

## Synthesis Polytetrafluoroethylene (PTFE) Nanoparticles via Adsorption of TFE Monomer onto Different Surfaces

**M. Yari\***

Chemistry Department, Islamshahr Branch, Islamic Azad University, Islamshahr, Tehran, Iran

**O. Moradi**

Chemistry Department, shaher-e- Gods- Branch, Islamic Azad University, Tehran, Iran

### Abstract

**Introduction:** The effects of different solid substrates including: carbon nanofibers (CNFs), activated carbon, alumina, silica, and poly vinyl pyrrolidone (PVP) were compared for high pressure synthesis of polytetrafluoroethylene (PTFE,  $(CF_2)_n$ ) nanoparticles via the adsorption of thermally synthesized tetrafluoroethylene (TFE,  $C_2F_4$ ) as monomer.

**Aim:** Syntheses and characterization PTFE nanoparticles and also in this paper, a new method is proposed for the synthesis of PTFE nanoparticles via adsorption of TFE monomer on different solid substrates.

**Materials and Methods:** Electron microscopy, FT-IR spectroscopy, and thermogravimetric analysis (TGA) were used for characterization of PTFE nanoparticles on different solid substrates.

**Results:** under similar conditions, the average diameter of the PTFE nanoparticles was around 90 nm for CNFs, 130 nm for PVP, 150 nm for alumina and around 200 nm for silica.

**Conclusion:** Different solid materials have various capacities for the formation of PTFE nanoparticles, depending on their size, shape, and their morphology. In fact, the amounts and the sizes of synthesized PTFE nanoparticles are strongly dependent on the nature of the solid surface substrate.

**Keywords:** Polytetrafluoroethylene, Radical polymerization, Tetrafluoroethylene, Adsorption, Carbon nanofibers

### Introduction

Fluoropolymers are technical polymers with very special properties and applications.<sup>[1]</sup> These materials are among the most versatile plastics thanks to their properties.<sup>[2]</sup> The thermal stability is the major feature of these polymers spurring their applications where high temperature exposures in polymers are encountered.<sup>[3]</sup> The stability of Fluoropolymers is derived mainly from the low polarizability as well as from the strong carbon-fluorine (C-F) bond energy of  $507 \text{ kJ mol}^{-1}$ , compared with typical energies of  $415 \text{ kJ mol}^{-1}$  for (C-H) or  $348 \text{ kJ mol}^{-1}$  for (C-C) bonds.<sup>[4, 5]</sup> The most important Fluoropolymers is PTFE.<sup>[6]</sup>

\*Corresponding author

PTFE has attracted much attention because of its excellent features such as extreme thermal stability, low friction coefficients, considerable biocompatibility, dielectric constant, few moisture absorption and chemical inertness.<sup>[7, 4]</sup> The special properties of PTFE arise because of its strong chemical bonding, the shielding of its carbon backbone by fluorine atoms, and the intermolecular interactions between its very long, helical,  $(CF_2)_n$  chains. These special chemical and structural features also give extremely high melt viscosity ( $\sim 10^{10}$ - $10^{12}$  poise)<sup>[7]</sup> and a negligible solubility in all common solvents.<sup>[8]</sup> These unique characteristics have lead to candidate PTFE in many widespread applications such as in electronics, mechanical engineering, aerospace, chemical industries, medical engineering, etc..<sup>[4, 9]</sup> The newest industrial applications of PTFE are its use as a matrix for polymer composites with a range of fillers, as material coating,<sup>[10]</sup> as super hydrophobic electro sprayed nanomaterials,<sup>[10]</sup> and as electrolyte membranes.<sup>[11]</sup> These all reveal the industrial applications of PTFE as well as the importance of the applicable methods for synthesis of PTFE.

For synthesis of PTFE, since the problems related to the preparation of the monomer, the polymer formed is highly expensive.<sup>[12]</sup> To prepare the monomer of PTFE, TFE is generally produced by the pyrolysis of chlorofluoroparaffins, especially chlorodifluoromethane ( $CHClF_2$ , R22) in the temperature range of 750–950 °C. The most widely used process for the commercial production of TFE is the direct pyrolysis of R22.<sup>[13]</sup> The synthetic process used for PTFE formation, is based on the radical polymerization mechanism in accordance with two different procedures. The first procedure is founded on the direct gas-phase polymerization process, whereas the other procedure is anchored on the aqueous dispersion polymerization process.<sup>[14]</sup> Since a complete description of gas phase synthesized polymer includes the size, shape, and the morphology of PTFE.<sup>[15, 16]</sup> Therefore, in the synthetic processes of PTFE, the generated polymer should be well characterized through the controlled process parameters to yield PTFE particles for specific applications.

One of the most important factors that affect the fantastic properties of the PTFE is the size of PTFE particles.<sup>[17]</sup> Recently, nanometer-sized PTFE particles have attracted much attention.<sup>[4, 10, 18-19]</sup> This is due to the unique physicochemical properties of PTFE nanoparticles.<sup>[18-19]</sup> Since the nano size of PTFE has some exceptional properties such as excellent electrical resistance, chemical inertness, mechanical and thermal stability, compared to the bulky PTFE particles, the PTFE nanoparticles play important roles in different parts of industry.<sup>[10, 12, 18]</sup> Therefore, despite the growing impact in the synthesis of PTFE particles, introduction of controllable methods for large scale synthesis of PTFE nanomaterial is important.<sup>[7]</sup>

In this paper, a new method is proposed for the synthesis of PTFE nanoparticles via adsorption of TFE monomer on different solid substrates. In this experiment, the effect of the active surface area of the solid supports for controlling the amount and also the size of the PTFE nanoparticles is investigated in detail.

## Experimental

### Reagents and solutions

Gases including  $CHClF_2$  (HCFC-22 or R22) and nitrogen with 99.998% and 99.900% purity percentages were purchased from "ISCEON, England " and "Parsbaloon, Iran", respectively. Silica, alumina, PVP, and molecular sieves (pore volume: 50Å) were from Merck, Darmstadt, Germany.

Highly purified CNFs with 250-400 nm internal diameter, and activated carbon were synthesized by chemical vapor deposition method at temperatures around 1300 °C in an inert atmosphere of argon using acetylene gas ("Parsbaloon, Iran") as a source of carbon and ferrocene (Merck, Darmstadt, Germany) as a source of catalyst.

## Apparatus

### Pyrolysis system for synthesis and direct adsorption of monomer on solid supports

The set up of the instrument has been shown in Fig. 1. The production line is quartz tubing (8 mm diameter, 90 cm length), that passes through a cubic furnace (Lenton, EF 11/8&AF 11/6). R22 was selected as the source of monomer (TFE). The furnace, 2500 W, was used for Pyrolysis of R22 and production of TFE in an inert atmosphere of nitrogen.

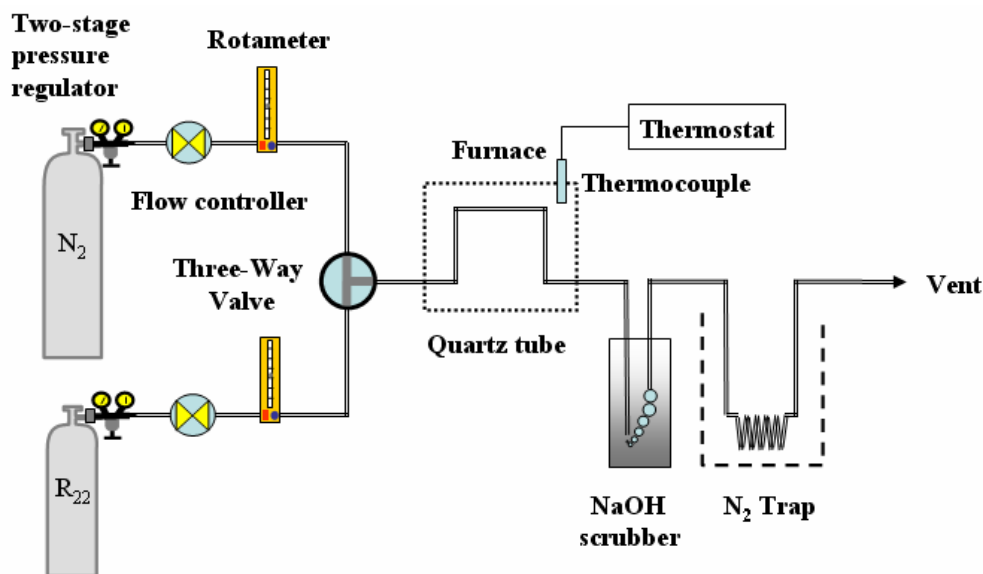


Fig. 1- Schematic of the pyrolysis instrument for synthesis and adsorption of TFE on different solid substrates.

Mass flow controllers were utilized to control the flow rate of R22 and nitrogen gas before introduction into the quartz tubing. The generated TFE was then carried towards the end parts of the production line by the flow of nitrogen and bubbled into a 500 ml vessel that was half filled with 5.0 M NaOH.

The outlet of the NaOH vessel was then connected to a glass U-Trap (internal diameter: 0.5 cm, width: 3 cm, height: 5 cm), located inside a vessel containing liquid nitrogen. Two valves (Three-way) were also positioned at the two sides of the U-Traps. Finally, the outlet of the U-Trap was directed towards the hood through silicone tubing.

After setting the temperature of the furnace, optimum flow rates of R22 and nitrogen as diluents were mixed and introduced into the quartz tubing. During the pyrolysis process, the synthesized TFE was then frozen inside the U-Trap using liquid nitrogen. At the end of the experiment, the two valves were closed and the U-Trap was disconnected from the pyrolysis production line and joined to the other system used to adsorb the TFE on solid supports.

In the adsorption process, suitable substrates such as CNFs, silica, alumina, molecular sieves and activated carbon were put individually inside several glass traps (internal diameter: 0.5 cm, width: 3 cm, height: 5 cm), connected sequentially to each other by silicon tubing. Then, the U-Trap containing the frozen TFE was connected to the end of the array of traps, using silicon tubing (0.5 cm internal diameter, 20 cm length). During the adsorption process, the temperature of the TFE inside the U-Trap was controlled via locating it inside a refrigerator.

In this experiment, scanning electron micrographs were obtained by SEM instrumentation (SEM, XL-30 FEG SEM, and Philips, at 20 KV). An atomic force

microscopy (AFM, DME-SPM, version 2.0.0.9) was also used for AFM images. spectroscopic methods including FT-IR spectrometry (Shimadzu FT-IR 8300 spectrophotometer) and X-ray diffraction (XRD, D8, Advance, Bruker, axs) were obtained for characterization of the PTFE nanoparticles. The TGA of the samples was analyzed using a lab-made TGA instrument.

#### Apparatus system for synthesis of PTFE nanoparticles

The set up of the instrument for synthesis of PTFE nanoparticles on different solid supports is shown in Fig. 2. It consists of T-shape tubing (schedule No. 160, model 4F2). A pressure gauge is located at one of the end parts of the T-tubing. Whereas, the other end part of the T-tubing is connected to the nitrogen cylinder (220 L, 200 bars) through a stainless steel valve to control the pressure of the reaction cell. The side-arm of the T-tubing (4.0 cm internal diameter, 15 cm height) is used to locate the copper reaction cells (0.5 mm internal diameter, 3 cm height) containing each type of solid substrate deposited with TFE for synthesis of PTFE nanoparticles. To control the temperature of the reaction for synthesis of the PTFE nanoparticles, the side-arm of the T-tubing was then located inside a beaker containing a solution of  $\sim 3.0$  M NaCl heated to around  $100^\circ\text{C}$ .

#### Procedure

For synthesis of TFE on solid substrates, the temperature of the furnace was set to  $950^\circ\text{C}$ . The flow rates of R22 and nitrogen for pyrolysis process in formation of TFE were set at  $300$  and  $5000\text{ ml min}^{-1}$ , respectively. This process leads to synthesize the TFE, which flows to the end parts of the production line and finally freeze inside the U-Trap, cooled with liquid nitrogen during  $\sim 1.5$  hour's time interval. Then, the two valves were closed and the U-Trap was disconnected from the production line.

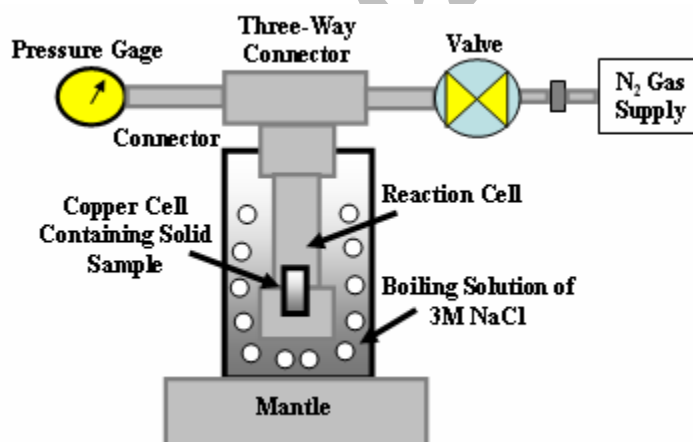


Fig. 2- Schematic of the polymerization instrument for synthesis of PTFE nanoparticles on different solid substrates.

Then, one of the valves first was connected to the one end of the traps, containing each type of solid support using silicon tubing. Afterward, in order to eliminate any memory effect related to the presence of nitrogen and air from the circulation line, the frozen TFE was let flow through the solid supports for about one minute time interval.

Finally, the other valve was connected to the other end part of the trap containing solid supports.

This was put away for 48 hours until adsorption process was completed, while the temperature of the U-Trap was controlled to around  $-10^\circ\text{C}$  via locating it inside a refrigerator.

For synthesis of the PTFE nanoparticles, several grams of each type of solid support was transferred into copper cell and positioned inside the side-arm of the system designed for polymerization process. About 2 ml of distilled water as initiator was also added into the

bottom of the side-arm of the designed system. The operating condition, applied to the system for polymerization process was the temperature of 100 °C and the pressure of 100 bars.

## Results and discussion

### Optimization of the operating parameters

For the adsorption of TFE as well as the formation of PTFE nanoparticles on the surface of different solid supports, several parameters such as the flow rates of R22 and nitrogen gas, the temperature of the furnace, the effect of liquid nitrogen on the purity of TFE, and also the optimum temperature and pressure were selected for the generation of PTFE nanoparticles.

In this work, FT-IR spectroscopy was used to measure the performance of each stage. This technique is appropriate to estimate the amount of TFE adsorbed on solid substrates. In the FT-IR spectra of TFE and PTFE, the  $\text{CF}_2$  stretching vibration occurs as the most intense IR absorption band, near  $1200\text{ cm}^{-1}$ . This band is a multiplet, and consists of three peaks at  $1240$ ,  $1215$ , and  $1150\text{ cm}^{-1}$ . Other major bands are located at  $641$ ,  $554$ , and  $515\text{ cm}^{-1}$  and are assigned to the C-F bending modes. The IR absorption band at  $2366\text{ cm}^{-1}$  is the overtone of  $\text{CF}_2$  stretching vibration. Also, the C-Cl stretch is a strong absorption at  $760\text{-}540\text{ cm}^{-1}$ .<sup>[20-23]</sup>

In this study, the R22 was used for the pyrolysis process in the production of TFE as monomer. R22 is a common reagent, used for industrial production of the TFE for synthesis of PTFE.<sup>[14]</sup> Usually, the pyrolysis process of R22 is performed directly at temperatures between  $750\text{-}950^\circ\text{C}$ , or at temperatures around  $650^\circ\text{C}$  using appropriate catalysts such as metal fluoride.<sup>[13, 24]</sup> Since the TFE is unstable, it can't be stored for long time. Hence, it should be polymerized as soon as possible. Therefore, for the formation of PTFE, an on-line system, it is needed to prepare the TFE.<sup>[25]</sup> The main limitation of the general polymerization technique is that, the produced PTFE are aggregated with each other to generate some bulky PTFE particles with large distribution in size.<sup>[26]</sup> This causes some difficulties in the synthesis of PTFE nanoparticles. To solve this problem, a novel method was proposed to control the size of PTFE nanoparticles via surface adsorption of TFE on solid supports. In this experiment, for simplicity, it was aimed to optimize the parameters related to the synthesis of the TFE monomers without using any catalysts.

To optimize the temperature of the pyrolysis process, the amount and the purity percentages of the TFE, synthesized individually at  $600$ ,  $700$ ,  $950$  and  $1000^\circ\text{C}$  at constant flow rates of  $400\text{ ml min}^{-1}$  for R22, and  $5000\text{ ml min}^{-1}$  for nitrogen gas were investigated using FT-IR spectroscopy.

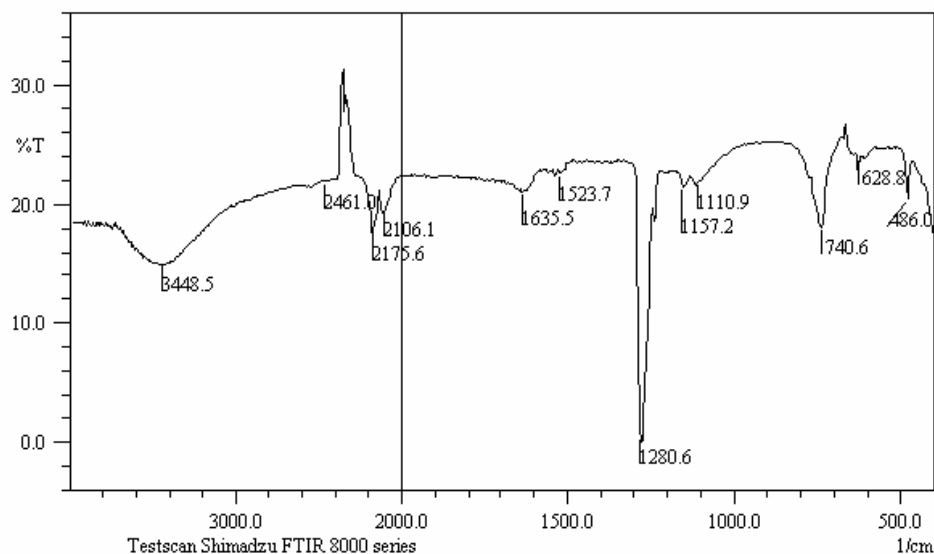


Fig. 3- The FT-IR spectrum of gaseous sample of TFE at the optimum conditions.

The FT-IR spectra of TEF exhibited maximum intensity for the  $\text{CF}_2$  stretching vibration at around  $1288 \text{ cm}^{-1}$  for the TFE, synthesized at temperatures between 900 to 1000 °C. Therefore, 950 °C was selected as optimum temperature in the generation of TFE monomer.

To optimize the flow rate of R22 in the pyrolysis process for synthesis of large amounts of highly purified TFE, several TFE samples were synthesized at 950 °C and at constant flow rate of nitrogen ( $5000 \text{ ml min}^{-1}$ ) and different flow rates of R22, ranging from 200 to 800  $\text{ml min}^{-1}$ . The synthesized TFE samples were also analyzed using FT-IR spectroscopy. Following the intensities of the absorption peaks related to the C-F and C-Cl bands at around 740 and  $1200 \text{ cm}^{-1}$ , respectively revealed that, the maximum suitable flow rate of R22 for the formation of TFE with maximum purity percentage was observed at a flow rate of  $300 \text{ ml min}^{-1}$  for R22. Therefore, this value was selected as optimum flow rate. Fig. 3 shows the FT-IR spectrum of the gaseous TFE sample as monomer, synthesized at 950 °C and at a R22 flow rate of  $300 \text{ ml min}^{-1}$ .

Since vapor of HCl vapor is considered as by-product in the synthesis process of TFE<sup>[27]</sup>, it is necessary to separate TFE from HCl vapors. To solve this problem, the synthesized TFE gaseous samples were bubbled into an aqueous basic solution. In this study, a solution of 5.0 M NaOH was selected. Therefore, the HCl vapors were easily separated from TFE. But this stage causes another difficulty. Bubbling of the TFE into aqueous solution causes the TFE to be moistened with water vapors. The presence of water vapors in the TFE causes some limitations in the adsorption behaviour of TFE on the solid supports. In this experiment, water vapors were easily separated from TFE, based on the significant difference between the freezing points of TFE ( $-142.5^\circ\text{C}$ ) and water.<sup>[14]</sup> In this experiment, liquid nitrogen was used to pre concentrate the TFE as well as to separate the TFE from water and nitrogen.

#### Characterization of the TFE and PTFE on different solid supports

In this experiment, the adsorptive behaviors of TFE on different solid substrates including: CNFs, alumina, silica, PVP, molecular sieves, and activated carbon were investigated using a lab-made TGA instrumentation system. To estimate the adsorption percentages, a trace flow of TFE ( $2.0 \text{ ml. min}^{-1}$ ) was passed through each solid support and

the changes of weight were recorded as shown in Fig. 4. In this study, maximum adsorption percentages were observed for CNFs and PVP, respectively.

The adsorption of TFE on solid substrates such as PVP and alumina were also evaluated using FT-IR spectroscopy as shown in Fig. 5. The results demonstrate that, solid supports such as CNFs, PVP, alumina, and silica are considered as appropriate supports for surface adsorption of TFE.

To evaluate the adsorption of the TFE on each solid support, the TGA of TFE adsorbed on different solid substrates were performed in an inert atmosphere of nitrogen with a temperature ramp of 5.0 °C/min. The TGA of TFE adsorbed on solid substrates was compared with each other as shown in Fig. 6. According to the thermo grams of the TFE deposited on solid substrates, a decrease in weight was observed at around 150°C. This is due to desorption of TFE from solid supports. As shown in Fig. 6, dissimilar behaviour was observed for different solid supports, depending on the morphology of substrate. Also, the last part of each trace (the plate obtained at low weight percentages) shows the quantity of TFE and reveals the capacity of each solid substrate for adsorption of TFE. This behaviour is also considered as another proof for maximum capacity of CNFs for the adsorption of TFE.

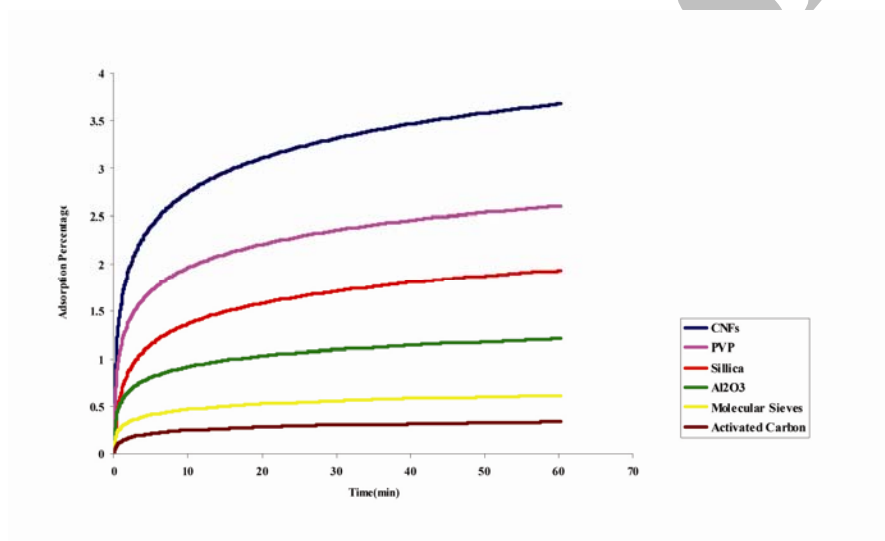


Fig. 4- The adsorptive behavior of TFE on different solid substrates using TGA instrumentation system.

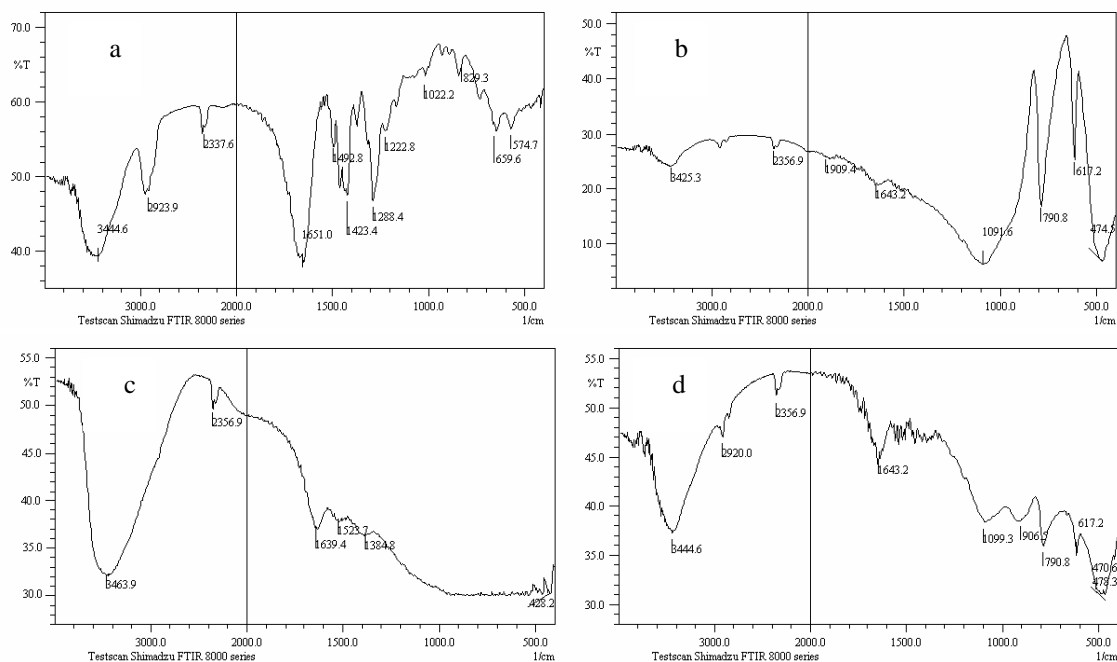


Fig. 5- The FT-IR spectra of solid supports on 100 folds of KBr for a: pure PVP, b: PVP deposited with TFE, c: alumina, and d: alumina adsorption with TFE

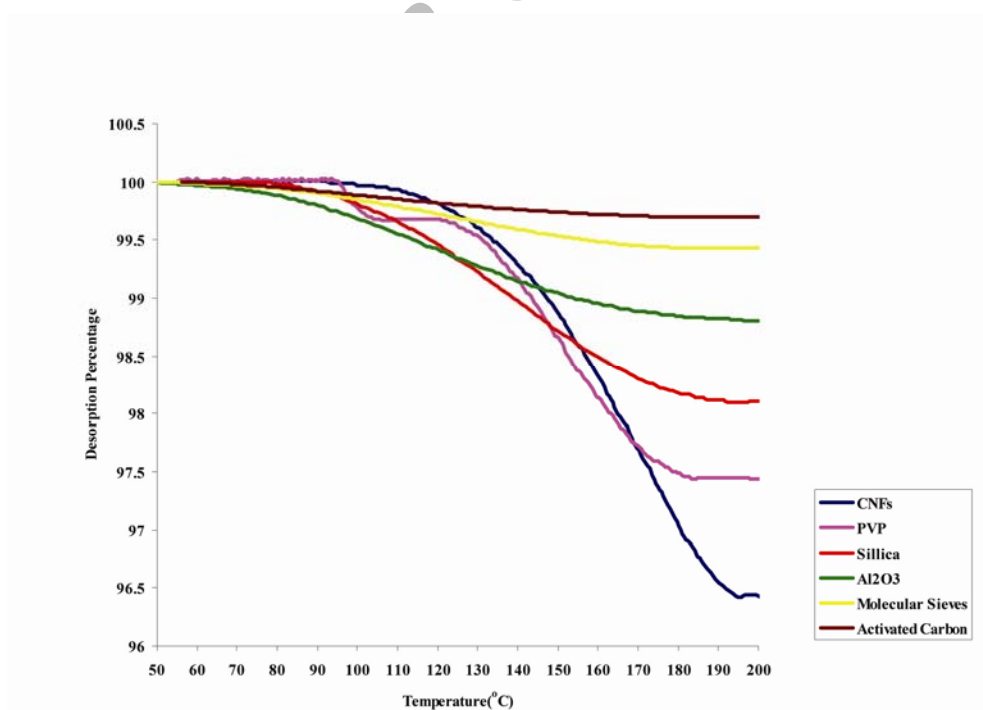


Fig. 6- Thermo gravimetric analysis of deposited TFE on different solid supports.

For polymerization process, the TFE deposited on each solid support was polymerized. In the polymerization process, the reported conditions for the synthesis of PTFE



are temperature of  $\sim 100$  °C and the pressure of  $\sim 100$  bars.<sup>[26]</sup> In this study, the same conditions were selected for the synthesis of PTFE nanoparticles.

In formation of PTFE nanoparticles, water vapors acted as initiator.<sup>[25]</sup> It seems that, the amounts of adsorbed TFE on each solid supports have strong influence on the termination reaction of PTFE nanoparticles.

The diameter of the PTFE nanoparticles depends on the size and the morphology of the solid substrate on which the TFE is deposited. Solid substrates such as CNFs, silica, alumina, molecular sieves, and activated carbon have different aspect ratio (surface-to-volume ratio). In this experiment, maximum adsorption of TFE was evaluated for CNFs. The smallest PTFE nanoparticles were also observed for CNFs according to the SEM (Fig. 7) and AFM images (Fig. 8) on highly orientated pyrolytic graphite. The histogram shown in Fig. 9, presents the frequency distribution of different sizes of synthesized PTFE nanoparticles on CNFs based on the AFM image.

The XRD patterns of PTFE on different solid substrates are also shown in Fig. 10. According to the XRD patterns, the strong peaks at  $2\theta=30^\circ$  correspond to the PTFE nanoparticles. The PTFE nanoparticles size was also determined from X-ray line broadening using "Debye-Scherrer" formula as:  $D=0.9 \lambda/\beta \cos\theta$ , where D is the average crystalline size,  $\lambda$  the X-ray wavelength used,  $\beta$  the angular line width at half maximum intensity, and  $\theta$  the Bragg's angle. According to the peak of PTFE nanoparticles correspond to the  $2\theta=30^\circ$  for  $\lambda=1.5473$  Å, the average sizes of PTFE nanoparticles on different solid substrates are estimated to around 90 nm for CNFs, 130 nm for PVP, 150 nm for alumina and around 200 nm for silica, which are in good agreement with the results obtained by AFM analyses.<sup>[28]</sup>

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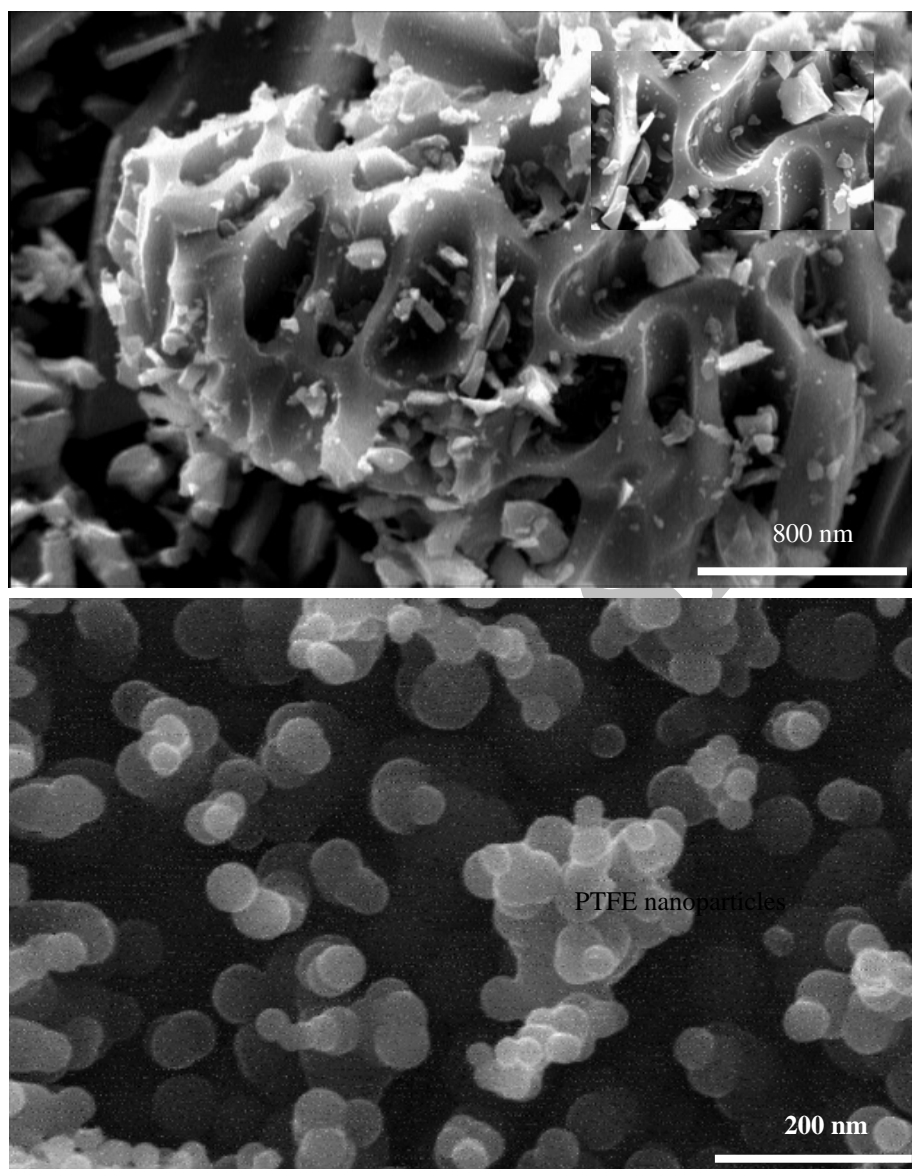


Fig. 7- SEM images of PTFE on CNFs.

The TGA showed that, the quantities of PTFE nanoparticles on each solid substrate under similar experimental conditions, were as  $3.53 \pm 0.09\%$  for CNFs,  $2.31 \pm 0.1\%$  for PVP,  $2.11 \pm 0.12\%$  for silica, and  $0.97 \pm 0.16\%$  for alumina. This reveals that, different solid substrates have various capacities for the deposition of TFE in formation of PTFE nanoparticles, depending on their size, shape and their morphology.

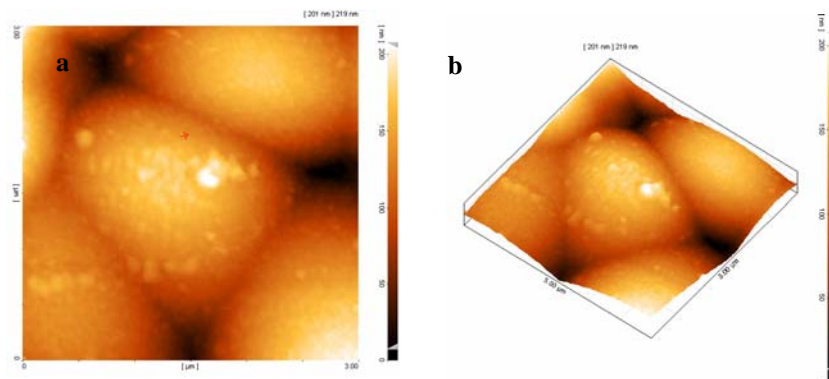


Fig. 8- The AFM images a: 2-D, and b: 3-D of PTFE on CNFs.

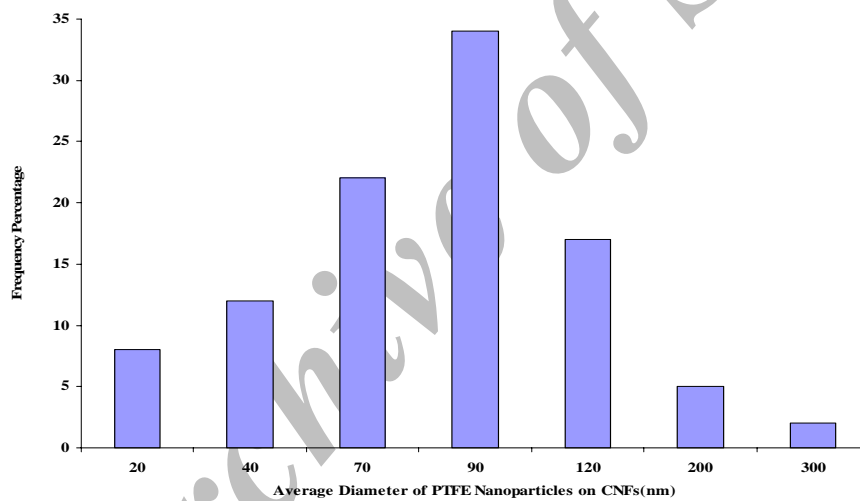


Fig. 9- The histogram showing the distribution of the PTFE nanoparticles on CNFs.

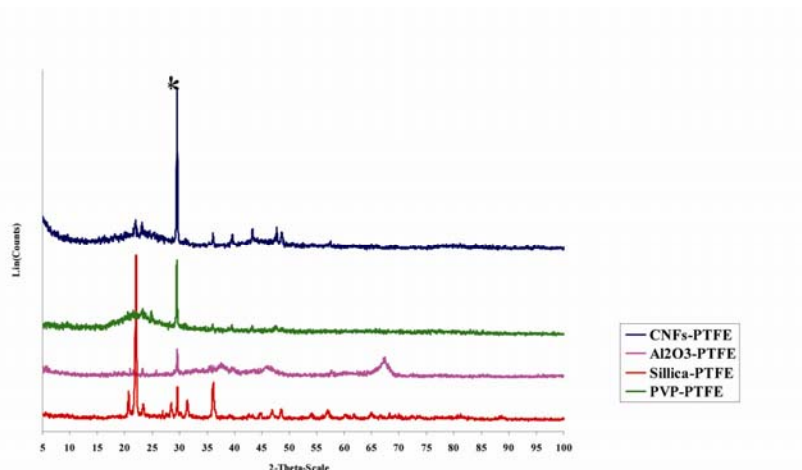


Fig. 10- The XRD patterns of the PTFE nanoparticles on different solid supports.

Also, as carbon nanomaterials have high specific surface area, they can act as suitable substrates for the deposition of large amounts of TFE. Comparing the amounts of PTFE nanoparticles on CNF substrate with other solid supports reveals higher percentage of PTFE nanoparticles, produced on CNFs. This is believed to be due to the high aspect ratio as well as the narrow size distribution of CNFs, which provide higher aspect ratio for the formation of PTFE nanoparticles. The high external surface area and the tubular structure of CNFs as support, allow rapid deposition of TFE to the active sites<sup>[28]</sup>. Also, high specific surface area of carbon nanomaterials prevents the mass transfer limitations in surface adsorption of TFE.<sup>[29]</sup>

## Conclusion

Different solid materials have various capacities for the formation of PTFE nanoparticles, depending on their size, shape, and their morphology. In fact, the amounts and the sizes of synthesized PTFE nanoparticles are strongly dependent on the nature of the solid substrate. The unique properties of CNFs as solid substrate act as a suitable support for the deposition of TFE. Consequently aspect ratio of solid substrates is very important in the deposition of TFE in the formation of PTFE nanoparticles.

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