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CHEMICAL RECYCLING OF SCRAP COMPOSITES

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ABSTRACT

There are no well-developed technologies for recycling composite materials other than grinding to produce fillers. New approaches are needed to reclaim these valuable resources. Chemical or tertiary recycling, conversion of polymers into low molecular weight hydrocarbons for reuse as chemicals or fuels, is emerging as the most practical means for obtaining value from waste plastics and composites. Adherent Technologies is exploring a low-temperature catalytic process for recycling plastics and composites. Laboratory results show that all types of plastics, thermosets as well as thermoplastics, can be converted in high yields to valuable hydrocarbon products. This novel catalytic process runs at 200°C, conversion times are rapid, the process is closed and, thus, nonpolluting, and no highly toxic gas or liquid products have been observed so no negative environmental impact will result from its implementation. Tests on reclamation of composite materials show that epoxy, imide, and engineering thermoplastic matrices can be converted to low molecular weight hydrocarbons leaving behind the reinforcing fibers for reuse as composite reinforcements in secondary, lower-performance applications. Chemical recycling is also a means to dispose of sensitive or classified organic materials without incineration and provides a means to eliminate or reduce mixed hazardous wastes containing organic materials.

INTRODUCTION

Fiber-reinforced composite materials offer high strength and stiffness, low weight, corrosion and fatigue resistance, and tailorability of properties to the structural designer. This unique combination of properties are used to increase the performance profile of military and civilian aircraft and vehicles, and the composite material content of these systems is increasing dramatically as each new generation is introduced. Recent additions to the Air Force inventory, the B-2, F117A, and F-22 (under development), are approaching the definition of "all composite aircraft" [1]. Increasing composites use in military and space

systems is expected to continue far into the next century [2,3] as is their use in commercial applications such as aircraft, recreation, and infrastructure components.

The vast majority of composites used today and projected for the future are polymer based. Most of those composites use thermosetting (crosslinked) polymers such as epoxies, phenolics, bismaleimides, polyesters, cyanate esters, and polyimides. Engineering thermoplastic matrix composites are beginning to be introduced and should see increased use in the future. Once a thermoset part is cured, it cannot be changed. Production parts with delaminations, high void content, or lack of dimensional control must be scrapped. Uncured or prepreg materials are also scrapped in large quantities from cutting losses and expiration of shelf life. There is currently no process available for recycling these materials, so they are landfilled with little regard for environmental effects or considerations for reuse.

The majority of high-performance composites have been developed to be temperature-resistant, stable structures. Their intractable nature makes them even more difficult to recycle or reuse than commodity plastics because of their cross-linked or thermally stable structures. Primary recycling (reuse in equivalent performance applications) of these materials is certainly unlikely, even with engineering thermoplastic-matrix composites. Thermoset-matrix composites cannot be changed once molded to shape because of their cross-linked chemical structure. Thermoplastic-matrix composites can be reformed; however, the severe processing conditions and ply orientation control required in high-performance applications make it unlikely that primary recycling will be applicable to most of those materials.

Secondary recycling (reuse in lower performance applications) approaches can be envisioned for both thermoset and thermoplastic composites. The majority of work on composites recycling that has appeared in the literature is concerned with grinding, chipping, or flaking the composite into suitable size to be used as filler in new molded composite parts [4,5]. Usually, the composite is ground into a fine powder with this approach. While that approach may be satisfactory for automotive sheet molding compounds, which are mostly filler to begin with, it will not provide the full value from the expensive fibers and resins used in high performance composites that may be achievable using other recycling processes. Other processes such as acid digestion or incineration in the case of glass-reinforced composites could be used to reclaim the fibers from some systems [6]. Those approaches generally appear impractical from an environmental point of view. Acid digestion uses harsh chemicals and conditions and creates a hydrocarbon/acid mixture that will require further processing. Incineration (quaternary recycling) is an option for carbon- and aramid-reinforced composites, but destroys what are valuable materials in the process and can be a source of pollution.

Chemical recycling [7,8] appears to be the most economical recycling method for high performance composites. A chemical recycling process separates the polymer from the valuable fibers as low molecular weight hydrocarbons. The fibers may then be reused as molding compounds, and the hydrocarbons reused as chemicals or fuels. Initial laboratory feasibility studies on chemical recycling of a variety of common consumer plastics, composites, and other organic materials show that this recycling process has the potential to economically recycle all types of polymer matrix composite materials. Results from those feasibility studies on composite materials are given in the following sections.

EXPERIMENTAL PROCEDURES

The composite chemical recycling studies were conducted in a prototype continuous feed reactor shown schematically in Figure 1. Catalyst composition and process parameters are proprietary and are not covered in this paper. Each composite feedstock was converted using an identical set-up and amount of catalyst. Gas samples were collected in gas sampling tubes.

Conversion products were analyzed using gas chromatography/mass spectroscopy following the procedure specified in EPA Method 8270 for semivolatile analysis. The conversion products were dissolved in methylene chloride before introduction into the gas chromatograph. Elution peaks were analyzed by mass spectroscopy and identified by matching with a library of 50,000 compounds.

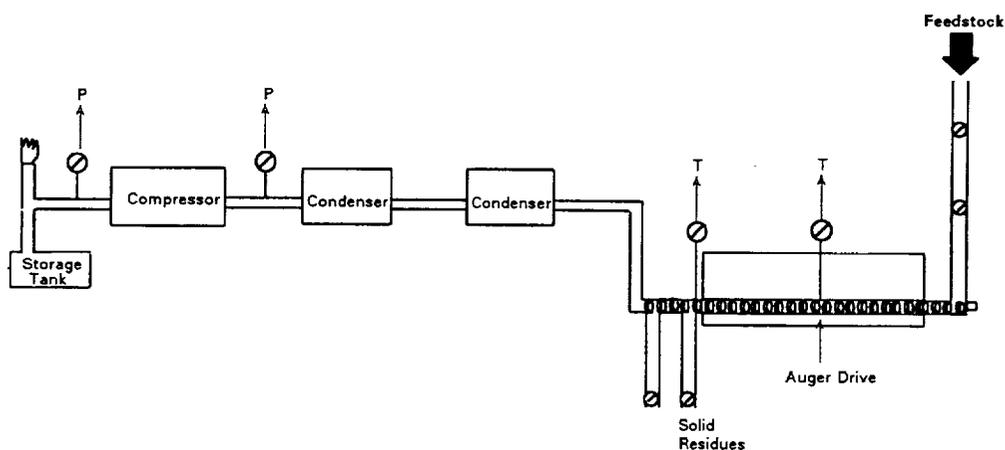


Figure 1. Schematic Tertiary Plastics Recycling System

RESULTS AND DISCUSSION

Two types of epoxy matrix laminates were studied with the low-temperature catalytic conversion process. The first composite was a sample of boron-

reinforced epoxy from an F-15 tail rudder. Samples from the tail rudder skin were pried from the honeycomb core and most of the paint removed before the conversion process. The F-15 boron/epoxy was converted in four minutes leaving 56 weight percent of fiber and glass scrim cloth residue. Separate weights were not obtained for the boron and glass. The epoxy appeared to be completely removed from the composite laminates leaving behind only fibers. The boron fibers were a loose unorganized mass. No evidence of epoxy could be found upon microscopic examination of the fibers.

The chemical composition of the composite used in the F-15 empennage structure has been published by the Air Force [9]. The composition and chemical structures in the Boron/Avco 5505 (now Textron) are given in Figure 2. Major conversion products (>4%) from the F-15 boron/epoxy sample and their chemical structures are given in Figure 3.

Analysis of Avco 5505

Composition		Weight Percent
Boron Fibers		60.1
Fiberglass Scrim Cloth		4.1
Resin Matrix	<u>phr</u>	} 35.8
Ciba ECN 1280	70.0	
Ciba 0510	30.0	
Diglycidyl Ether Bisphenol A	3.0	
Dicyandiamide	5.4	
Crosslinked Elastomer	?	

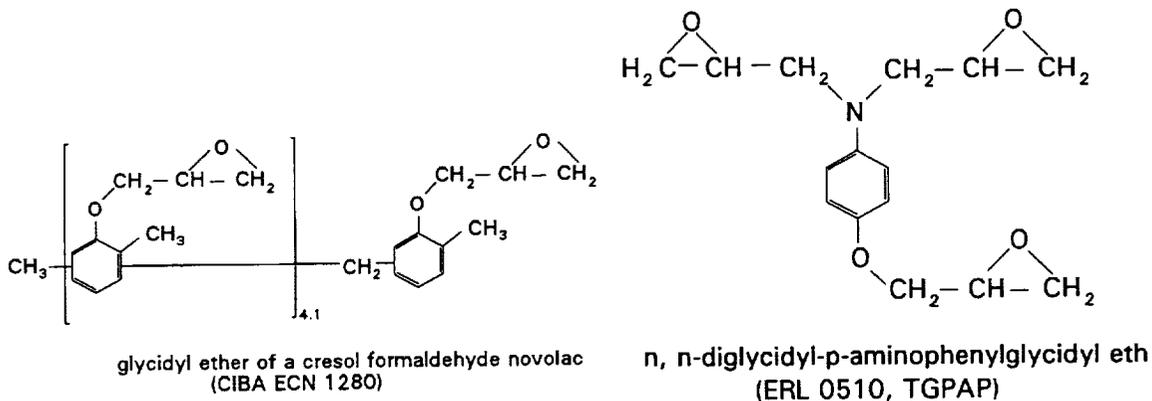
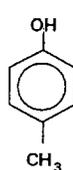
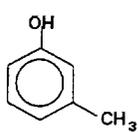
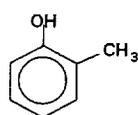
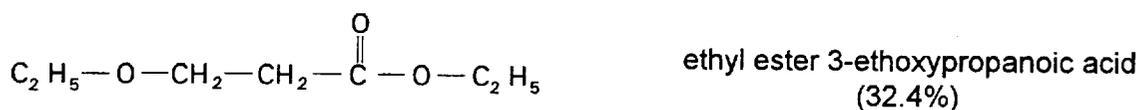
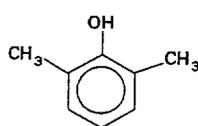
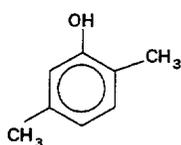
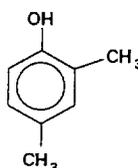


Figure 2. Composition of Avco 5505 Boron/Epoxy Used in F-15 Tail Rudder [9]

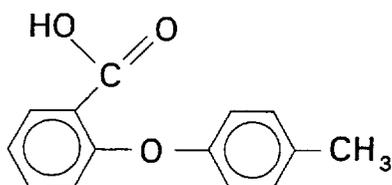
Comparison of the major conversion products from the boron/epoxy F-15 rudder (Figure 3) and the starting epoxide structure shown in Figure 2 shows that the conversion process scissions the methylene and ether linkages to form valuable low molecular weight hydrocarbons from what was an intractable cross-linked epoxy. A high concentration of ethyl ester of 3-ethoxy-propenoic acid is seen. This compound was also seen in the conversion products from other epoxies [10] and appears to be a recombination product from the glycidyl groups found in all epoxy resins.



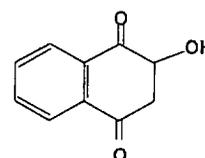
methyl phenols
(5.0%)



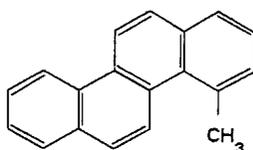
dimethyl phenols
(7.8%)



2-(4-methylphenoxy) benzoic acid
(7.9%)



2-hydroxy-1,4-naphthalenedione
(12.4%)



4-methyl/crysene
(5.4%)

Figure 3. Chemical Structures of F-15 Boron/5505 Epoxy Major Conversion Products

The second epoxy matrix laminate studied was a unidirectional 24-ply carbon fiber-reinforced system from Hexcel Corporation designated F584. The carbon/F584 conversion reaction was complete after 4.5 minutes. The remaining carbon fibers represented 69 weight percent of the original composite. No other residues were observed. On a volume basis, 69 weight percent carbon fibers corresponds to 61 volume percent, which is the normal fiber volume range for this type of composite.

The carbon fibers remained as single-ply sheets that could easily be spread apart. In that form, the carbon fibers are readily reusable as reinforcements for molding compounds. Major conversion components of the F584 epoxy system are given in Figure 4.

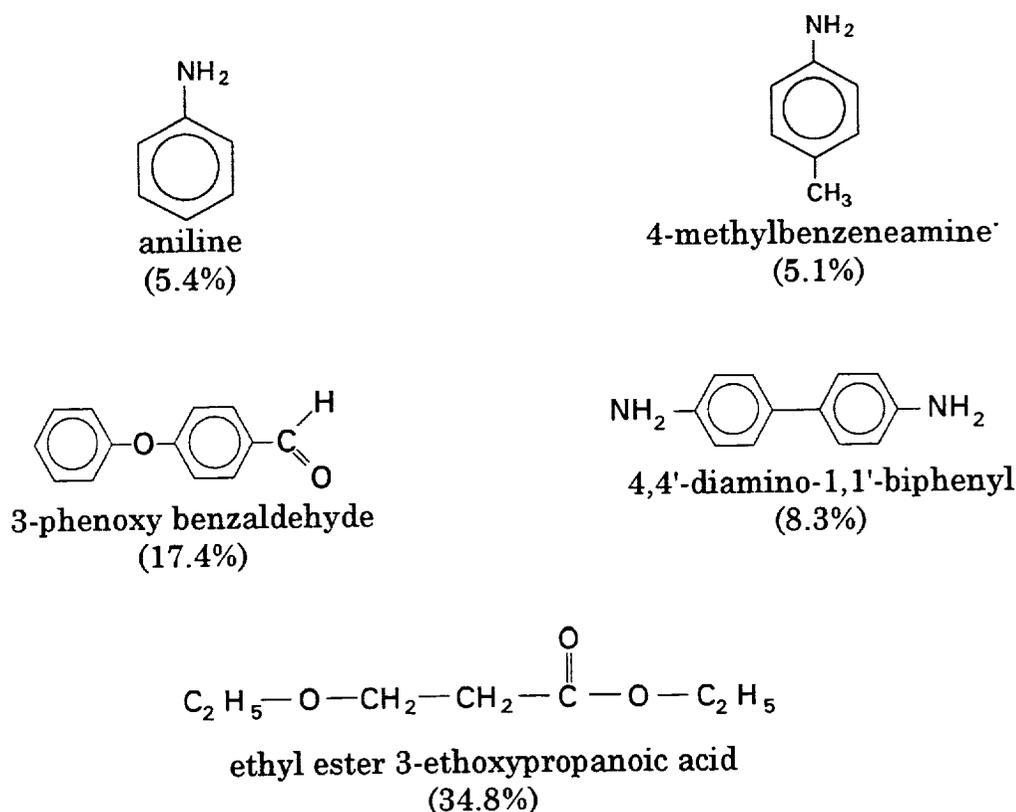


Figure 4. Conversion Products from F584 Epoxy

The starting epoxy components in the Hexcel F584 matrix system are proprietary and unknown to the authors. Examination of the major products for the F584 epoxy (Figure 4) shows that there are several aromatic amine compounds (aniline, methyl aniline, diamino biphenyl), which likely indicates that this epoxy is an aromatic amine-cured system.

Analysis of the gas fraction given off from carbon/F584 epoxy conversion showed 98.4% propylene. Propylene likely comes from the glycidyl groups that have been scissioned from the ether linkages during conversion.

The third composite studied is a high-temperature polyimide matrix system. Polyimide and bismaleimide matrix composite materials are preferred for high-temperature applications near engine ducts and for future aircraft such as the high-speed civil transport. The most common polyimide matrix system in use is PMR-15, which is formed by a condensation reaction between the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid, 4,4'-methylenedianiline, and the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid [11]. The resultant structure is shown in Figure 5.

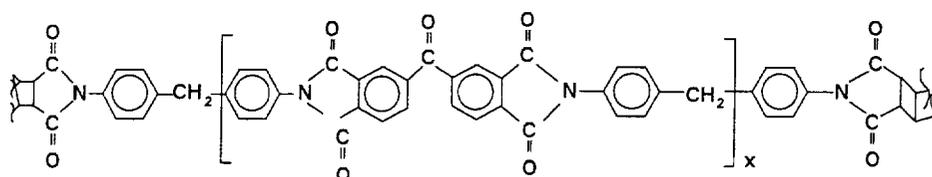
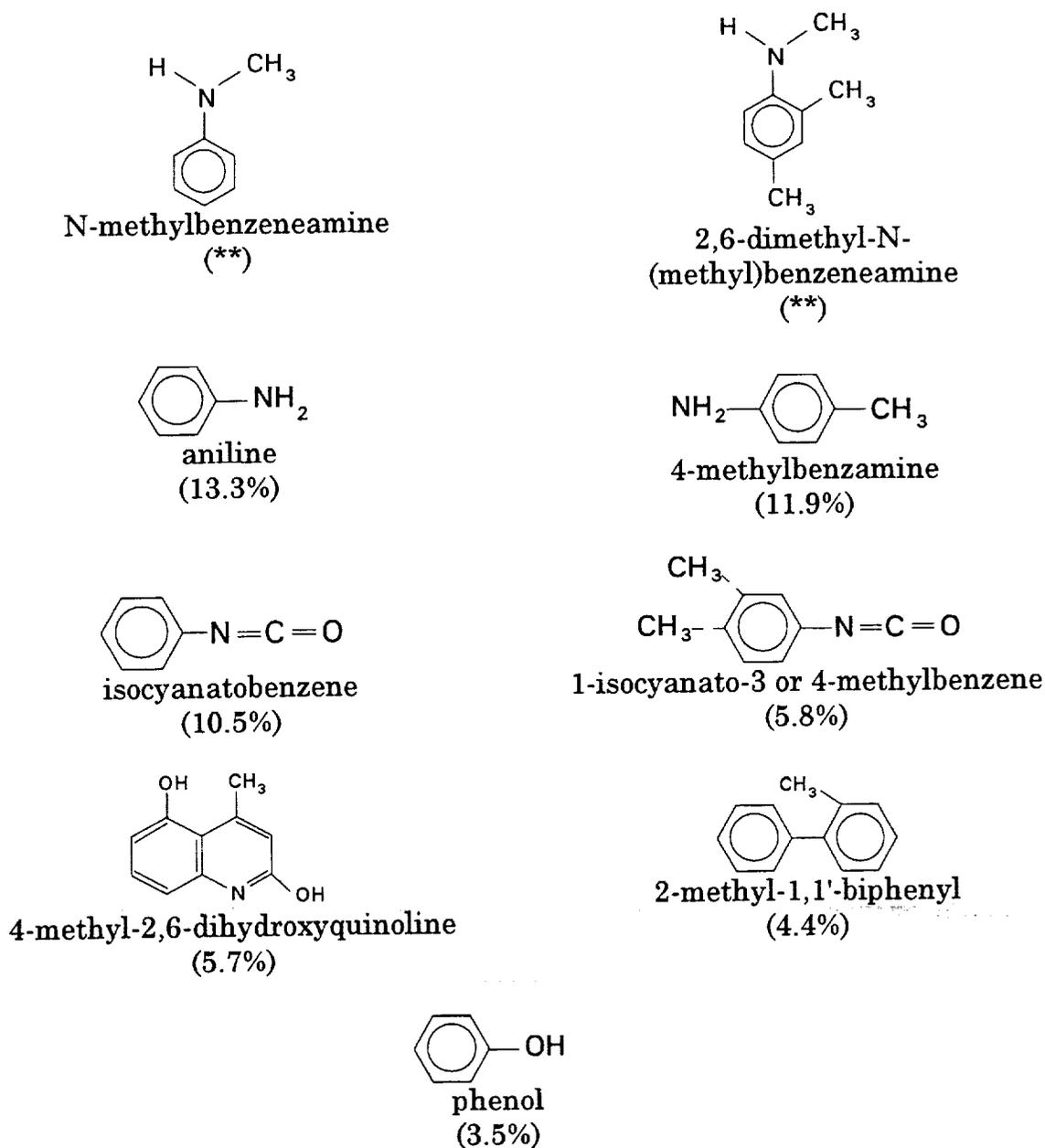


Figure 5. Chemical Structure of Cured PMR-15 Polyimide

The carbon/PMR-15 composite was converted only very slowly. A yellow gas evolved three minutes into the reaction. After 20 minutes, enough tar coated the reaction vessel to take an analysis sample, but the composite was not completely broken down. The persistence of the PMR-15 is a further demonstration of the high thermal stability of these materials. Analytical results for the PMR-15 conversion products are shown in Figure 6.

Comparison of the product structures shown in Figure 6 with the PMR-15 structure (Figure 5) reveals that the catalytic conversion reaction is scissioning the imide rings to make a variety of substituted phenyl compounds and recombination structures. This is an encouraging result and may indicate that even these very stable polymer structures can be broken down completely if the conversion process parameters are optimized.



**Combined total is 28.6%.

Figure 6. Chemical Structures of PMR-15 Conversion Products

The last example is an engineering thermoplastic matrix composite: polyetheretherketone (PEEK) reinforced with carbon fibers. Analysis of the clear liquid evolved from the carbon/PEEK sample and the structure of PEEK are given in Figure 7. Ninety-nine percent of the liquid conversion products from PEEK are phenol and hydroquinone. These are two common and valuable

organic compounds. Producing these compounds in such high yields and purities will likely result in good economics for recycling of PEEK matrix waste components.

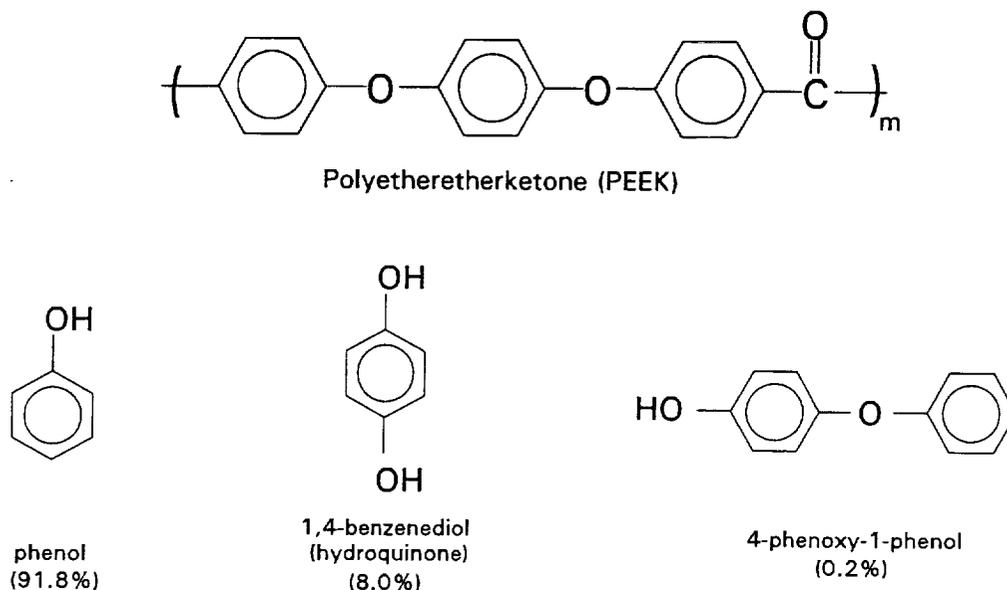


Figure 7. Chemical Structure of PEEK and its Conversion Products

PROCESS ECONOMICS

The economics of low-temperature, catalytic conversion of high performance composites is difficult to assess accurately at this early stage of development. There are numerous unknowns such as gathering and transportation costs for the waste, volumes of waste available, and markets for the conversion products and reclaimed fibers. Nevertheless, it is beneficial to ignore these unknowns and perform an elementary economics analysis to show the economic viability of the tertiary recycling process.

A 10-ton/day unit operated 330 days per year can recycle 6.6 million pounds of composite or about 15% of current DoD production. Such a plant could be expected to be highly profitable if the hydrocarbons were sold at a price equivalent to that of crude oil and the carbon fibers were sold for use in molding compounds at \$2.00 per pound, which is equivalent to the cost of buying virgin glass with the superior properties of carbon fibers.

removing the polymer from the composite mixture, the expensive reinforcing fibers are recovered in a form that allows their economical reuse in molding compounds. This versatile process may be used to solve many current and future solid and hazardous waste problems with organic-based materials. Because the conversion process is totally closed, no adverse environmental effects are produced. In addition, a preliminary economic analysis shows that recovery of valuable hydrocarbons and fibers from these wastes could be highly profitable.

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