A Mild Reduction Route to PTFE Degradation at Low Temperature

Guifu Zou, Dabin Yu, Changlong Jiang, Guangcheng Xi, Yitai Qian,* and Houbo Zhang
Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

(Received June 25, 2004; CL-040737)

Poly(tetrafluoroethylene) has been degradated by a benign method at low temperature. Metal K plays an important effect in this process. The mild and economical route may be applied to decompose other polymers with hard degradation.

With the environment protecting consciousness improved, scientists have payed much attention to deal with the waste. However, efficient disposing of solid pollutans is always one of the most challenging to chemists. In addition, the minimizing energy consumption (low reaction temperature) of chemical manufacturing is also required to modern chemical industry. Therefore, the introduction of new methods, mild and economical conditions, is still in demand.

Poly(tetrafluoroethylene) (PTFE) is a plastic material with excellent heat and chemical resistance, low friction coefficient, and little water absorption etc., so it is widely used in our life.[1] However, the waste PTFE materials may become persistent solid pollutants, which are difficult to degrade in the environment.[2] Traditionally, the waste PTFE was decomposed by thermal treatment over 500 °C.[3] Up to now, many new degradation methods have been applied to deal with PTFE.[4–8] However, these reactions either require high reaction temperature, or employ organic solvents. Thus it is required to search for a benign and low energy consumption method to PTFE degradation. Herein, we use a mild reduction method to degrade PTFE in a sealed system at 180 °C. In this process, metal K acts as not only the reductive but also the reaction 'solvent', so the toxic organic solvent can be avoided. Moreover, as PTFE is facilely dissolved in metal K, it is favorable to reduce the reaction temperature. Besides, carbon nanospheres formed by PTFE degradation have potential application as reinforcement materials for rubber,[9] supports for catalysts,[10] and anodes in lithium ion second batteries.[11] The obtained KF can be used as solder, basic catalysis and so on.[12] Therefore, the 'green' route may be feasible method to PTFE degradation in the present.

All reagents are commercially available and used without further purification. In a typical experiment, metal K (0.200 g) and microsized PTFE powder (0.100 g) were added into a stainless steel reactor with 10 mL after the reactor was purged with nitrogen gas for 5 min to exclude the air. The reactor was sealed and maintained at 180 °C for 30 h. Then the reactor was cooled to room temperature naturally. The products were collected and washed with absolute ethanol to remove a spot of residual K. The obtained samples were washed continually with distilled water and absolute ethanol several times. Finally the samples were dried in vacuum at 40 °C for 6 h.

The products were determined by XRD on a Philips X'Pert PROSUPER X-ray powder diffractometer using Cu Kα radiation ($\lambda = 1.54178$ Å). The scanning electron microscopy (SEM) images were taken on a HITACHIX-650 scanning electron microscope. The transmission electron microscopy (TEM) images were captured on a HITACHI 800 instrument using an acceleration voltage of 200 kV. Information about the vibrational properties of the carbon material was obtained by Raman spectroscopy using an argon-ion laser at an excitation wavelength of 514.5 nm.

Figure 1 shows the Raman spectrum of the samples. There are two strong peaks at 1350 and 1590 cm^{-1}. The peak at 1350 cm^{-1} could be assigned to the vibrations of carbon atoms with dangling bonds in planar terminations of disordered graphite. The peak at 1590 cm^{-1} (G-band) corresponds to an E_{2g} mode of graphite and is related to the vibration of sp^2-bonded carbon atoms in a 2-dimensional graphite layer.[13] Compared with the G-band at 1580 cm^{-1} for the graphitic carbons,[14] the G-band of the products shifts towards a higher wavenumber due to the less orderly arrangement of the carbon atoms.[8]

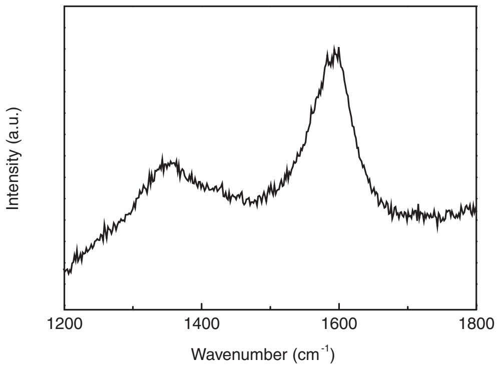

Figure 1. Raman spectrum of the products which shows G-and D-graphite peaks at 1350 and 1590 cm^{-1}, respectively.

The SEM image of the samples is exhibited in the Figure 2a. In the typical SEM image, it can be found that the PTFE is almost degradated into carbon spheres with diameter of 500–800 nm. There are a few carbon nanoparticles on the surface of the carbon spheres. TEM image of the samples is shown in Figure 2b, it also reveals that the samples mostly consist of carbon spheres. The inset in Figure 2b shows the selected area electron diffraction of the carbon sphere. The dispersed rings indicate that the carbon sphere has low crystallization, which also can be revealed by the Raman spectrum and XRD pattern (in Figure 3b). It may be related to the low reaction temperature. In addition, the obtained carbon spheres may be applied in rubber industry, supports for catalysts and so on.

In our experiment, the temperature is an important factor to PTFE degradation. When the reaction temperature is below 70 °C, the PTFE degradation could not be found even if the reaction is proceeded for one week. While the temperature is increased to 100 °C, most PTFE are degraded into the carbon particles. Moreover, the PTFE could be completely degraded into carbon nanospheres at 180 °C only if the reaction proceeds for

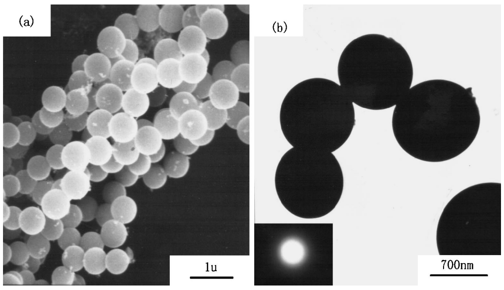

Figure 2. (a) SEM and (b) TEM images of the products; inset (in the Figure 2b) shows SAED of the carbon sphere.

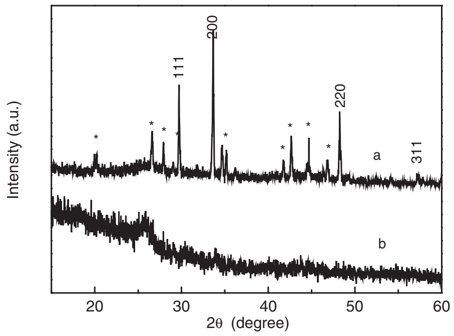

Figure 3. (a) and (b) XRD patterns of the samples, not washed by the distilled water, and the final products, respectively.

30 h. It may be caused from the fact that the PTFE is easy to dissolve in metal K (mp 64 °C), thus it is favorable to expedite reaction process. Herein, metal K acts not only as the 'solvent' but also the reducer. It can be concluded from the following.

Figure 3a shows the XRD pattern of the products that are not washed using the distilled water. All the sharp and broad reflection peaks can be indexed to cubic KF (JCPDS Card File, 04-0726), small quantity of orthorhombic $KF.H_2O$ (marked with asterisks) and low crystalline carbon. Figure 3b is a typical XRD pattern of the as-obtained products. Based on the above, the reaction process can be represented as follows:

$$-(CF_2-CF_2)-_n + 4n\ K = 2n\ C + 4n\ KF$$

It is the similar process in the literature.[5] In addition, some other metals (such as Mg, Zn, Fe, etc.) instead of metal K are used as the starting material, but the PTFE can not be degraded even if the reaction temperature is increased to 300 °C. Therefore, it is important to PTFE degradation to find a kind of metal with low melting point and strong reducibility.

In summary, PTFE powders have been favorably degraded into carbon nanospheres at 180 °C by a mild reduction process. The possible reaction mechanism is also discussed. The metal K, used as not only reducer but also 'solvent', may play a key role in the PTFE degradation. Because the process is closed, uses no toxic reagent, and proceeds at low reaction temperature, this reduction route may be applied to degrade other stable polymer with high melting point.

We thank the financial support from the National Natural Science Funds and the 973 Projects of China.

References

1 a) T. G. Vargo, J. A. Gardella, J. M. Calvert, and M. S. Chen, *Science*, **262**, 1711 (1993). b) J. M. Bellon, L. A. Contreras, J. Bujian, and A. Carrera-San Martin, *Biomaterials*, **17**, 2367 (1996).
2 a) J. C. Wittmann and P. Smith, *Nature*, **352**, 414 (1991). b) G. M. Simon and W. Kaminsky, *Polym. Degrad. Stab.*, **62**, 1 (1998).
3 D. A. Ellis, S. A. Mabury, J. W. Matin, and D. C. G. Muir, *Nature*, **412**, 321 (2001).
4 T. T. Liang, Y. Yamada, N. Yoshizawa, S. Shimidzu, and A. Oya, *Chem. Mater.*, **13**, 2933 (2001).
5 A. Huczko, H. Lange, G. Chojecki, S. Cudzilo, Y. Q. Zhu, H. W. Kroto, and D. R. M. Walton, *J. Phys. Chem. B*, **107**, 2519 (2003).
6 J. Hlavaty and L. Kavan, *Carbon*, **37**, 1029 (1999).
7 A. Yasuda, N. Kawase, T. Matsui, T. Shimidzu, C. Yamaguchi, and H. Matsui, *React. Funct. Polym.*, **41**, 13 (1999).
8 X. G. Yang, C. Li, W. Wang, B. J. Yang, S. Y. Zhang, and Y. T. Qian, *Chem. Commun.*, **2004**, 342.
9 H. Ismail, P. K. Freakley, and E. Sheng, *Eur. Polym. J.*, **31**, 1049 (1995).
10 E. Auer, A. Freund, J. Pietsch, and T. Tacke, *Appl. Catal.*, **173**, 259 (1998).
11 S. Flandrois and B. Simon, *Carbon*, **37**, 165 (1999).
12 a) M. Malsushita and S. Liu, *Weld. J.*, **79**, 295S (2000). b) T. Seki and H. Hattori, *Catal. Surv. Asia*, **7**, 145 (2003).
13 J. W. Liu, M. W. Shao, X. Y. Chen, W. C. Yu, X. M. Liu, and Y. T. Qian, *J. Am. Chem. Soc.*, **125**, 8088 (2003).
14 J. S. Qiu, Y. F. Li, Y. P. Wang, C. H. Liang, T. H. Wang, and D. H. Wang, *Carbon*, **41**, 767 (2003).

Published on the web (Advance View) August 7, 2004; DOI 10.1246/cl.2004.1150