Decomposition of Polytetrafluoroethylene by Grinding with Strontium Oxide

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Polytetrafluoroethylene (PTFE) was ground with SrO using a planetary ball mill in air. The grinding stimulates the solid reaction between PTFE and SrO at room temperature. PTFE is decomposed by the solid reaction and fluorine in PTFE is transformed into strontium fluoride. The results show that it is possible to mineralize highly stable polymer PTFE by grinding with proper additive.

Polytetrafluoroethylene ($[CF_2CF_2]_n$, PTFE) is one of the most widely used plastic material because of its very excellent properties such as stability against heating, chemical reagents, weathering and mechanical wearing. Since it has such excellent properties, it is difficult to dispose of the waste PTFE plastic after utilization except for thermal decomposition. Considering the necessity to avoid the release of toxic gas in waste treatment and the difficulty to do so in the thermal treatment, new method is required to treat the waste polymers containing halogens in order to lighten the environmental burden.

It is found that mechanochemical method provides a new method to decompose toxic organic substances.[1–3] As one basic research on non-thermal treatment of waste plastic containing halogen elements,[4,5] PTFE was chosen and ground with some additives at room temperature. Although it is known that mechanical treatment of polymer will degrade it and molecular weight of the polymer decreases to relatively low level,[6–9] the basic unit (monomer part) remains unchanged after the mechanical treatment. It is different in the mechanochemical process where an active chemical is added during grinding so that not only degradation but a real reaction takes place. Our preliminary experiments have shown that it is possible to transform fluorine from PTFE into fluorides with fluorite structure by grinding it with relatively unstable oxides of alkaline earth elements, which have high solid reactivity against grinding. Among these oxides, SrO has shown best results, namely shortest grinding time to complete the reaction. On the other hand, BaO is so unstable that it changed into carbonate and hydroxide during grinding in air and showed no reactivity with PTFE.

The grinding operation was conducted using a planetary ball mill running at 700 rpm. PTFE taken as monomer unit (CF_2) and SrO were mixed in ratio 1:2 of Sr to F and 2 grams of the mixture were put in a zirconia pot for grinding. SrO was obtained from High Purity Chemetals Lab., Japan and used as received.

Figure 1 shows the X-ray diffraction patterns of the PTFE and ground mixture for different times. Peaks of PTFE are still observed in pattern of the 30-min ground sample though very weak. On the other hand, pattern of the sample ground for 60 min or more is confirmed to belong to that of SrF_2. We did observe the gas release when opening the mill pot and the gas was confirmed to be CO gas by the gas checking tube. Taking the results into account, a reaction stimulated by the grinding is considered as follows:

$$[CF_2CF_2]_n + 2n\,SrO \;=\; 2n\,SrF_2 \;+ 2n\,CO \quad (1)$$

The white powders of the starting sample have been changed into black ones after reaction, which suggest that carbon-like sample is formed besides SrF_2. In fact, it seems to be difficult for all the carbon atoms to bind oxygen into CO and part of them may be left free. Formation of CO gas conflicts with our purpose for waste disposal. Proper grinding conditions to avoid CO gas formation and leave all carbon composition as free carbon are under investigation. Other possible additives such as CaO instead of SrO are also under investigation.

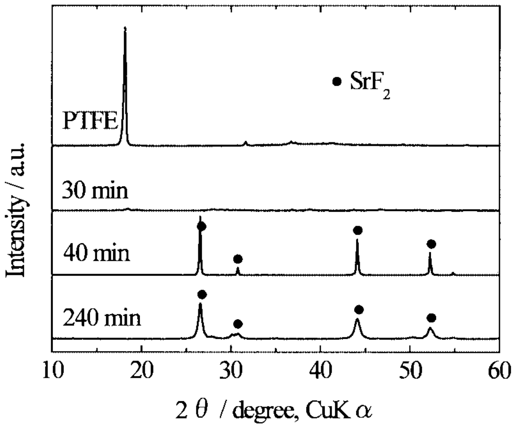

Figure 1 X-ray diffraction pattern of PTFE and mixture ground for different times.

Figure 2 shows C1s spectra of the original PTFE and 240-min ground sample. Since each carbon atom has been bound with fluorine atom, the peak position of C1s for PTFE has high binding energy of about 293 eV compared to a reference bind-

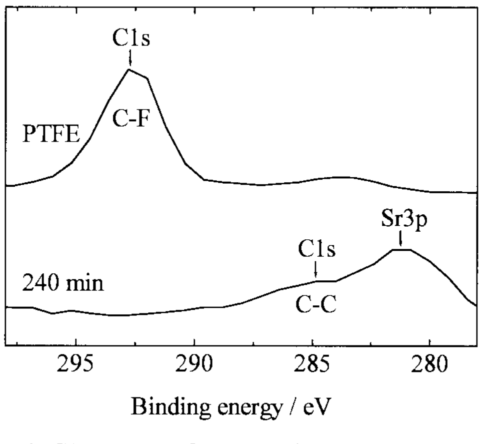

Figure 2. C1s spectra of PTFE and 240-min ground sample.

ing energy of 285 eV for carbon bound to itself. This peak has disappeared from the spectrum of 240-min ground sample and a very small broad peak at 285 eV binding energy is observed instead. These results indicate that the binding state of carbon in the ground sample has been changed from with fluorine to with itself. Therefore, no binding between C–F exists after the mechanochemical reaction.

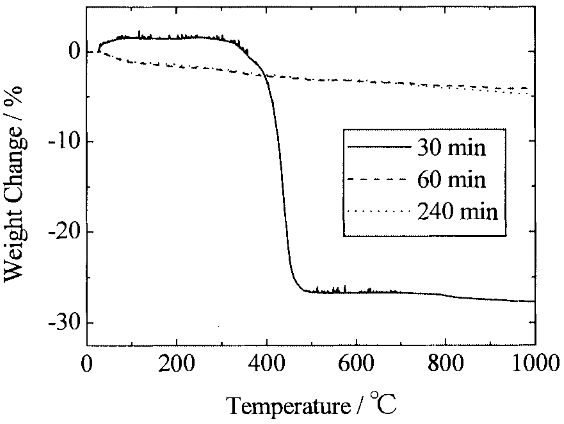

Figure 3. TG curves of the ground samples.

Figure 3 shows the results of thermogravimetric analysis which was conducted in air. PTFE is decomposed by heating in air at about 400 °C as shown by weight loss of the 30-min sample. About 28% weight loss is obtained for this sample and this amount is near the starting ratio of PTFE of 32.5% before grinding. Contrary to this result, the rapid weight loss around 400 °C has diappeared with the sample ground for 60 min or more. It indicates that no PTFE exists in the sample after the above reaction. Very slow continuous weight loss up to about 5% within 1000 °C is obtained with the sample ground for 60 min or more. 5% weight loss is suggested to come mainly from the burning of amorphous carbon formed during grinding. Carbon composition analysis of the ground samples will be conducted after satisfactory separation from fluoride.

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