THERMAL DECOMPOSITION OF PMC FOR FIBER RECOVERY[a]

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Abstract

This paper describes efforts by Argonne National Laboratory to develop a process to recover carbon fibers from polymer matrix composite (PMC) materials. The polymer material in the matrix may be a thermoplastic or a thermoset. Samples of panels containing PMC fibers were obtained and used in our bench-scale testing program. We tested three different methods for recovering these PMC fibers: thermal treatment, chemical degradation, and cryogenic methods (thermal shock treatment). The first two methods were effective in separating the carbon fibers from the polymeric substrate; the third method was not satisfactory. Carbon fibers separated from the polymer substrate using the thermal treatment method were submitted to Oak Ridge National Laboratory for analysis and evaluation. The results indicated that the carbon fibers had been cleanly separated from the polymer matrix. Their intrinsic density was 1.8473 g/cm^3 and their electrical resistivity was 0.001847 ohm-cm, compared to an intrinsic density of 1.75–1.9 gm/cm^3 and an electrical resistivity of 0.0002–0.002 ohm-cm for virgin fibers produced from polyacrylonitrile (PAN). Although we were not sure that the samples we processed were originally produced from PAN, we used the PAN fibers for comparison. It was also demonstrated that the surface of the recovered fibers could be reactivated to energy levels equivalent to those of reactivated virgin fibers from PAN. A comparison of the mechanical properties of the recovered fibers (without surface treatment) with those of surface-treated virgin fibers from PAN revealed that the ultimate tensile strength and the elongation at brake values are about 1/3 the values for the virgin fibers. The modulus for the recycled fibers (31.4 million pounds per square inch [psi]) was about the same as that for the virgin PAN fibers (31.2 million psi). The reason for the lower tensile strength and elongation is not clear: we plan to investigate it further as part of the process improvement study that is now underway. Process economics appear very promising, and a payback of less than two years is likely.

Introduction and Background

Because of their high strength-to-weight ratios, carbon-fiber-reinforced polymer matrix composite (PMC) materials are finding increasing applications in the aerospace industry. These materials are also being evaluated for use in the automotive industry. The major barriers to their widespread use are their high cost and the uncertainty about whether they can be recycled when vehicles reach the end of their useful lives. Argonne National Laboratory is working to develop a process to recover these high-value carbon fibers and to assess the potential for recycling them into useful products.

Experimental Work

Thermal Treatment Method

Experiments were conducted using PMC pieces measuring about 2 in. × 2 in. × 1/8 in. or about 6 in. × 6 in. × 1/8 in. The samples were placed in an electrically heated oven at different temperatures within the range of 350°F–1,200°F. The oven was placed in an explosion-proof hood equipped with high-efficiency particulate air (HEPA) filters. The gas/vapor products were cooled down to near-ambient temperature using tap water, and the resulting gas and liquid samples were sent for chemical analysis. The excess gas was vented to the hood. Some of the experiments were conducted in ambient air and some in a nitrogen atmosphere. At temperatures greater than 500°F, the carbon fibers were completely freed from the polymer given enough residence time; at 1,200°F, the required residence time was less than 5 minutes. Longer residence times were required at lower temperatures. The recovered carbon fibers comprised between 45% and 55% of the total original sample weight. On average, about 50% of the samples' weight was the polymer substrate that was pyrolized and/or oxidized during the heating process.

Examination under a magnifying glass revealed that the recovered fibers were completely free from any visible contamination and from each other (see Figure 1). Individual hair-like fibers could be pulled out using a pair of tweezers. Samples that were heated in air did not show any physical damage that could result from oxidation. This finding confirms the stability of the recovered fibers in the temperature range that was tested.

Carbon fibers separated from the polymer substrate using the thermal treatment method (at 1,200°F) were submitted to Oak Ridge National Laboratory for analysis and evaluation. The results showed that these fibers had been cleanly separated from the polymer matrix. Their intrinsic density was 1.8473 g/cm^3 and their electrical

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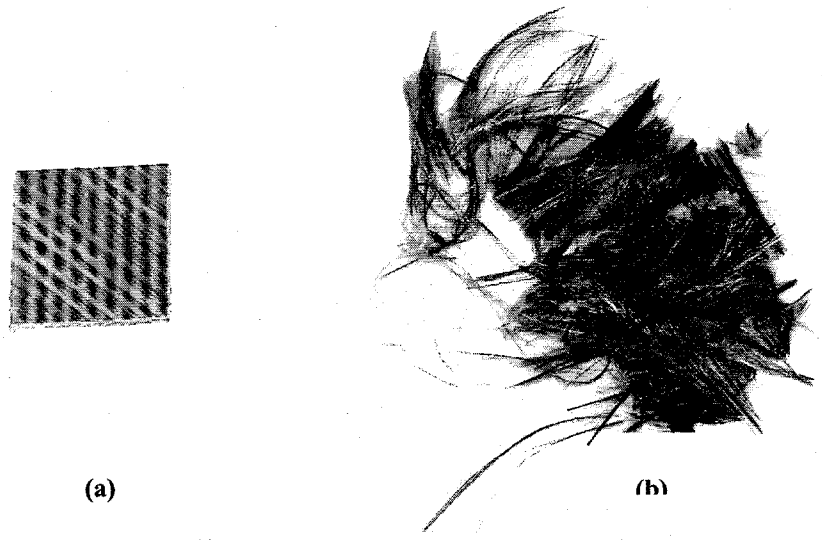

(a) (b)

Figure 1. (a) PMC Sample, (b) Recovered Carbon Fibers

resistivity was 0.001847 ohm-cm, compared to an intrinsic density of 1.75–1.9 gm/cm^3 and an electrical resistivity of 0.0002–0.002 ohm-cm for virgin fibers produced from polyacrylonitrile (PAN). Although we are not sure that the samples we processed were originally produced from PAN, we used the PAN fibers for comparison. It was also demonstrated that the surface of the recovered fibers could be reactivated to energy levels equivalent to those of reactivated virgin fibers from PAN. A comparison of the mechanical properties of the recovered fibers (without surface treatment) with those of surface-treated virgin fibers from PAN revealed that the ultimate tensile strength and the elongation at brake values are about 1/3 of the values for the virgin fibers. The modulus for the recycled fibers (31.4 million pounds per square inch [psi]) was about the same as that for the virgin PAN fibers (31.2 million psi). The reason for the lower tensile strength and elongation is not clear; the temperatures that we used may be too high or the residence times too low. We plan to investigate both of these possibilities as part of the process improvement study that is now underway.

The composition of the gas and liquid effluent streams for this process depends on the composition of the substrate material and on whether heating takes place in air or in nitrogen. The gas/vapor products from one of the samples that was heated in nitrogen at 1,200°F were cooled down to near ambient temperature, and the resulting gas and liquid samples were sent for chemical analysis. The gas sample contained N_2, O_2, CO_2, CO, and only trace amounts of hydrocarbons. The liquid sample was analyzed for semivolatile compounds; it contained about 30 such compounds, including (in descending order) 2,2,6,6, tetramethyl-4-piperidinone (73 ppm), aniline (49 ppm), 4-methyl benzene amine (33 ppm), 4-methyl-3-pente-2-one (22 ppm), 4-amino-4-methyl-2-pentanone (20 ppm), and benzonitrile (20 ppm). Therefore, this stream will have to be incinerated at high temperatures (with heat recovery) or disposed of as a hazardous waste.

Chemical Degradation Method

Argonne also conducted experiments in which 1-in. × 1-in. × 1/8-in. pieces of PMC material were placed in hot triethylene glycol/water and tetraethylene glycol/water solutions. At temperatures greater than about 450°F, the fibers were freed from the polymer matrices within a matter of a few minutes, depending upon the solution temperature. The liberated fibers were washed using fresh water and allowed to dry in the hood.

Fibers recovered by means of the chemical degradation method were also submitted for analysis. Initial results indicated that these fibers were more brittle than those recovered by means of the thermal treatment method and were coated with a thin film of an unidentified material. We believe that the thin film coating on the fibers was a residual layer of glycol. The brittleness of the fibers may be due to residual thermoset polymeric residue that was not completely removed during chemical processing.

Thermal Shock Treatment

Argonne also conducted experiments in which the PMC samples were exposed to very large temperature gradients to determine whether the difference in expansion coefficients of the fibers and the polymeric materials would be sufficient to break the bond between the two. The samples were first placed in liquid nitrogen for about 10 minutes and then rapidly transferred to a beaker containing boiling water. The results were not satisfactory. No apparent delamination was observed.

On the basis of the experimental results described, we concluded that the thermal treatment method is the most

promising of the three techniques tested for recovering carbon fibers from PMCs. Development of this process is continuing at Argonne.

Pilot-Testing of the Thermal Treatment Method

The next step in the effort to develop and commercialize the thermal treatment process is to conduct pilot testing. We plan to use a specially designed rotary kiln (Figure 2) to confirm process performance, generate data for a reliable cost analysis of the process, and develop the necessary scale-up and design data for a larger field-demonstration system. We also plan to recover sufficient fibers to produce products suitable for product testing.

The annulus of the double-barreled rotary kiln will be used as a combustion chamber to burn the polymer decomposition products in a separate chamber away from the PMC material that is being treated. The combustion products will be exhausted to an after burner to complete the destruction of pollutants that may have survived in the combustion chamber. This design will allow significant heat recovery by the rotating drum and prevent the combustion products and the polymer decomposition products from entering the rotating drum. The recovered fibers will exit the drum over a perforated conveyor that allows air through to recover heat from the fibers. Detailed design of the pilot unit is under way. The rotary kiln will measure 1 ft in diameter and will be designed for a variable residence time of up to 30 min.

Related Recycling Activities

Argonne has also conducted experiments similar to those described above for recovering glass fibers from fiberglass insulation and integrated electronic circuit boards. We successfully recovered the glass fibers from the urea-phenolics resins in the insulation material and separated the fiberglass mats from the metal plates in the circuit boards by means of both thermal treatment and chemical degradation methods. These results suggest that these two techniques are effective in recovering fibers from a variety of fiber-containing materials.

Economic Analysis

A preliminary economic analysis of the thermal treatment process for recovering carbon fibers from PMC materials was conducted for a plant processing 1,000,000 lb/yr of PMC material. We assumed that the PMC material contained 50% (by weight) carbon fibers. The analysis showed that such a plant would have a payback on the order of about one year, as shown in Table 1. The short payback period is attributable primarily to the high value of the fibers. The least expensive carbon fibers are worth about $5.50/lb, and the higher-quality fibers are worth well over $12/lb. We used a value of $3/lb in our cost analysis for the recovered fibers, assuming that they can be used only in short-fiber applications.

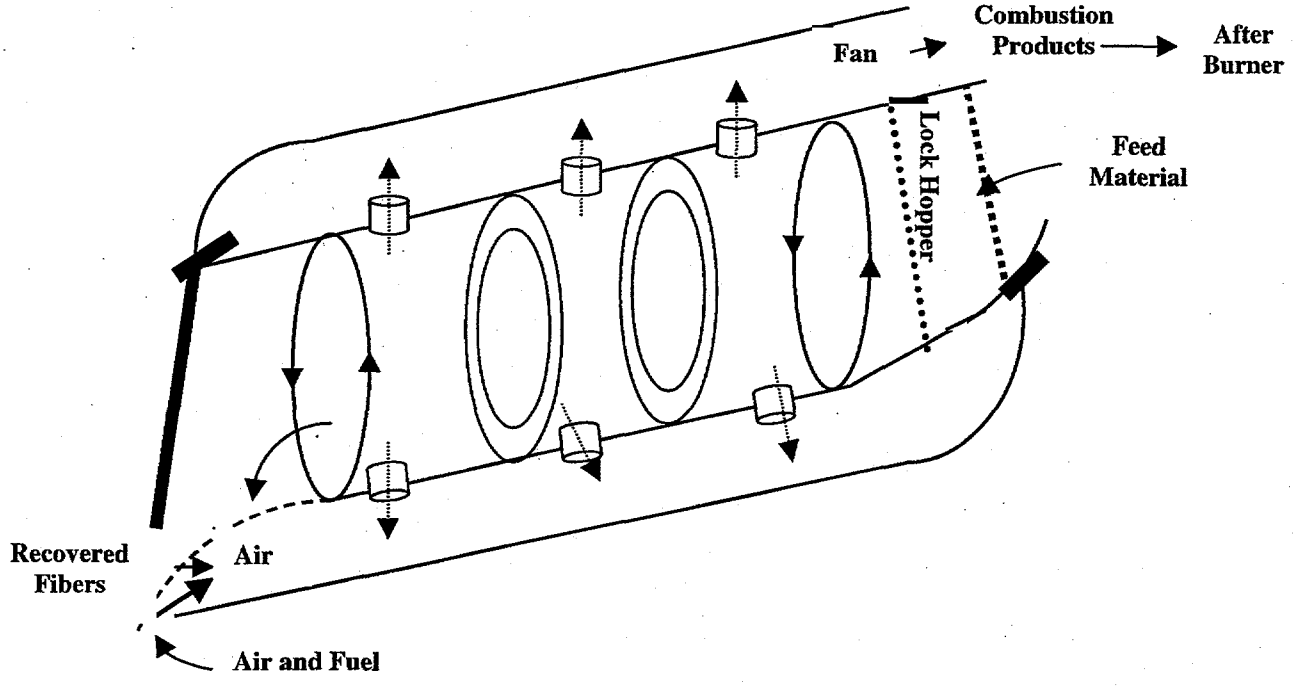

Figure 2. Double-Barreled Rotary Kiln

TABLE 1 Process Economics (Annual Basis) for Carbon Fiber Recovery from Obsolete Polymer Matrix Composite Materials

BASIS	
Total PMC processed (1,000 lb/yr)	1,000
Mass fraction carbon fibers in feed	0.50
REVENUES (thousand $/yr)	
Carbon Fibers (at $3.00/lb)	1,500
Other	0
TOTAL REVENUES	**1,500**
OPERATING COSTS (thousand $/yr)	
Feedstock (credit for avoided disposal)	-10.0
Chemicals	3.0
Waste disposal	0.0
Utilities	87.5
Labor	50.0
Maintenance	15.0
TOTAL OPERATING COSTS	**145.5**
NET INCOME (thousand $/yr)	**1,354.5**
CAPITAL COST (thousand $)	**1,500.0**

Conclusions

The thermal treatment method is a technically feasible and economically attractive approach to recover carbon fibers from polymeric matrices. The technology also applies to other fiber- containing waste materials such as fiberglass insulation.