The Effect of Polymerization Temperature on the Properties of Polyvinyl Fluoride Polymerization in Supercritical Carbon Dioxide

Wei Liu, Yanzhong Zhang*, Huaiyun Chang, Rong Cai and Peiliang Ma
Zhejiang Research Institute of Chemical Industry Co., LTD, No. 387 Tianmu Mountain Road, Hangzhou, China
Email: zhang.yanzhong@sinochem.com

Abstract. The ongoing search for environmentally friendlier alternative to the organic solvents used in chemical processes has led to the development of technologies based on supercritical carbon dioxide (scCO₂), which is non-flammable, non-toxic and relatively inert fluid. Polymer chemistry does not escape this trend. Fluoropolymers prepared in scCO₂ have many special properties, which are different from fluoropolymers that use water as the reaction medium, this paper studies the effect of polymerization temperature on polyvinyl fluoride polymerization in supercritical carbon dioxide. The results show that as the polymerization temperature increases, the intrinsic viscosity and shear viscosity of the polymer gradually decreases; at the same time, the increasing of polymerization temperature leads to higher proportion of irregular structure of the polymer, which causes lower melting point and lower crystallinity, and the film prepared by the resin also exhibits a higher visible light transmittance. The above results show that the resin polymerized in supercritical carbon dioxide can impart better performance to conventional polymerization, which expands the potential application fields of the resin.

Keywords. Polyvinyl fluoride resin, supercritical carbon dioxide, polymerization temperature, polyvinyl fluoride film.

1. Introduction
The density and dielectric constant of supercritical carbon dioxide (scCO₂) are close to conventional solvents, so its property is basically the same as that of liquid solvents. At the same time, its viscosity is very small and close to gas, so it has a high mass transfer rate. Due to the inherent compressibility of scCO₂, it is an ideal substitute for traditional solvents [1].

scCO₂ being characterized by a low dielectric constant ξ-2, is thus a good solvent for nonpolar molecules with low molecular weight [2]. Indeed, in the field of polymer synthesis, scCO₂ presents many advantages compared to conventional solvents. Dry polymers can be obtained by simple depressurization of the reactor at the end of the polymerization. Moreover, its low toxicity and cost, high mass transfer and diffusivity, and low viscosity which limits the Trommsdorf effects, make CO₂ as an interesting alternative solvent. In the last decades, intensive research dedicated to polymerization reactions in this medium also demonstrated higher and faster conversions of monomer to polymer with high molecular weight [3]. Most organic monomers and initiators are soluble in liquid and scCO₂, whereas most polymers are insoluble in CO₂ [4-7]. This behavior defines a precipitation polymerization. Continuous precipitation polymerization in scCO₂ should be applicable to a wide variety of industrially important monomers.
It is reported in the literature that fluoropolymers prepared using water as a medium will produce carboxyl groups, and polymers containing carboxylic acid ends, which need to be hydrolysis at high temperature or to be fluorinated [8]. If without treated, problems such as decomposition, discoloration, and release of hydrogen fluoride will occur during processing at relatively low temperature. Since radical species are inert towards CO$_2$, atom transfer radical polymerization (ATRP), reversible addition–fragmentation chain transfer polymerization (RAFT), nitroxide-mediated radical polymerization (NMP) was also investigated in CO$_2$ mainly in heterogeneous polymerization processes [9, 10].

Fluoropolymers prepared in scCO$_2$ have many special properties, which are different from fluoropolymers that use water as the reaction medium. Polyvinyl fluoride (PVF) prepared in scCO$_2$ has low branching rate, high crystallinity and relatively high thermal stability [11]. In this article, the effect of different polymerization temperature on the performance of polyvinyl fluoride and the processing performance of the resin polymerized by different processes were studied.

2. Experimental

2.1. Main Raw Materials and Equipment
Vinyl fluoride, purity $\geq 99.99\%$, Zhejiang Research Institute of Chemical Industry Co., LTD.; 4,4’-Azobis(4-cyanovaleric acid), purity $\geq 98\%$, Aladdin; CO$_2$, purity 99.99\%, Hangzhou Chengfeng Gas Co., Ltd.; DMF, purity $\geq 98\%$, Eastman Chemicals (Nanjing) Co., Ltd. DMAc, purity $\geq 98\%$, Eastman Chemicals (Nanjing) Co., Ltd.

Twin screw extruder: HT-25 Nanjing Rubber and Plastic Machinery Factory Co., Ltd.
Biaxial stretching machine: Guilin Electrical Equipment Scientific Research Institute Co., Ltd.

2.2. Preparation of PVF Resin in scCO$_2$
The initiator 4,4’-Azobis(4-cyanovaleric acid) is dissolved in a small amount of deionized water, and fed into the autoclave that already contains CO$_2$ through the metering pump. The temperature in autoclave is increased to the setting value. And vinyl fluoride monomer is simultaneously injected to a predetermined pressure of 7.5MPa. The pressure of autoclave is maintained by continuously replenishing vinyl fluoride monomer. About 2 hours later, stop adding vinyl fluoride monomer and remain autoclave temperature about 10 minutes, then reduce the autoclave temperature slowly to room temperature through cooling water in jacket. Finally, release the CO$_2$ in the autoclave to obtain a white snowy polymer powder (PVF resin).

2.3. Preparation of PVF Film
Firstly, 10kg PVF and 15kg DMAc are added into the mixer, followed by a mechanical stirring at a speed of 800rpm for 30min. Secondly, to eliminate bubble, the mixture is stayed remain for 10 minutes. Finally, transparent PVF film is obtained by extruding, casting, biaxially stretching and solvent volatilizing.

2.4. Testing and Characterization
DSC: The melting point and enthalpy of the resin was measured using a PE Diamond DSC analyzer under the protection of N$_2$. The amount of N$_2$ is 50 mL/min, and the amount of sample is about 4 mg. The temperature is raised to 220°C (+10°C/min) and keep for 5 minutes, then decreased to room temperature (-20°C/min), and finally increased to 220°C (+10°C/min). Sample’s melting enthalpy during the process should be recorded.

$^{19}$F NMR: The molecular chain microstructure determination in the sample was performed on the Bruker AVANCE III HD nuclear magnetic resonance instrument. Use deuterated dimethyl sulfoxide as the solvent, the mass concentration of the solution is about 1\%, the test temperature is 120 °C, the sampling time is 0.5 s, the pulse angle is 90°, and the delay time is 1 s.
Rheology measurement: Melt viscosity (40% by weight PVF dispersed in DMF) is measured using a Malvern capillary rheometer at 140°C, from 10 s\(^{-1}\) to 10000 s\(^{-1}\).

Intrinsic viscosity: Add 0.05g of PVF resin sample into a 25 ml volumetric flask, dissolve it in DMF at 110°C for 48 hours; The intrinsic viscosity is measured using Ubbelohde viscometer with three-point method.

Crystallinity test: The crystallinity of PVF resin was measured by X’Pert PRO type diffractometer. The tube pressure and tube current are 40kV and 40mA, respectively, the radiation source is CuK\(_\alpha\) (0.1541 nm), and the data is read in the range of 2θ=10°~80°.

Visible light transmittance test: Cary 5000 UV-Vis was used for the test, spectral range 380nm-800nm.

3. Results and Discussion

3.1. Characterization of PVF Resin

![Graph](image)

**Figure 1.** The relationship between intrinsic viscosity and polymerization temperature.
Figure 2. The relationship between shear viscosity and shear rate. (a:75°C; b:80°C; c:85°C; d:90°C.)

It can be seen from figure 1 and figure 2 that with the increasing of the polymerization temperature, the intrinsic viscosity of the resin shows a definite decrease. As the polymerization temperature increases, the decomposition rate of the initiator accelerates and the molecular weight of the polymer becomes smaller. At the same time, it appears that the shear viscosity of the resin also becomes smaller, especially at high shear rate. Shear thinning of the shear viscosity exists at all resin at different polymerization temperature.

Figure 3. DSC curve of PVF resin at different polymerization temperature.
It can be seen from figure 3 that the polymerization temperature reduces the melting temperature of the resin while also reducing the crystallinity of the resin. The same tendency can also be found from the XRD spectrum of the resin at different polymerization temperature.

![Figure 4. XRD spectra of PVF resin at different polymerization temperature.](image)

The XRD spectra of PVF resin at different polymerization temperature was shown in figure 4. By calculation, the crystallinity and crystallite size of the resin through different polymerization temperature are shown in table 1.

Table 1. The crystallinity and crystallite size of the resin at different polymerization temperature.

| Polymerization temperature | Degree of crystallinity /% | Crystallite size /nm |
|----------------------------|-----------------------------|----------------------|
| 90°C                       | 16.34                       | 5                    |
| 85°C                       | 18.70                       | 6.1                  |
| 80°C                       | 26.71                       | 7.5                  |
| 75°C                       | 29.42                       | 9.9                  |

Table 2. $^{19}$F NMR of resin at different polymerization temperature.

| Polymerization temperature | Head-head/ tail-tail % | Head-tail % |
|----------------------------|-------------------------|-------------|
| 90°C                       | 9.0                     | 90.1        |
| 85°C                       | 9.8                     | 89.3        |
| 80°C                       | 11.6                    | 88.5        |
| 75°C                       | 13.2                    | 86.1        |

There are two main peaks at -178ppm~ -182ppm and -189ppm~ -197ppm, corresponding to the fluorine atom of the head-tail structure and the fluorine atom of the head-head (or tail-tail) structure respectively; There are three groups of smaller peaks at -147ppm, -163ppm, -220ppm, which are derived from fluorine atoms at the branching of the head-to-tail structure, fluorine atoms at the branching of the head-to-head structure, and fluorine atoms at the end group (CH2F) [12]. It can be seen from table 2 that with the increasing of the polymerization temperature, the higher ratio of the head-to-head structure that
maybe led to the reduction of crystallinity and crystalline size significantly, this phenomenon is consistent with the results of DSC and XRD.

3.2. Characterization of PVF Film

The transmittance of transparent film which was prepared from resins at different polymerization temperature was evaluated, as shown in figure 5.

![Transmittance of film at different polymerization temperature](image)

**Figure 5.** Transmittance of film at different polymerization temperature.

The structural irregularity caused by the high polymerization temperature leads to the differentiated visible light transmittance of PVF film, especially when the polymerization temperature reaches 90°C, it exhibits a visible light transmittance comparable to commercial ETFE film.

4. Conclusions

Vinyl fluoride polymerized in supercritical carbon dioxide shows many excellent properties. In this article, we focus on the effect of polymerization temperature on the properties of polyvinyl fluoride resin. The results show that with the increasing of the polymerization temperature, the intrinsic viscosity and shear viscosity of the resin shows a definite decrease. Interestingly, we found that the polyvinyl fluoride with high polymerization temperature has a larger proportion of head-head structure, lower crystallinity, and lower crystallite size, and the resin with more irregular structure caused by high polymerization temperature produced to the higher visible light transmittance of PVF film.

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