

# The Continuous Depolymerization of Filled Polytetrafluoroethylene with a Continuous Process

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**ABSTRACT:** A new method for beneficiating unfilled as well as filled polytetrafluoroethylene (PTFE) waste has been developed. This process does not use any carrier gas while forming the depolymerization products. It enables polymer manufacturers and end-users to reuse and adds value to filled fluorocarbon polymer waste. The filler material was qualified by means of scanning electron microscopy and thermogravimetric analysis and the success of the depolymerization process inside a rotating kiln was proved by visual observation. The PTFE was depolymerized inside a kiln-type reactor declined at a 5° angle, with a central rotating paddle screw to scrape the inner wall of the reactor, which was able to operate within the tempera-

ture range of 600–800°C and pressure range of 10–90 kPa. Different ratios of the useful products tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and octafluorocyclobutane (OFCB) were produced. The optimum conditions for TFE production are 600°C and 10–30 kPa, for HFP production it was 800°C and 10 kPa, and for OFCB production 600°C and 90 kPa. Temperatures of 700°C should be avoided as this leads to considerable amounts of undesirable HFE and OFP as well as the very toxic PFIB. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 264–271, 2008

**Key words:** PTFE; depolymerization; pyrolysis; filler; continuous

## INTRODUCTION

It is a well-known fact that polytetrafluoroethylene (PTFE) has a relatively high-melting point, is chemically inert, has a high surface tension, is not biodegradable, and is generally very stable. Therefore, special uses for PTFE are possible, for example, chemical and thermal resistant coatings on cookware, high resistance chemical containers, gaskets, and thermally stable parts with unique mechanical properties in industrial machinery, etc. The mechanical properties of PTFE can further be enhanced by adding fine particulate powder (filler) to the virgin polymer, for example glass, bronze, carbon, stainless steel, etc. The amount of filler can be up to 60% by mass of the PTFE. The particle size of the filler materials can be in the range of 1–150 µm.<sup>1</sup>

The inert properties of PTFE can unfortunately also be a disadvantage from a waste point of view. PTFE waste can be in the form of shavings, turnings, off-cuts, chunks, etc., and can sometimes amount to as much as 50% of the initial material. It is not possible to reuse PTFE waste by melt-processing as is the case with other polymers, for example polyethylene. Unfilled PTFE waste can be ground into a fine powder form and can be reused as a filler material in,

for example, paint and cement. Grinding is not an option for filled PTFE and currently all filled PTFE is regarded as an unwanted waste. This forces PTFE processors and manufacturers to dispose of these types of PTFE waste in landfill sites. This is an expensive option, due to the cost associated with landfilling, the loss of the highly valuable fluorine values that are contained in the waste, and the long-term negative environmental effects due to the non-biodegradability property of the waste PTFE.

The processes for depolymerizing PTFE via pyrolysis and especially under subatmospheric pressure are extensively described in the literature.<sup>2–4</sup> One of the reasons for depolymerizing PTFE is to recover the F-values in the form of tetrafluoroethylene (TFE), hexafluoropropylene (HFP), and octafluorocyclobutane (OFCB), which can be used for producing new perfluorinated products. Depolymerization of PTFE is done at temperatures between 600 and 900°C and at or below atmospheric pressures (between 10 and 90 kPa) in an inert atmosphere. Special precautions have to be taken when working at subatmospheric pressures, because TFE and oxygen (that may accidentally leak in) can under certain conditions form an explosive mixture.<sup>5</sup> When PTFE is depolymerized, perfluoroisobutylene (PFIB), which is extremely toxic at very low concentrations, is also formed under certain conditions.<sup>6</sup> It is therefore desirable to avoid such conditions and to take the necessary safety precautions. Various ways of heating can be used, for example, resistance heating (where the de-

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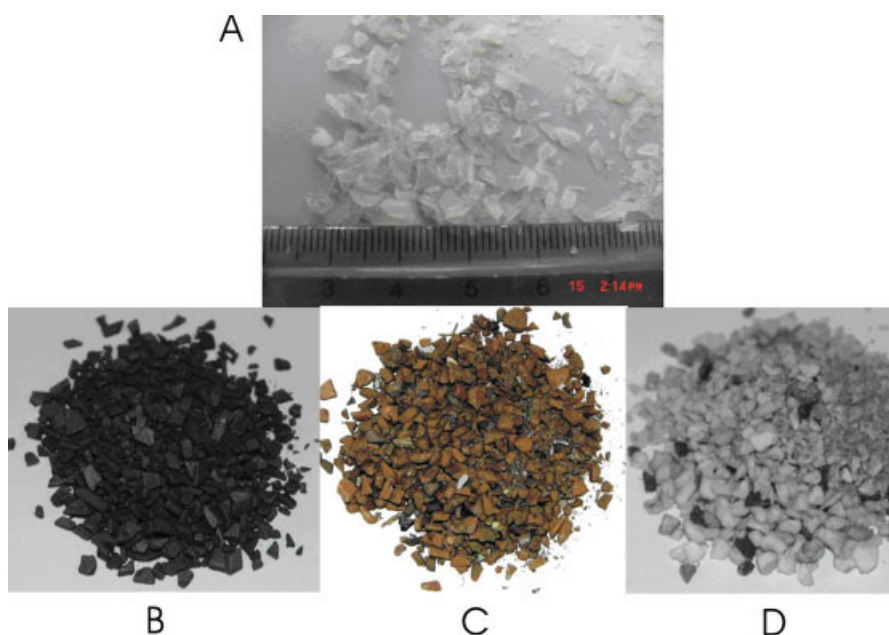
polymerization reactor is externally heated by means of an electrical heater), steam heating<sup>7-9</sup> (where the depolymerization reactor is additionally heated by the introduction of steam into the reactor), heating with super-heated gas (where earth gas or oil burners are used to heat the depolymerization reactor), or induction heating (where the heating of the reactor is accomplished by induction from the coil of an induction generator that is situated around the reactor).<sup>10</sup> The use of steam has the additional advantage that it reduces the partial pressure of decomposed PTFE with a resulting increase in the TFE yield, at ambient pressure. The disadvantage of using steam is the amount of waste generated during this process. Small amounts of HF dissolved in the steam make the steam not useable for a second time. These small amounts of HF are most probably formed by the reaction between some of the highly reactive fluorine radicals and steam. Therefore it has to be scrubbed, thereby increasing the operating cost. The HF also forces the material of construction to be of a high specification, which is more expensive, increasing the capital cost of such a system.

The literature regarding the depolymerization of PTFE revealed that most of these experiments were performed on a laboratory and batch scale,<sup>10-13</sup> and not in a continuous mode on bench, pilot, or commercial scale by means of a complete, continuous, and comprehensive "vacuum fluoropolymer waste conversion system." This is especially true for filled PTFE, where the filler material and non-depolymerized fraction have to be removed on a continuous basis.

Meissner et al.<sup>14</sup> reported results on the production of TFE, HFP, and C<sub>4</sub>F<sub>8</sub> isomers (including OFCB) that formed during the pyrolysis of unfilled PTFE in a semi-batch laboratory-scale process. This research was done in a reactor with a PTFE feed rate of 250–1000 g h<sup>-1</sup> and nitrogen as a carrier gas that also served to reduce the partial pressure of the product gases. The products were frozen in sample holders and analyzed by means of a gas chromatograph. Van der Walt<sup>10,15,16</sup> described a process that was able to convert clean, unfilled PTFE into high purity TFE in a continuous process. This system was not able to depolymerize filled PTFE because the filler accumulated inside the reactor, which eventually blocked. The depolymerization of filled PTFE with a continuous process, requires a different reactor design, whereby the reactor is able to separate the product gases and the filler material and dispose of the filler on a continuous basis, while the PTFE is depolymerized.

#### WASTE PTFE CHARACTERIZATION

When filled PTFE is to be depolymerized on a continuous basis, several additional aspects need to be considered compared to a system. For example, the thermal and physical properties of the filler material at the desired depolymerization temperature have to be known in order to avoid product gas contamination because of possible volatilization of the filler material. Further, good flow properties of the filler material after depolymerization through the reactor



**Figure 1** Typical granules from suppliers with measurement units in cm. Picture A is of unfilled PTFE, B is of graphite-filled PTFE, C is of bronze-filled PTFE, and D is of glass fiber-filled PTFE. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

and at the solid discharge of the system must be ensured. It was experimentally determined that the depolymerization of certain polymers causes the reactor to block.

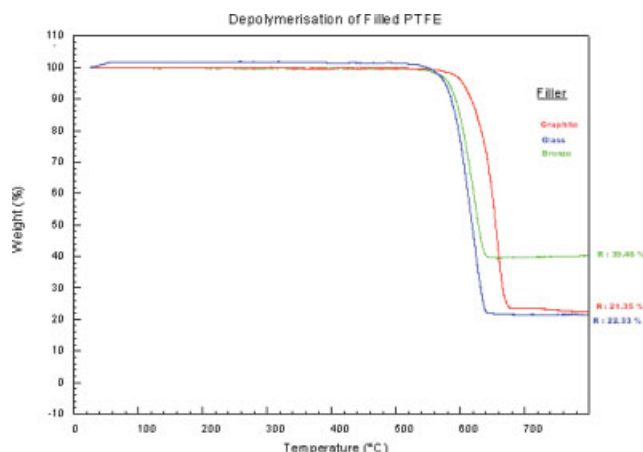
In this study, four types of free-flowing granulated PTFE were investigated, namely graphite, glass fiber, bronze-filled, and unfilled PTFE (Fig. 1). Pure filler material was also obtained from the suppliers for evaluation purposes. The filled PTFE samples as well as the filler material were analyzed using different analytical methods.

### Thermogravimetric analysis

Thermogravimetric (TG) analysis was used to determine the amount of filler in the feed material as well as the thermal stability of the filler at the depolymerization temperatures that were used in this study. A Perkin Elmer PGS2 TG analyzer was used and 4.5–5 mg PTFE samples were analyzed. The sample was heated at a heating rate of 10°C/min and with a nitrogen flow of 30 mL/min.

Results obtained from the TG analysis are presented in Figure 2. Filled PTFE samples were analyzed and found to have different amounts of filler material encapsulated in the PTFE. In the samples that were investigated, it was found that the bronze-filled PTFE contained almost 40% bronze filler, the glass fiber-filled PTFE 22% glass fibers and the graphite-filled PTFE, 21% graphite.

As can be seen from Figure 2, the graphite filled PTFE depolymerized at a higher temperature than for the bronze and glass fiber-filled PTFE. A possible explanation for this higher depolymerization temperature of the graphite filled PTFE is dependant on the different thermal properties of the filler material.



**Figure 2** Thermo gravimetric curve of filled PTFE. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### SEM/EDS analysis

The unused filler (filler not yet incorporated into PTFE) was examined with a Scanning Electron Microscope (SEM) and the chemical composition thereof was confirmed by an energy dispersive X-ray spectrometer (EDS) detector. The graphite filler consisted mainly of carbon with only traces of sulphur. The glass fiber filler mainly consisted of silicon and the bronze filler was confirmed to be a tin–copper alloy. It can therefore be concluded that these fillers contained no compounds that be volatilized during depolymerization and consequently cause contamination of the product gas.

According to the SEM analysis, the particle size distribution of all the fillers was between 10 and 100  $\mu\text{m}$ . However, the glass-fibers were needle-like fibers of 50–100  $\mu\text{m}$  long and 10  $\mu\text{m}$  in diameter. SEM micrographs of the different filler materials are presented in Figure 3(a–d). Figure 3(a) presents the micrograph of the filler material before it was introduced into the PTFE matrix. Figure 3(b) presents a micrograph of glass fiber filler material after the depolymerization process. Some finely-divided PTFE matter can still be seen on the filler material. The bronze and graphite filler particles [Fig. 3(c,d)] were finely-divided particles of irregular shape. It was found that the filler materials that were tested were free-flowing and therefore should not present a problem in a typical declined reactor where the filler has to be removed from the reactor on a continuous basis.

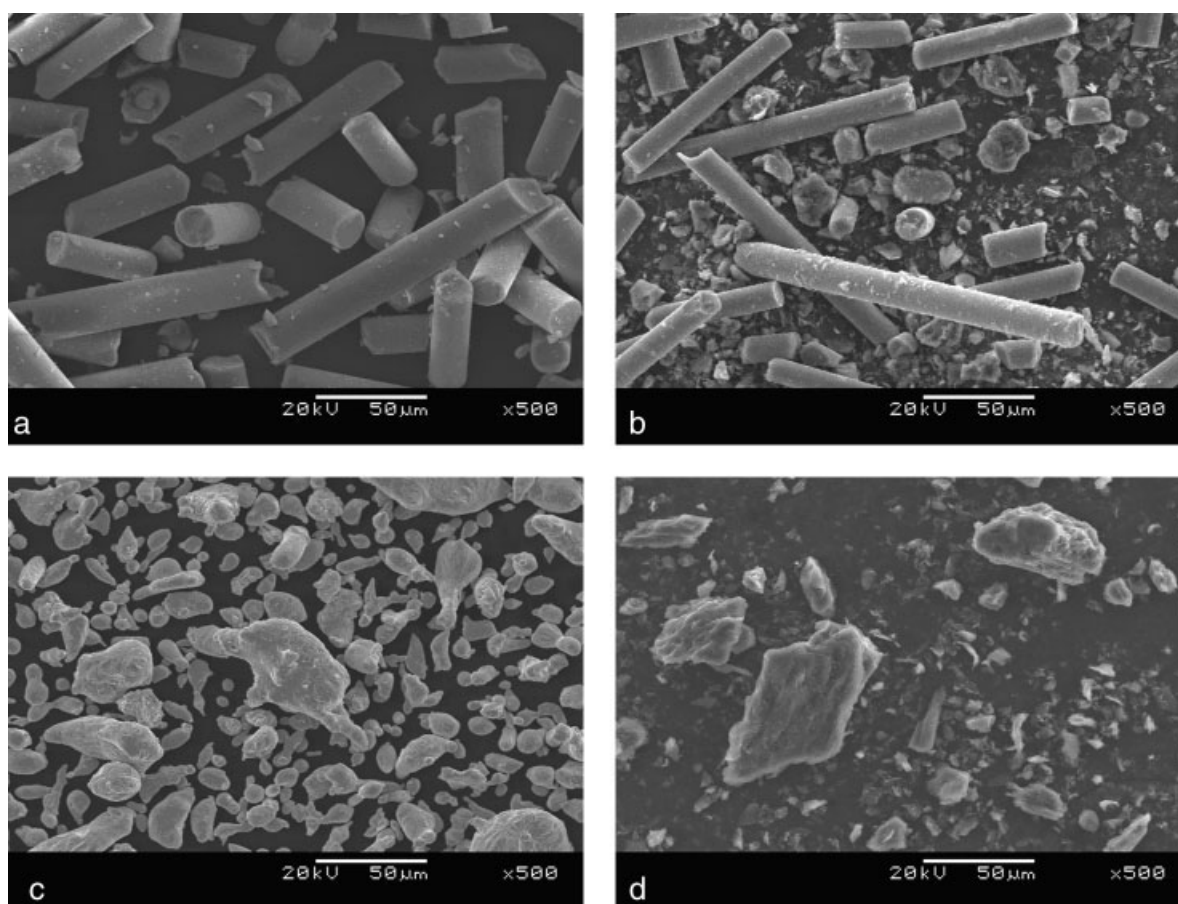
### Visual inspection of the depolymerization process

The flow properties of filled PTFE under hot conditions were investigated by visually observing the depolymerization process. If the PTFE should stick to the walls during depolymerization, it would be difficult to use a tubular reactor because bad heat transfer of the PTFE will cause incomplete depolymerization and eventually lead to blocking. For this experiment, a 50 mm diameter, 100 mm long, open-ended stainless steel tube-reactor was used to observe the flow of PTFE at the depolymerization temperature. This very basic, reactor was situated inside a muffle oven where the depolymerization process of filled PTFE took place. A thermocouple was inserted into the tube reactor and positioned against the inner wall in an attempt to measure the wall temperature directly.

This system was operated inside a well-ventilated fume cupboard because of the toxicity of some of the gaseous depolymerization products.

The muffle oven and tube-reactor temperature was increased from ambient to a temperature of 600°C over a 2-h period. During this heating cycle a 5 g





**Figure 3** (a) SEM micrographs of glass-fiber filler. (b) SEM micrographs of the glass fiber filler residue after depolymerization. (c) SEM micrographs of bronze filler. (d) SEM micrographs of graphite filler.

glass fiber-filled PTFE sample was introduced at 400°C into the front end of the reactor. While turning the reactor, the glass fiber-filled PTFE was completely depolymerized and the residue (filler) was discharged from the lower end. The experiment continued until no PTFE was left inside the reactor.

It was observed that the PTFE did not stick to the sides of the reactor during the depolymerization process. While the tube reactor was repeatedly rotated through 45°, the photo presented in Figure 4, was taken during the depolymerization process.

It was observed that at 400°C the glass fiber filled-PTFE exhibited a sweaty texture and slid back when the kiln was rotated through 45°. At 450°C, the PTFE had a fluffy texture but it was still solid and slid back when the kiln was rotated through 45°. At 500°C the PTFE formed a high viscosity cake, but did not stick to the kiln wall. It still slid back when the tube was rotated through 45°. At 520°C, the PTFE became opaque to transparent in appearance, but still slid back when the kiln was rotated through 45°. At 550°C, the volume of the PTFE seemed to increase. In appearance it was now totally transparent and started to form a thick and viscous liquid. At 580°C the PTFE started to “boil” (sublimate) and

white gas fumes appeared. This thick viscous mass rolled back when the tube was rotated through 45°, without sticking to the walls. The volume reduced rapidly at 590°C as the material was vaporized. Only the undepolymerized filler residue remained.

This experiment proved that filled PTFE could be depolymerized on a continuous basis inside an inclined reactor, that hot PTFE inside the reactor did not stick to the sides of the reactor but slid back to the bottom of the kiln during rotation, and that the PTFE as well as the undepolymerized filler moved easily through the reactor.

It can therefore be concluded that filled PTFE can be depolymerized on a continuous basis in a declined reactor such as a rotary kiln. No problems are expected regarding the sticking of hot PTFE to the reactor walls, and the filler material also free-flows through the lower, back end of the reactor where it can be discharged.

#### THE DEPOLYMERIZATION OF PTFE IN A PADDLE REACTOR

It is a well-known fact that solid low molecular mass PTFE compounds tend to deposit on the colder parts



**Figure 4** Kiln rotated manually through 45° at 400°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

of a PTFE depolymerization system. This is observed especially when PTFE needs to be depolymerized on a continuous and a long term basis. The build-up of these deposits leads to impaired heat transfer and eventually to blockages. To address this problem, a tubular, kiln type reactor, with rotating paddles that continuously scraped the wall of the reactor in order to remove any deposits, was developed.<sup>17</sup>

This system is schematically presented in Figure 5. The reactor and paddle screw was made of Inconel and had an inside diameter of 150 mm and length of 1 m. The tube had an inlet on the top of the feed-side and two outlets at the top and bottom of the product-side. A screw feeder supplied PTFE continuously from a hopper to the inlet of the reactor. A quench probe was mounted onto the top outlet of the reactor. The purpose of the quench probe is to “freeze” the depolymerization products at certain conditions in order to obtain TFE, HFP, and OFCB as a stable product gas mixture and therefore to prevent the formation of unwanted saturated CF-products. However, the filler residue was accumulated through the bottom outlet of the reactor. The filler collector system consisted of a double-valve airlock to allow for the continuous removal of the solids into a solids residue hopper.

Two externally mounted heaters supplied a maximum of 6 kW of power to the system. Temperature controllers were used to regulate the energy input in order to sustain the preset temperature. The centrally mounted paddle screw consisted of two parts namely a short screw below the feeder inlet, while equally spaced paddles, at right angles to one another, occupied the rest of the axis. The purpose of the screw was to enhance the flow of the PTFE through the reactor. The paddles scraped the sides of the reactor with a small clearance. The scraping

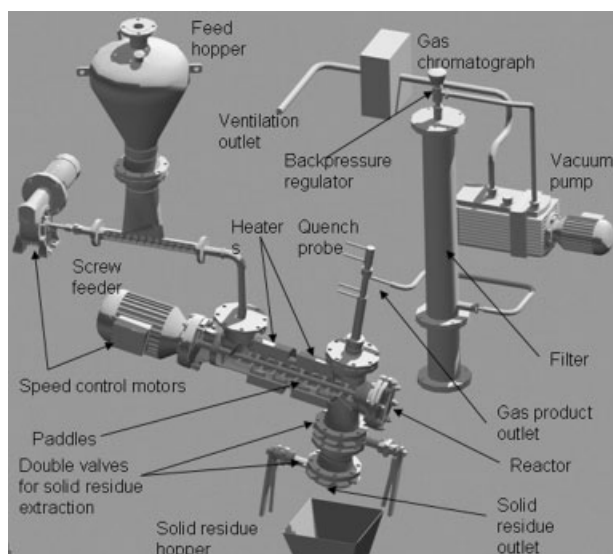
action of the paddles against the sides prevented the filler residue from sticking to the sides and blocking the reactor, and also increased the heat transfer between the PTFE and the hot wall. The reactor was mounted onto a stand of which the angle could be easily adjusted. The temperature of the reactor outer wall was measured by means of a type K thermocouple.

The temperature, pressure, paddle rotation speed, and reactor angle could be varied depending on the product composition needed. The temperature was varied between 600 and 800°C and the pressure from 10 to 90 kPa (ambient pressure).

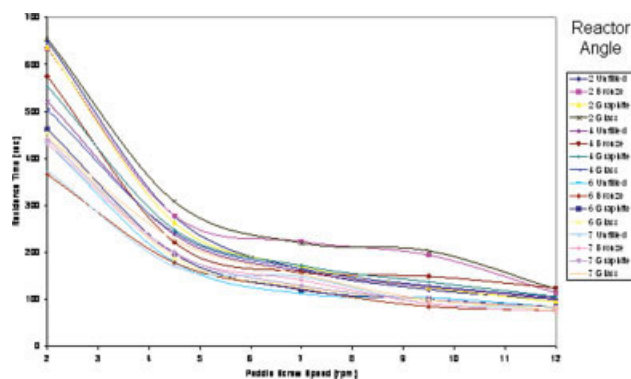
After the gas passed through the quench probe, any fine particular matter, that might still be carried within the gas stream was filtered out before the gas was analyzed by a gas chromatograph. A dry vacuum pump was used inline not to contaminate the product stream.

### Reactor residence time optimization

To measure the residence time of the solid particles, a series of tests needed to be done. During these tests the reactor angle and paddle rotation speed was varied for the different filled PTFE samples. At each setting a fixed mass of filled PTFE was introduced into the reactor while the paddle was rotating. The time measurement was started at that moment up until all the PTFE was fed through the reactor and the mass was recorded at 5 s intervals. After data collection the first derivative of the mass readings were calculated and the peak value (graph of time vs. dm) used as the effective residence time.



**Figure 5** Three dimensional presentation of paddle-reactor system.



**Figure 6** Residence time of different filled PTFE samples at different reactor angles as a function of paddle rotation speed. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

When the mean residence time is plotted against the paddle rotation speed for the different angles, (2, 4, 6, and 7 degrees declined as presented in Fig. 6), it was determined that the residence time of PTFE inside the reactor increases as the angle decreases and the rotation speed of the paddle screw decreases as can be expected. The mean residence time of the PTFE varied between 74 s for bronze-filled PTFE at a reactor angle of 7° and paddle screw speed of 12 rpm, to 655 s for glass fiber-filled PTFE at a reactor angle of 2° and a paddle screw speed of 2 rpm. The residence time change because of a change in reactor angle and is not as significant as with a change in paddle rotation speed. It was subsequently decided to work with a reactor angle of 5°. Figure 6 presents the dependence of the residence time on the filler material as a function of different reactor angles and different paddle rotation speeds.

Generally, the trends of the different samples at the different parameter settings were the same. From Figure 6, it can be seen that the mean residence time was less sensitive at paddle rotation speeds of >5 rpm. At a low speed (2 rpm) though, the residence time increased significantly, in most cases almost doubling the time the samples spend in the reactor.

Another parameter that was investigated was the reactor angle. The effect of the reactor angle on the residence time was greater at slow paddle rotation speeds than at high rotation speeds. The general

trend was an increase in the residence time with decreasing reactor angle. This was the case for all four the samples.

The sharp increase in the residence time for all the reactor angles, when the paddle rotation speed was decreased from 4 to 2 rpm, can be attributed to the increasing effect of friction at slow paddle rotation speeds. At the higher rotation speeds where the friction component is not as severe, the residence times can be up to 100% less.

To choose a paddle rotation speed and a reactor angle where experiments can be performed, the sensitivity of the system to change had to be evaluated. For example at paddle rotation speeds of higher than 6 rpm, there was little change in residence time when the reactor angle is varied. However, at a paddle rotation speed of 2 rpm, the residence times varied considerably when the reactor angle was changed. At a paddle rotation speed of ~ 4.5 rpm, there was a significant change in residence time when the reactor angle was varied, but the change was manageable. Therefore, this is the preferred operation speed used during experimentation.

#### Depolymerization efficiency of the paddle-reactor

Table I is a presentation of the amount of filler residue (by mass) that was generated when 5 kg of different filled and unfilled PTFE samples were depolymerized in the paddle oven over a 10 h run. The PTFE was fed at 0.5 kg h<sup>-1</sup> at a 5° angle and a rotation speed of 4.5 rpm. The temperature of the reactor was 600°C and the pressure 90 kPa. The filler was collected on a continuous basis in the filler collector.

The depolymerization efficiency was determined by using the following equation:

$$\text{Depolymerization Efficiency}(\%) = \left( \frac{z - y}{z - x} \right) \times 100\% \quad (1)$$

From Table I, it can be seen that the depolymerization efficiency of the paddle reactor at the set conditions was generally >85 %. Longer residence times would improve the efficiency, but the additional cost to accomplish this might not be worth the effort.

**TABLE I**  
The Amount of Residue (by Mass) of the Undepolymerized Material Collected at the Solid Discharged of the Paddle Screw Reactor

Material	Mass PTFE fed (z) (kg)	Filler in PTFE (x) (kg)	Residue collected (y) (kg)	Depolymerization efficiency (%)
PTFE (unfilled)	5.0	0	<0.05	>99
PTFE (bronze-filled)	5.0	1.97	2.35	87
PTFE (graphite-filled)	5.0	1.19	1.52	91
PTFE (glass fiber-filled)	5.0	1.19	1.63	88



**TABLE II**  
**The GC Analyses of the Product Gas After Depolymerization of Graphite-Filled PTFE in the Paddle Reactor (vol %)**

Pressure (kPa (abs))	Temp (°C)	TFM (%)	HFE (%)	TFE (%)	OPF (%)	HFP (%)	OFCB (%)	PFIB (%)
10	600	2.47	10.63	28.43	0.00	49.06	9.42	ND
30	600	5.64	17.04	30.79	9.42	30.22	6.89	ND
60	600	2.24	9.41	27.67	7.79	34.18	14.65	4.07
90	600	0.15	1.74	14.91	1.59	28.82	47.20	5.59
10	700	6.22	16.48	2.92	20.20	26.31	6.79	21.09
30	700	3.36	14.96	12.17	21.96	28.32	3.76	15.47
60	700	4.97	19.71	1.33	22.70	20.71	4.48	26.09
90	700	4.25	25.61	2.82	10.77	39.65	3.08	13.82
10	800	4.00	23.53	3.49	12.99	47.91	ND	8.07
30	800	7.26	32.28	1.17	11.76	40.60	ND	6.93
60	800	9.39	36.16	0.94	9.16	36.20	1.84	6.30
90	800	17.40	48.18	0.44	7.36	18.65	1.47	6.50

ND, not detected.

It was found that this type of reactor system was able to depolymerize filled as well as unfilled fluoropolymers without any blockages. No operational difficulties were experienced after 10 h of operation. The same experimental conditions were used for all the depolymerization experiments. Longer residence times might be needed for the filled PTFE to be depolymerized more efficiently.

After the exploratory experiments were concluded, the system was set up in such a manner as to optimize the depolymerization of graphite-filled PTFE. The reactor was tilted at a 4° angle and the paddle screw was set at 7 rpm, corresponding to a solids residence time of ~ 2 min. The calculated gas residence time is ~ 60 s for a mass flow rate of 1 kg h<sup>-1</sup> filled PTFE. The reactor was operated at 600, 700, and 800 °C while the pressure was set at 10, 30, 60, and 90 kPa. Table II presents the results of the product analyses (GC) after graphite-filled PTFE was depolymerized in the Paddle reactor.

It is clear that the product distribution is quite different from that produced by Van der Walt<sup>10,16</sup> with respect to the formation of high yields of HFE, OPF, HFP, and TFM at most temperatures and pressures, and small concentrations of TFE. A possible reason for this could be an increased residence time of the intermediate products inside the paddle reactor with respect to the reactor used in previous work.<sup>10,16</sup> The formation of each product will be discussed separately below.

#### The formation of TFM

TFM is formed in significant amounts (up to 17.4%) at 800°C and 90 kPa. At 600 and 700°C, the formation of this product with pressure increased although the yield at 700°C was twice as high as at 600°C. At 800°C, the yield increased as the pressure increased. This molecule can only form if a CF<sub>3</sub>• radical collides with a fluorine donor. At 600, 700, and

800°C, the CF<sub>4</sub> formation competes with the HFE and OPF formation. Because of stoichiometric reasons carbon deposits are formed.

#### The formation of HFE

The HFE formation at 600°C decreased as the pressure increased. This might be due to an increase in the amount of PFIB that formed. At 700–800°C, the HFE yield increased as the pressure increased and the yield peaks at almost 50% at 800°C and 90 kPa.

#### The formation of TFE

At 600°C, the TFE yield dropped as the pressure increased. The same trend was observed at 700 and 800°C, but surprisingly much smaller amounts of TFE was found (<5%). The highest TFE yield (30.79%) was found at low pressure (10 kPa) and low temperature (600°C).

#### The formation of OPF

A maximum OPF concentration (22.7 %) was found at 700°C and 50 kPa. At higher and lower temperatures the yield was dropped.

#### The formation of HFP

Three maxima were observed. The first (49%) at 600°C and 10 kPa, the second (~ 38 %) at 700°C and 90 kPa, and the third (~ 48 %) at 800°C and 10 kPa. A large low-concentration dip was observed at 700°C and 50 kPa. This is in the same region as the OPF maximum.

#### The formation of OFCB

The OFCB concentration increased as the pressure was increased at 600°C. A sharp rise in concentration was observed and a maximum yield of 47.2% was

obtained at 600°C and 90 kPa. At 700 and 800°C the concentration dropped significantly to below 10%.

The formation of PFIB

The PFIB yield produced by the Paddle reactor was significantly higher (26.09% max) than that was previously reported (1.7%). At 700°C and 60 kPa the highest yield was observed. This is in the same region as the OFP maximum and the HFP minimum. For safety reasons this temperature region must be avoided.

PFIB is not one of the wanted products and along with the toxicity hazard; it is one of the by-products that must be avoided as far as possible.

## CONCLUSION

Different aspects of the depolymerization process were tested in order to build a system able to convert filled PTFE on a continuous basis into useful products. Graphite-, glass fiber-, and bronze-filled PTFE samples and the corresponding filler materials were evaluated. SEM investigations of the unreacted filler materials as well as after the depolymerization process were conducted. The composition of the filler material was confirmed to make sure that no product contamination can take place during depolymerization. The filled PTFE samples were also analyzed in a TGA and the stability of the fillers were tested at the depolymerization temperatures. It was found that these filler materials did not decompose during the depolymerization reaction and will therefore negatively influence the depolymerization process.

The depolymerization process was visually observed in a laboratory size rotating kiln that was tilted at an angle of only a few degrees. It was found that the PTFE depolymerized completely and did not stick to the wall of the reactor during rotation. The un-depolymerized filler material was discharged without problems at the lower end of the kiln. These observations were used as the basis for the design of a reactor that can depolymerize filled as well as unfilled PTFE under subatmospheric pressures and with no carrier gas. Such a system was subsequently developed. This system consisted of a paddle-reactor with a screw feeder to feed the filled PTFE into the reactor that was inclined at an angle 5°. This reactor was stationary and was fitted with a centrally-mounted paddle-screw, which enhanced the movement of the feed material through the reactor. The paddles also exert a scraping action onto the inner wall of the reactor to prevent any possible residue from blocking the reactor. The outlet of the reactor was designed to separate the solid residue (inert filler material) from the depolymerized gas. When the

gas exits the reactor it is quenched and analyzed. The solid residue is extracted *in situ* with the double valve system into a residue-disposal hopper.

The residence time of the different filled PTFE samples were measured as a function of paddle rotation speed and reactor angle at room temperature. At a paddle rotation speed of ~ 4.5 rpm, there was a significant change in residence time when the reactor angle was varied, but the change was manageable. Therefore, this is the preferred operation speed used during experimentation. It was found that this system could depolymerize filled and unfilled PTFE without any problems on a continuous basis for more than 12 h.

Experiments were also conducted at different temperatures (600–800°C) and pressures (10–90 kPa). Depending on these conditions the system was able to produce different ratios of TFE, HFP, and OFCB. It was found that the optimum conditions for TFE production are 600°C and 10–30 kPa, for HFP production it was 800°C and 10 kPa and for OFCB production 600°C and 90 kPa. A temperature of 700°C led to considerable amounts of undesirable HFE and OFP as well as the very toxic PFIB. At all conditions typically 5% of the PTFE is converted to TFM and associated carbon production. Only at high temperatures and pressures this compound is produced at considerable amounts (7–17%).

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