Thermal Activation Technology of Oxide Semiconductors and its Applications to the Environmental Field

Jin MIZUGUCHI

Faculty of Textile Science and Technology, Shinshu University
Ueda, 386-8567 Japan
E-mail: jimmizu@shinshu-u.ac.jp
Tel & Fax: +81-268-71-0868

Abstract
Thermal activation of semiconductors (TASC) has been investigated with special attention to its applications to the environmental problem caused by polymer-related wastes. TASC is our novel technology which enables us to decompose any polymers, in an instant, into H2O and CO2. This is based on our accidental finding that the semiconductor exhibits no catalytic effects at room temperature; whereas significant oxidative properties will appear when heated at elevated temperatures at about 350-500 °C. The present effect has been interpreted as arising from thermally generated defect electrons (“hole”) formed in the valence band of the semiconductor. The initial TASC-process for polymer decomposition is to capture bonded electrons from the polymer to create there unstable radicals. Then, the radicals travel throughout the polymer to make the whole polymer unstable, resulting in the fragmentation of the giant molecule into small pieces such as ethylene and propane. Finally, the fragmented molecules react with oxygen in air to give H2O and CO2 (i.e. complete combustion). The present review describes the TASC technology together with its applications to the recovery of reinforcing fibers from FRPs (fiber reinforced plastics), reclaim of rare-earth powders from resin-bonded rare-earth magnets, and repair of partially damaged FRPs.

Keywords: Fiber reinforced plastic, recycling, resin-bonded magnets, repair of partially damaged FRPs, volatile organic compound
1. Introduction

As is well known, FRPs (fiber reinforced plastics) are characterized by high mechanical strength, lightweight, etc. For these reasons, FRPs are widely used in construction-related areas, as those of aircrafts, ships, etc. However, these outstanding properties of FRPs can, in turn, cause a serious problem as to the wastes for disposal or recycling [1]. At the moment, the FRP wastes are mostly landfilled, although partly used for the cement kiln fuel [2,3].

A variety of technologies for recycling FRP wastes have been tested at a lab or a pilot scale at universities and industries. Today, recycled fibers are, in most cases, cut and milled by recycling companies. These fibers reclaimed are short in length and also random in orientation. The technologies involved are classified into thermal, chemical, or mechanical processes. Both thermal and chemical processes attempt to separate the carbon fibers from the polymer matrix; whereas mechanical recycling processes typically use mechanical size-reduction technologies to change the FRP wastes into a usable form, such as filler. The thermal processes use various methods of pyrolysis to breakdown the polymer matrix of the composite into gaseous and/or liquid components. Pyrolytic processes are usually carried out in atmospheric pressure, or oxygen-depleted atmospheres, or under vacuum. Chemical processes [4,5] use catalysts or reactive solvents in order to decompose the polymer matrix into its liquid components. These chemical reactions are at times conducted at high pressures and in sub-/supercritical fluids [6,7]. On the other hand, our TASC process (i.e. thermal activation of semiconductors) described below is an entirely new technology based on semiconductor physics [8-11].

Today, recycled fibers are, in most cases, cut and milled by recycling companies. The cost for removal of polymer matrix will vary depending upon the type of binder and the size (thickness) of the waste being fed into the equipment for binder removal. The lower selling price would be for less-demanding applications, such as milled fiber for electrically conductive molding compounds. The higher selling price would be for higher performance applications, such as sheet molding compounds, bulk molding compounds, and injection molding compounds, where fiber length has a significant impact on the fiber’s mechanical properties. In our case, we aim at the latter application by keeping the recovered carbon fiber as long as possible.

The present review describes the TASC technology as well as its applications to the recovery of reinforcing fibers from FRPs [12,13] and also to its related topics: reclaim of rare-earth powders from resin-bonded rare-earth magnets [14] and repair of partially damaged FRPs [15].
2. Outline of the TASC technology together with an example of polymer decomposition [9-11]

We begin with the destruction mechanism of a giant molecule into H₂O and CO₂ by TASC, as shown in Fig. 1. This technology allows us to decompose a giant molecule into H₂O and CO₂, in an instant, through the fragmentation of the giant molecule by radical splitting. The destruction process is composed of the three major steps: 1. Creation of radicals by oxidation caused by thermal activation of semiconductors. 2. Fragmentation of a giant molecule by radical splitting. That is, the unstable radicals propagate throughout the polymer at 350-500 °C to make the polymer unstable, resulting in the fragmentation of the giant molecule into tiny molecules such as ethylene, propane, etc. [11]. 3. Then, the fragmented molecules react with oxygen in air to give rise to H₂O and CO₂ (i.e. complete combustion).

We describe below one example of complete decomposition of polycarbonate (PC) which is currently used as the substrate for compact discs. [9]. Fig. 2 shows the result of PC decomposition in the presence or absence of TiO₂ used as the semiconductor. We carried out our experiment using two glass tubes, each of which contains PC chips. These were heated in air at 500 °C for 30 min. The PC in the absence of TiO₂ melted around 200 °C and then boiled, ending up with the carbonization as shown. This is a typical result when a plastic is roasted in air. On the other hand, no trace of PC was recognized in the presence of TiO₂. Here remain just white powders of TiO₂. Gas analysis of the decomposition product was made by mass spectrometer. Fig. 3((a) shows the result of the experiment carried out in air. We see peaks of N₂ (28) and O₂ (32) that are components of air, as well as peaks of H₂O (18) and CO₂ (44). Furthermore, we observe a peak of Ca (40). This is due to a metallic soap of Ca used as a lubricant in PC for optical discs. The present result indicates that the PC whose molecular weight is around 25,000 has entirely been decomposed into H₂O and CO₂ in an instant. On the other hand, when the experiment was carried out under vacuum as shown in Fig. 3(b), we see a number of small fragments. However, these fragments disappear in an oxygen atmosphere, leaving behind only two peaks of H₂O and CO₂. This clearly indicates that oxygen is absolutely necessary for the disappearance of fragment peaks. On the basis of these experiments as well as the ESR measurements for radical concentration [10,11], we proposed the destruction mechanism as shown in Fig. 1.

Then, an important question arises as to what kinds of semiconductors can be used for decomposition, and what kinds of materials can be decomposed. Those semiconductors which are stable at high temperatures in an oxygen atmosphere come into
consideration. This means that oxide semiconductors are the semiconductor of choice. For example, TiO₂, ZnO, Cr₂O₃, α-Fe₂O₃, etc. Among these, we are particularly interested in Cr₂O₃ that is the most stable compound having a melting point of about 2200 °C. As for the materials to be decomposed, all kinds of thermoplastic and thermosetting polymers, Diesel exhaust which includes benzene, toluene, and PM, tar, tobacco smoke, VOC (volatile organic compounds) as well as offensive odor.

3. Decomposition of FRPs: Carbon-fiber based FRP (CFRP) [13]

3.1 Sample preparation

Carbon fiber textiles (Torayca Cloth CO6343) were obtained from Toray Industries, Inc. Carbon fibers are usually surface-modified with functional groups such as –COOH, C=O, and -OH, as shown in Fig. 4. When an epoxy resin is used as the polymer matrix for FRP, a low-molecular epoxy resin is coated onto the carbon fibers as a sizing agent in order to enhance the affinity between fiber and polymer matrix (Fig. 4). However, details on these sizing materials are not available in open literature.

Carbon fiber fabrics were impregnated with an epoxy-resin of XNR6815 and a hardener of XNH6815 from Nagase Chemtex Corporation, using a Vacuum Assisted Resin Transfer Molding (VARTM) machine. Then, the plates were cured at room temperature for 24 h, followed by post curing at 50 °C for 12 h.

The CFRP plate was sandwiched between two Cr₂O₃-coated honeycomb-substrates (see below) and heated in a furnace at 400 °C in air for 10 min. The temperature was adjusted to 400 °C because the carbon fiber reacts with oxygen in air above 450 °C to yield CO₂. The carbon fibers were perfectly recovered with the TASC technology as though these were virgin textiles.

3.2 Decomposition of FRPs and recovery of carbon fiber fabrics

For carbon fiber recycling to become fully commercialized, there are important factors to make a recycling process both technically and economically feasible. Especially, the cost for removing the polymer matrix of the composite plays a crucial importance. To achieve this, we looked closely into the destruction mechanism again and focused on the formation of free radicals and their propagation (Fig. 1). Then, we felt convinced that the free radicals multiply spontaneously to induce the radical splitting, leading to the fragmentation of the giant molecule into small pieces such as ethylene, propane, etc. This prompted us to believe that we have only to create “seed radicals” in FRP in the initiation process, and all the rest proceeds automatically. To sum up, it is sufficient for the FRP plate to be mechanically in contact with Cr₂O₃ in order to create radicals in the initiation process. This is achieved in the following way.
Fig. 5 shows a Cr$_2$O$_3$–coated honeycomb substrate colored green due to Cr$_2$O$_3$. We simply put an FRP plate on it and then sandwiched by another honeycomb, so that the FRP plate is mechanically in contact with Cr$_2$O$_3$. Then, the plate is heat-treated in air in a furnace.

Fig. 6(a) shows a CFRP plate before TASC treatment. Fig. 6(b) is the plate after TASC treatment at 400 °C for 10 min in air. Polymer matrix was entirely decomposed, giving rise to clean carbon-fiber textiles. No trace of carbonaceous deposits was recognized either on the woven textiles.

Figs. 7(a) and 7(b) show the SEM (scanning electron microscope) pictures for one single carbon fiber (i.e. one filament), before use and after recovery. No significant difference is recognized in appearance between them.

Fig. 8 shows the Raman spectra of carbon fibers, before use and after recovery, that are characterized by two peaks at about 1600 and 1350 cm$^{-1}$. The peak at 1600 cm$^{-1}$ (G band) is characteristic of the highly oriented pyrolytic graphite; whereas the peak around 1350 cm$^{-1}$ (D band; so to speak, disorder-induced peak) appears when the graphite includes some amorphous or diamond-like structures [16]. However, no significant difference is found in peak position.

Fig. 9 shows the X-ray diffraction diagrams for carbon fibers, before use and after recovery. The diffraction peaks are typically characterized by the graphite structure [17]. Here again, no significant difference in diffraction angle is recognized between the samples, before and after TASC treatment.

3.3 Mechanical strength of the CFRP based on the recovered carbon-fibers

The mechanical strength of the FRP is known to largely depend on the following three factors: 1. mechanical strength of the carbon fibers, 2. surface modification of the carbon fiber, and 3. sizing agent applied on the surface-modified carbon-fibers. The surface modification as well as the application of the sizing agent is usually assumed for the epoxy-resin based FRP, as shown in Fig. 4. There is another influential factor in the TASC process: i.e. annealing of carbon fibers. Namely, the temperature increase/decrease run during the TASC process exerts a profound influence on the mechanical properties of the recovered carbon, especially the annealing after the TASC treatment. Therefore, the annealing must carefully be carried out in such a way as to remove internal stress as much as possible.

According to our characterization on the recovered carbon fibers [13], the surface modification (-COOH, C=O, -OH in Fig. 4) is found to be kept even after TASC treatment as shown by XPS measurements. On the other hand, the sizing agent has entirely been removed at about 260 °C as revealed by TGA (thermogravimetric analysis) measurements.
Since no information was available on the sizing agent, we regarded an epoxy-resin of XNR6815 before curing (see section 3.1) as a sizing agent and prepared its acetone solution for dip coating. Then, the recovered carbon fiber fabric was dip-coated with the sizing agent and the relevant factors were optimized so as to improve the mechanical properties of recovered FRPs. Finally, we have achieved a value of about 90% of the mechanical strength of the virgin FRP. Further improvement can presumably be achieved in collaboration with carbon fiber manufacturers that have enough know-how about the sizing agent as well as the manufacturing process of carbon fibers.

3.4 Continuous equipment of the FRP decomposition system of the tunneling type

Most recently, we have constructed a continuous equipment of the FRP decomposition system of the tunneling type. The schematic diagram of the equipment is shown in Fig. 10(a). At the inlet, we feed waste FRPs into the furnace that are sandwiched by two catalyst-coated honeycombs. At the outlet, we obtain recovered carbon-fiber textiles. Exhaust heat due to the reaction of fragmented molecules with oxygen is recovered and transferred to the inlet. The length of the 500 °C zone is about 1 m, and the transfer rate of FRPs is about 100 mm/min. The process requires about 10-20 min duration and is currently capable of processing FRP wastes up to 200 mm in wide, 1000 mm long and 3 mm thick. The process can be energy self-sufficient using the fragmented molecules (processed by TASC from polymer matrix) as an energy source (see section 2). Fig. 10(b) shows the prototype of our continuous equipment of the FRP decomposition system of the tunneling type.

4. Recovery of rare-earth powders from resin-bonded rare-earth magnets [14]

Rare earth metals are nowadays widely used as materials for permanent magnets, polishers of optical glasses, catalysts, phosphors, magnet-optic storage system, etc. The amount of the reserve is said to be about 130 million tons, of which about 48.3% is held by China. In addition, the production of rare earths is centered on China and its market share is about 97% in 2009. The present situation reflects the state of oligopoly (i.e. a state of seller’s market). Because of this, the supply of rare earth metals can easily be influenced by political situations and thus be unstable at times. In addition, the price has been constantly and drastically rising every year. In order to obviate these problems, it is urgently necessary to break up the rare-earth suppliers into several countries other than China. At the same time, we need to accelerate the reclaim and reuse of rare earth metals from the disposals. In view of the above situation, an attempt has been made to reclaim rare earth metals from resin-bonded magnets by decomposing only polymer matrix alone, utilizing the TASC technology.
Resin-bonded magnets are made of magnetic powders together with a minute amount of polymers used as the binder and manufactured by means of injection molding in combination with thermoplastic polymers, or compression molding together with thermosetting polymers. Bonded magnets are especially preferred because the magnets of desired shapes can easily be prepared with low costs.

Two kinds of bonded magnets J16 and K12, based upon the composition of Nd-Fe-B/Sm-Fe-N, were obtained from Nichia Corporation. These are tablet magnets (size: 10 mm in diameter and 7 mm in height). The magnets are prepared by injection molding using polyamide 12 (PA12) as the binder for J16, or using polyphenylene sulfide (PPS) for K12.

Bonded magnets of Wellmax S3A (Composition: Sm-Fe-N) were purchased from Sumitomo Metal Mining Co. These are also tablets prepared by injection molding using PA as the binder: 20 mm in diameter and 13 mm in height.

First, the bond magnets were coated with a dispersion layer of Cr$_2$O$_3$ or $\alpha$-Fe$_2$O$_3$ (thickness: about 5 $\mu$m) by dipping the magnets into an acetone suspension containing powders of Cr$_2$O$_3$ or $\alpha$-Fe$_2$O$_3$. Next, the bond magnets were heated at 500 °C for 20 minutes in air in a muffle furnace in order to decompose the polymer binder into H$_2$O and CO$_2$ on the basis of our TASC technology. The successful result is shown in Fig. 1.

5. Repair of partially damaged FRPs with reinforcing fibers intact [15]

FRPs are widely used in construction related areas. However, once FRPs are partially damaged, there is no way to repair it with embedded reinforcing fibers intact. Currently, so called “scarf method” is used for partial repair which proceeds in such a way as to mechanically remove the damaged area (i.e. both polymer and reinforcing fibers) by a disk grinder, followed by an application of a prepreg together with a binder tape. However, the mechanical strength of the repaired part is greatly diminished because the reinforcing fibers were entirely severed during the repair process. In view of the present situation, a trial has been made to repair partially damaged areas with embedded reinforcing carbon fibers intact, utilizing the TASC technology.

TASC allows us to remove the polymer matrix alone in damaged areas of CFRP in the presence of thermally activated semiconductors while retaining the embedded fibers intact. The polymer-eliminated area is then refilled with an epoxy resin to complete the repair. The repair process is shown in Fig. 12, and the experimental setup is illustrated in Fig. 13. In our experiment, an IR lamp was used together with an ellipsoidal mirror to locally heat the damaged area, using TiO$_2$ as the semiconductor. The FRP plate used for the experiment was prepared as described in section 3.1.
Figs. 14(a) and 14(b) show the CFRP plate before and after heat treatment. Fig. 14(c) is a magnified picture of the carbon fiber fabric. The carbon fiber textile looks really undamaged. The thickness of the polymer-removed area is about 1 mm, and this can easily be controlled by changing the heating power.

6. Conclusions
The TASC technology as well as its applications have been reviewed in the present paper. The conclusions can be summarized as follows:

1. Thermal activation of semiconductors has been applied to the recovery of reinforcing fibers from various FRPs, and the embedded fibers have been isolated without any damage. This is a 100%-dry process.
2. The FRP based on the recovered fabric exhibits about 90% of the mechanical strength of the virgin FRP.
3. A continuous equipment of the FRP decomposition system of the tunneling type has been constructed.
4. The TASC technology can also be utilized to recuperate metals from resin-bonded magnets.
5. A novel repair method for partially damaged FRPs has been presented which allows us to keep the reinforcing fibers intact.
6. More research is still required for applications development to bring the TASC technology to full commercialization.
References:


Figure captions:

Fig. 1  Schematic diagram of the destruction mechanism of polymers.

Fig. 2  Decomposition of polycarbonate in the presence or absence of TiO₂ used as the semiconductor.

Fig. 3  Mass spectra of the decomposition product: (a) in air and (b) under vacuum.

Fig. 4  Schematic illustration of the modified surface of carbon fibers and the additional surface treatment with sizing agents.

Fig. 5  Cr₂O₃-coated honeycomb substrate colored green due to Cr₂O₃.

Fig. 6  CFRP plate: (a) before and (b) after TASC processing.

Fig. 7  SEM pictures for one single carbon fiber: (a) before and (b) after TASC processing.

Fig. 8  Raman spectra of one single carbon fiber before and after processing.

Fig. 9  X-ray diffraction diagrams of carbon fibers before and after processing.

Fig. 10  Continuous equipment of the FRP decomposition system of the tunneling type: (a) schematic illustration and (b) prototype.

Fig. 11  Pictures for the tablets before TASC (top) and the reclaimed powders after TASC (bottom): J16 and K12 treated with Cr₂O₃, and Wellmax S3A treated with Cr₂O₃ or α-Fe₂O₃.

Fig. 12  Schematic diagram of the repair process.

Fig. 13  Experimental setup for the repair system.

Fig. 14  Pictures for CFRPs: (a) before TASC processing, (b) after TASC processing, and (c) magnified view of the reclaimed carbon fiber textile.
1. Oxidation by holes: creation of radicals
2. Radical splitting: fragmentation of giant molecules
3. Reaction with oxygen: complete combustion

Fig. 1 Schematic diagram of the destruction mechanism of polymers TASC.

Fig. 2 Decomposition of polycarbonate in the presence or absence of TiO₂ used as the semiconductor.
Fig. 3 Mass spectra of the decomposition product: (a) in air and (b) under vacuum.

Fig. 4 Schematic illustration of the modified surface of carbon fibers and the additional surface treatment with sizing agents.
Fig. 5 Cr$_2$O$_3$-coated honeycomb substrate colored green due to Cr$_2$O$_3$.

Fig. 6 CFRP plate: (a) before and (b) after TASC processing.
Fig. 7 SEM pictures for one single carbon fiber: (a) before and (b) after TASC processing.

Fig. 8 Raman spectra of one single carbon fiber before and after TASC processing.

Fig. 9 X-ray diffraction diagrams of carbon fibers before and after TASC processing.
Fig. 10 Continuous apparatus of the FRP recycling system of the tunneling type: (a) schematic illustration and (b) prototype.
Fig. 11 Pictures for the tablets before TASC (top left and right) and the reclaimed powders after TASC (bottom left and right): J16 and K12 treated with Cr$_2$O$_3$ (left), and Wellmax S3A treated with Cr$_2$O$_3$ or $\alpha$-Fe$_2$O$_3$ (right).

Fig. 12 Schematic diagram of the repair process.
Fig. 13  Experimental setup for the repair system.

Fig. 14  Pictures for CFRPs: (a) before TASC and (b) after TASC processing, and (c) magnified view of the reclaimed carbon fiber textile.