrations.

Low surface energy of fluorinated coating allows architectural fronts to remain clean. Contrary to silicone-based coating which tends to get rapidly dirty and then it must be washed off to get rid of settled dust. Decreasing brightness due to external exposure is usually taken for result of settling dust, as well as polymer surface degradation. Low surface energy coatings have poor affinity to dust, and consequently high bright retention after external exposure [8]. With an adequate sequence of processing steps, PVDF can be made piezo-, pyro- and ferroelectric forms depending on preparation conditions and which are usually α, ß, γ and δ. The beta phase is the more difficult and the most interesting polar phase to obtain from the technological point of view.

Gregorio and Borges [9] have investigated the effect of solvent type and temperature on the formation of α and ß phases from solution cast PVDF. They have used three solvents with different boiling points; N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP) and hexamethyl phosphoramide (HMPA). Infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) revealed that the type of phase formed depends on the crystallization rate of PVDF, which its turn is determined by the evaporation rate of the solvent.

On the other hand, Gregorio [10] has studied the alpha, beta, and gamma crystalline phases of poly(vinylidene fluoride) films prepared at different conditions using Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), wide angle X-ray scattering-(WAXD), polarized light optical microscopy (PLOM), and scanning electron microscopy (SEM). The sudy showed that solution crystallization at T <70 °C always results in the β phase regardless of the solvent used.

In 2011, Silva et al. [11] have studied the effect of drawing on the crystal-amorphous interphase, remanent polarization and dielectric properties of α-PVDF films. Calorimetric analyses and X-ray diffraction results indicated that drawing increases the degree of crystallinity and reduces the crystal-amorphous interphase. The same author has studied the effect of drawing on the dielectric properties and polarization of pressed solution cast ß-PVDF films [12]. The results allowed verification of the effect of drawing on and structure of the resulting and structure on the dielectric properties, remanent polarization, and coercive field of beta-PVDF.

The objective of this study is to verify the effect of the solvent type, conditions of dissolution and evaporation temperature on the formation of each crystalline phase of PVDF, using several solvents with distinct boiling points. Since different boiling points result in different evaporation rates and, consequently, in different crystallization rates of PVDF

EXPERIMENTAL

The PVDF powder used was Hylar 5000 from Ausimont. The organic solvent used was, dimethylformamide (DMF). This solvent was chosen because of its distinct boiling point (Tb) and for being good ones of PVDF. Infrared spectra (FTIR) were obtained using a Perkin-Elmer Spectrum 1000 spectrophotometer. PVDF was dissolved in the solvent at different temperatures and for different times.

RESULTS AND DISCUSSION

In order to study the effect of conditions of dissolution and evaporation temperature on PVDF crystallinity phase, three polymer solutions have been prepared. For the first one, PVDF was dissolved in DMF at 40 ° C for 2 hours in a solution; for the second, it was at 70 °C for 2 hours and for the last one, it was dissolved at 90°C for 6 hours.

The results showed that for the first solution (40 °C, 2h),it was found that the appearance of a peak at 614cm^{-1} which is the characteristic of phase α and a wide bands corresponding to the two crystalline forms; α and ß mixed (see Figure1).

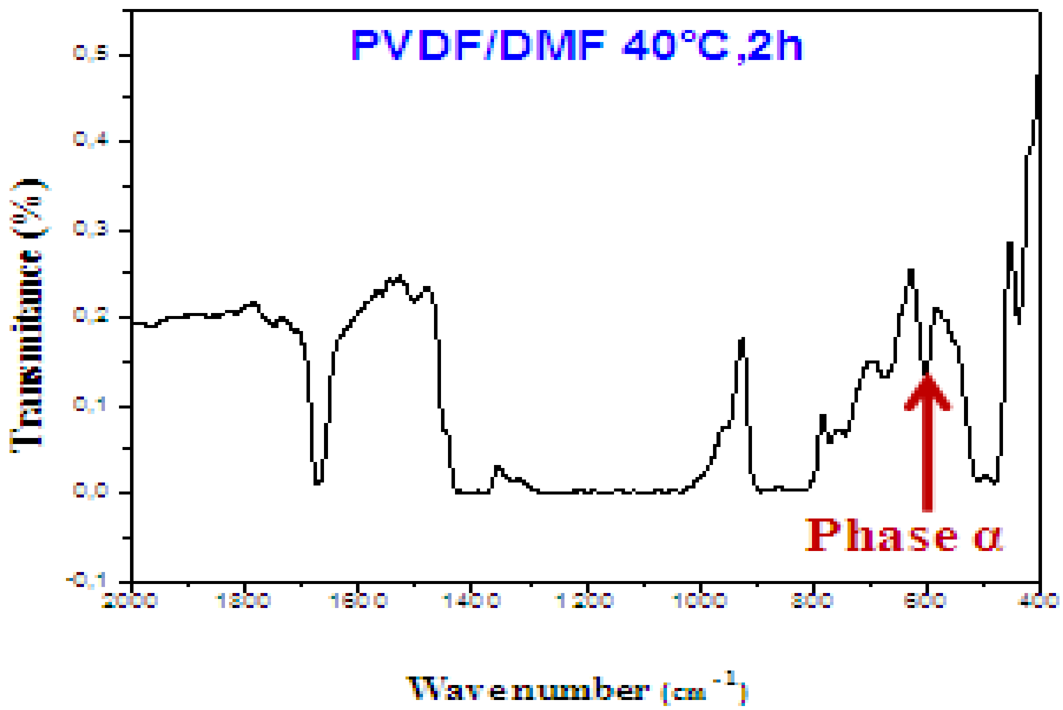

Fig. 1 FTIR spectrum of the first solution

For the second solution (70 °C, 2h), various characteristic peaks of α phase were detected at 487, 533, 614, 796 and 976 cm^{-1}(see Figure 2).

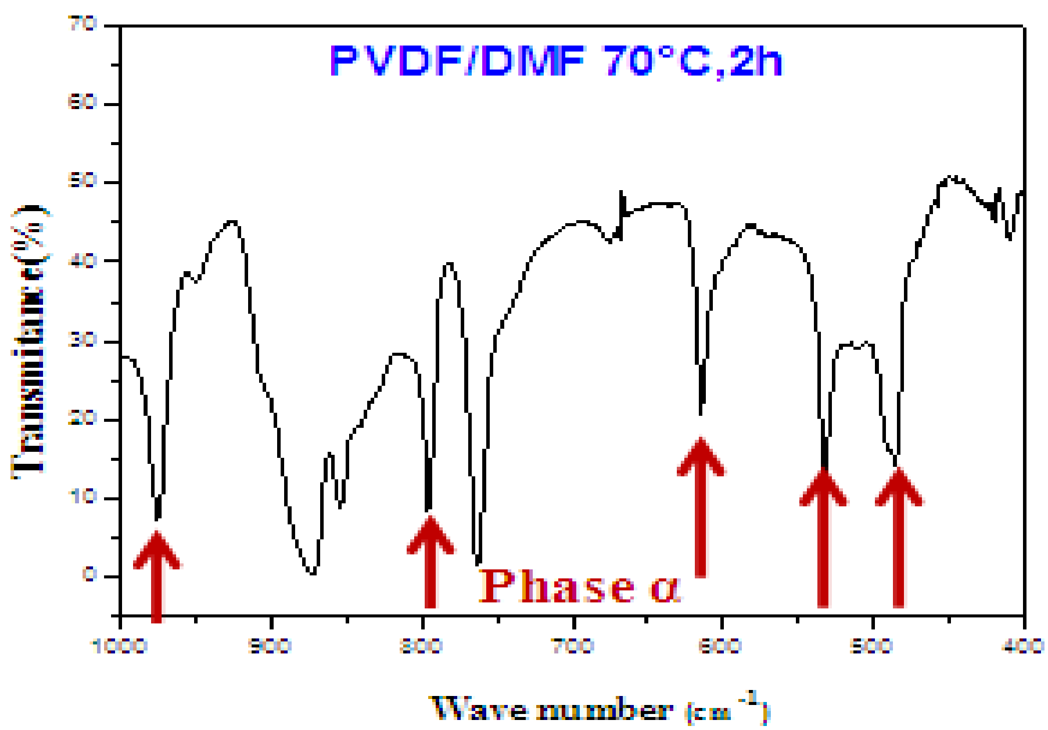

Fig. 2 FTIR spectrum of the second solution

In the third solution (90°C, 6h), two peaks of ß-phase were observed at 510 and 841 cm^{-1}. Such result was confirmed by Gregorio which has many research works concerning the different crystallinity phases of PVDF [7-10] (see Figure3). The author also confirms that low evaporation solvent rates favor the formation of the trans planar ß-phase.

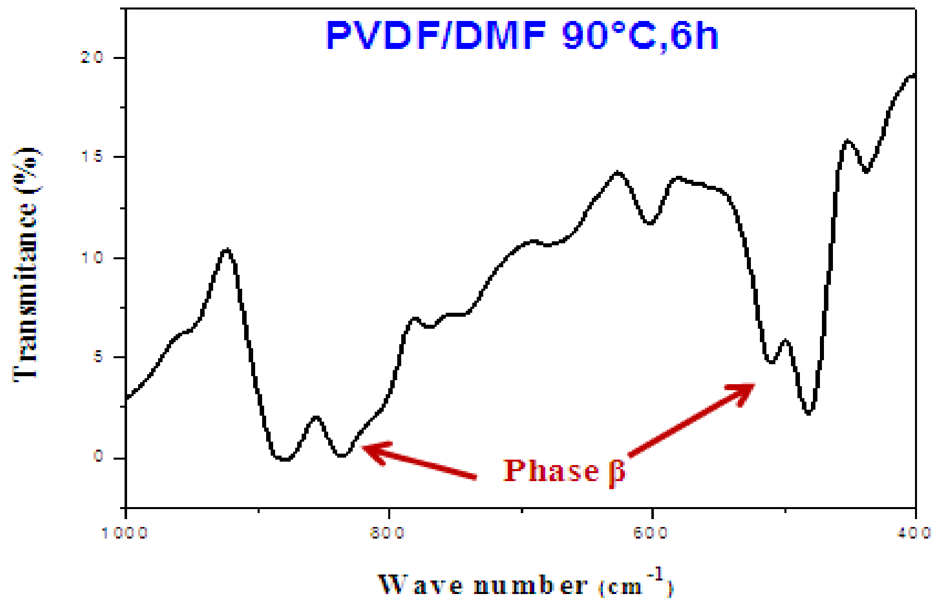

Fig. 3 FTIR spectrum of the third solution

In summary, we can say that a long and low evaporation solvent rate (40°C, 6 h) favor the formation of the trans planar ß-phase [9] . The different crystalline phases (α and ß) are shown in Figure 4.

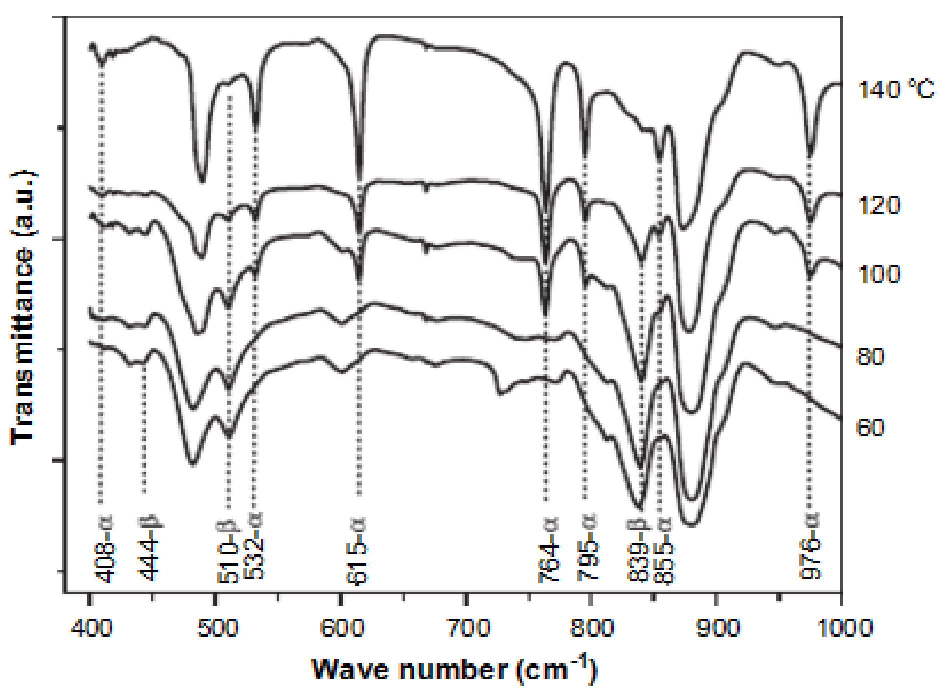

Fig. 4 FTIR spectra of the films cast from DMF solution at different temperatures [9]

CONCLUSIONS

The obtained results showed that conditions of dissolution and evaporation temperature effect the PVDF crystallinity phase: The first solution (40 °C, 2h) showed the appearance of characteristic phase of α peak and wide bands corresponding to the two crystalline forms α and ß mixed. The second solution (70°C, 2h) showed various characteristic peaks of α phase at 487, 533, 614, 796 and 976 cm^{-1}. The third solution (90°C, 6h) showed two peaks of ß-phase at 510 and 841 cm^{-1}.

REFERENCES

[1] O. Faria and R.L Moreira, Effect of PMMA addition on characterization and morphology of PVDF, Polymer, 10 (1999) 421.
[2] K. Saito, S. Miyata, T.T. Wang, Y.S. .Jo and R. Chujo, Macromolecules, 19 (1986) 2450.
[3] D.A. Sciler and J. Sheirs(Fad), PVDF in the Chemical Process Industry, Wiley, Chichester (1997) 487.
[4] F. Zouai, F. Z. Benabid, S. Bouhelal, M. E. Cagiao, D. Benachour & F. J. Baltá Calleja, Nanostructure and morphology of poly(vinylidene fluoride)/polymethyl (methacrylate)/clay nanocomposites: correlation to micromechanical properties, *J Mater Sci*, 52, 4345–4355, (2017).
[5] F.Z Benabid, L. Rong, D. Benachour, M. E. Cagiao, M. Ponçot, F. Zouai, S. Bouhelal and F. J. Baltá Calleja, Nanostructural characterization of poly (vinylidene fluoride)-clay nanocomposites prepared by a one-step reactive extrusion process, *J Polym Eng,* 35(2), 181–190, (2015).
[6] J.S. Noland, N.N. Hsu, R. Saron and J.M. Scmitt Adv. Chem.Ser. 15(1971) 1199
[7] P. Tekely, F.Laropretre and L. Monnerie Polymer.26 (1985) 1081.
[8] J. Mc Cann, Surface Coatings 8 Aust.(1990) 27.
[9] R. Jr. Gregorio and D.S. Borges, Effect of crystallization rate of the formation of the polymorphism of solution cast poly (vinylidene fluride), Polymer, 49 (2008) 4009-4016.
[10] R. Gregorio Jr., Determination of the α, ß and γ Crystalline Phases of Poly(vinylidene fluoride) Films Prepared at Different Conditions, Journal of Applied Polymer Science, 100 (2006) 3272–3279.
[11] A. B. Silva, C. Wisniewski, J. V. A. Esteves and R. Gregorio JR., Effect of Drawing on the Crystal–Amorphous Interphase, Remanent Polarization and Dielectric Properties of α-PVDF Films, Ferroelectrics, 413 (2011)220-230.
[12] A. B. da Silva, C. Wisniewski, J. V. A. Esteves and R. Gregorio Jr., Effect of drawing on the dielectric properties and polarization of pressed solution cast ß-PVDF films, J. Mater. Sci., 45 (2010) 4206–4215.