ELECTROCHEMICAL POLYMERIZATION AND DEPOSITION ON CARBON FIBERS

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Abstract - *The electrodic polymerization on graphite fibers of a variety of monomers having different types of functional groups has been investigated. An electrodeposition technique has also been developed for polymer coating of graphite fibers running continuously through an electrolytic cell containing polymers with ionizable groups. Unidirectional composite specimens were prepared by embedding the coated fibers in an epoxy matrix, and the effect of the interphase polymer was studied through variations in their impact, interlaminar shear, and flexural strengths in comparison to those of composites fabricated from commercially treated and untreated fibers. It is found that the introduction of the polymer interphase results in significant improvements in composite properties and that the extent of improvements is controlled by the nature of the polymer interphase. The molecular weight, chemical composition, and crosslinking of the interphase polymer are some of the molecular parameters modifying the effects observed. This method of interphase modification has also been applied to minimize the electrical hazards of fiber lofting from graphite composites.*

INTRODUCTION

The remarkable strength enhancement and resistance to fracture that is achieved by the incorporation of strong fibers in low-strength, low-modulus matrix is determined to a great extent by the existence of several polymer-fiber interfaces. Compatibility between the fiber and the polymer matrix is one of the most important considerations in developing useful composites. Adequate bonding between matrix and fiber is essential to permit the fiber to be loaded to its maximum strength. However, the preferential failure of the interface of a composite may increase fracture toughness by deflecting cracks perpendicular to the direction of the fiber alignment. Thus, there exists a dual requirement in the properties required of the interface.

Applications involving graphite fibers have advanced significantly in recent years in view of the fibers being readily available at a realistic price. A major initial drawback in their application for the reinforcement of polymers was the low interlaminar shear strengths that resulted. Work in the area of interfacial relationships in reinforced polymers has led to the development of various surface modification techniques that result in improved compatibility between the fiber and the polymer and led to improved interlaminar shear strengths (1-3). The disadvantage of these surface modification techniques is that the shear strength improvements are attained at the expense of the impact strength.

Research on asbestos and glass-fiber composites has shown that the introduction of a polymer interlayer between the fiber and the polymer matrix leads to signficant alterations in the mechanical properties of composites (4-8). A comprehensive program of research has been initiated in our laboratories to investigate the applicability of electrochemical processes for the formation of such a polymer layer on carbon fibers through electropolymerization and electrodeposition. Electropolymerization involves the polymerization of monomers in an electrolytic cell; electrodeposition utilizes the migration of preformed polymers carrying ionized groups to the oppositely charged electrode. The major advantage of utilizing these electrodic processes is that a uniform polymer layer of controlled thickness and variable structure and properties can be expected to be formed.

The results to-date of our investigation along these lines have amply confirmed the expectations based on the concepts mentioned above (9-12). Only the salient features of these results are summarized here.

In addition to the study of the improvements in mechanical properties of polymer composites arising from the electrochemical coating of the reinforcing graphite fibers, a new scope has been added to our investigation of interphase modification by electrodic processes; it concerns the problem of electrical hazards that could be caused by the release of conductive

fiber fragments from graphite composites (13).

Recent reports from NASA have identified the potential problems that may arise when carbon fibers are accidentally released into the environment, as in the event of a fire involving graphite fiber composites (14). Because of their light weight, airborne carbon fibers can float like dust particles, and if they come to rest on electrical circuits, can cause shorts or arcing resulting in power failures or equipment damage. A prospective solution to these problems resides in devising organic coatings for graphite fibers which can provide, in case of fire, a relatively nonconducting layer of char or other material that might result in fiber 'clumping' minimising the fiber release or, in the event of fiber release, prevent or minimise the chances for electrical contact within electrical equipment. The techniques of interphase modification by electropolymerization and electrodeposition have therefore been extended to form organophosphorus and polyimide coatings on graphite fibers. Such coatings can be expected to promote char formation on the fiber surface. Furthermore, in the case of organotitanate coatings, the formation of a thermally stable and nonconducting layer of titanium dioxide would also be expected. The first part of this study (15) is also included here.

BACKGROUND

In the present investigation, the effect on composites properties of introducing an inter-layer of polymer on carbon fibers by electrodeposition or electroinitiated polymerization has been studied. In discussing interface tailoring, it is useful to recognize that the fiber and matrix are bridged in the composite not by a fine interface but by an interphase polymer. The properties of the interphase polymer can be significantly different from the bulk polymer properties. When a polymer coating is formed on the fiber by electrodeposition, the properties of the interphase are further modified by the polymer coating.

Electropolymerization

With electrochemical polymerization, the electrode process is the source of active species that initiate polymerization. Following the early lead of Kolbe (16), it was established long ago that free radicals are produced in electrochemical oxidation or reduction; but it is only recently that such radicals, and other species formed electrolytically, viz., cations and anions have been used to initiate polymerization reactions. This allows their rate of generation to be controlled, and mechanisms to be studied in the formation of both linear and crosslinked polymers. An additional feature is the effect of the field of the electrode on the growth of the polymer chain. While previous studies on electropolymeriza-tion have almost exclusively been concerned with polymerization in the reaction solution, Bogenschütz and co-workers demonstrated that metal (electrode) surfaces can be coated by the polymers formed (17-19) during electropolymerization. These and subsequent studies of polymerization on electrode surfaces were reviewed recently (20).

The research on the electropolymerization of monomers on graphite fiber and on the effects of such a polymer interphase on the properties of polymer composites made from the coated fibers was seen to offer many advantages. Polymerization can take place on graphite fiber electrodes, with initial wetting of the fiber by the monomer possibly leading to better adhesion of the polymer formed thus. The structure and properties of the polymer coating could be varied by employing different vinyl and cyclic monomers not only in homopolymeri-zation but also in copolymerization, with and without crosslinking monomers. Furthermore, in electropolymerization occurring by electrodic processes initiated on graphite fiber electrodes, chemical bond formation, i.e., polymer grafting to the graphite fiber, may also be introduced. These are advantageous features because of the potential interphase in graphite fiber composites. As was pointed out earlier, these properties of the interphase polymer are of critical importance in determining the behavior of composites prepared from the fibers.

Electrodeposition

In principle, both anodic and cathodic deposition of polymers should be possible. In anodic deposition, the electrode to be coated is suspended as the anode of an electrical circuit in a bath containing the polymer. In the current study, electrodeposition has been conducted using graphite fiber as the anode.

The polymer used for anodic deposition has free acid or acid anhydride groups attached to the polymer chain. At this stage, the polymer is usually hydrophobic. The hydrophobic-hydrophilic character of a resin can be varied to some extent by the chemical groups incor-porated into the backbone of the polymer chain. The acid groups used for these materials are generally carboxyl groups. When the acid groups are neutralized with a base, a salt of the polymer is formed which can ionize in water. This polymer salt can be water soluble or at least water dispersible. When dispersed in water, the particle sizes are on the border-line between solution and colloids.

An electrodeposition polymer can be visualized as a suspension of polymer particles with the ionized carboxyl groups sticking out of the surface so that the particle carries a negative charge. The repulsion between like charges keeps the polymer dispersed in water. These charges also enable the particles to migrate towards the anode during electrodeposition. The efficiency of polymer deposition depends on the ratio of the molecular weight of the polymer to the number of free acid groups.

A wide variety of polymers with anionic, carboxyl functional groups were selected for electrodeposition (12). The molecular parameters that were varied in these polymers were (i) the molecular weight, (ii) the chemical composition, (iii) length of side chains, and (iv) crosslinking. The reactivity of the carboxyl functions with epoxy groups prompted the choice of epoxy resin as the matrix polymer. It was expected that the carboxyl groups of the electrodeposited polymer will react with the epoxy matrix to form a strong interfacial bond. The various factors pertaining to the effect of interphase polymers on composite mechanical properties have been studied by the introduction of an appropriate range of copolymers at the interface.

RESULTS AND DISCUSSION

Electrodeposition

Uniform polymer coatings were formed on graphite fibers by electrodeposition operating at 10 volts, 2.5% solids content in electrolytic bath, 1 minute deposition time and a washing period of 5 minutes in the solvent medium used in the electrolytic bath. Equipment was built for continuous deposition on fiber tows. The exterior layer of electrodeposited polymer was easily washed off in 5 minutes washing time; but the residual inner layer of polymer was not removed even after 30 minutes of washing.

From a perusal of the many studies that have been made on the mechanism of carboxylate-stabilized systems (21,22), it is seen that the following reactions can contribute to the formation of a polymer film on the graphite fiber anode:
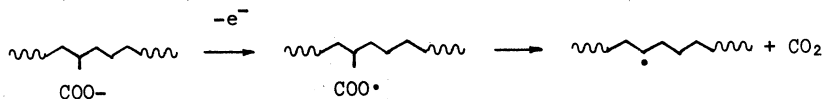
(1) Electrolysis of water

  a) $H_2O \rightarrow OH\cdot + H^+ + e^-$

  b) $2\ OH\cdot \rightarrow H_2O + O\cdot$

  c) $2\ O\cdot \rightarrow O_2$
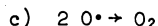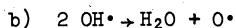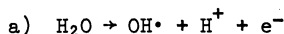
(2) Reaction of the Carboxylate ion with H^+

$$\sim\sim\sim C \overset{O}{\overset{\|}{-}} O^- + H^+ \longrightarrow \sim\sim\sim C \overset{O}{\overset{\|}{-}} OH$$
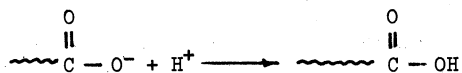
Thus the protonation of the soluble polycarboxylates results in the precipitation at the anode of the insoluble acid. Furthermore, concentration coagulation could also occur at the electrode. However, the initially precipitated and deposited polymer layer would be "compacted" on the fiber surface and will be present as the insoluble acid film while the exterior layers including those resulting from concentration coagulation would be more easily solubilized by the basic solvent medium.

Anodic oxidation of the carboxylate by a Kolbe reaction is another possible reaction in anodic deposition (22):

$$\sim\sim\sim \underset{COO-}{\wedge\!\!\!\wedge} \sim\sim\sim \xrightarrow{-e^-} \sim\sim\sim \underset{COO\cdot}{\wedge\!\!\!\wedge} \sim\sim\sim \longrightarrow \sim\sim\sim \wedge\!\!\!\wedge \sim\sim\sim + CO_2$$

The polymer radicals produced thus can recombine to form crosslinked polymer or interact with the graphite anode to form a graft polymer. Both types of reaction would lead to the formation of an insoluble polymer layer strongly bonded to the fiber surface.

Composite Properties

Results for composite specimens containing 50 percent volume fraction of fiber (V_f) were read from plots of interlaminar shear and impact strengths against V_f. These are summarized in Table 1 (12).

The most striking feature of the results is the general improvement in shear, impact and flexural strengths caused by the incorporation of an electrodeposited polymer interphase. Thus increase in shear strengths is not accompanied by a corresponding loss in impact strength as is generally observed in various methods of surface treatment. Since the

various steps in this new technique have not been optimized, it is the relative improvements
in strength values determined in this study which are of significance. The results are
similar to those noted in other studies of the effect of the interfacial layer on toughness
and impact strength of glass and asbestos reinforced composites (4,6,8). In these studies
also, encapsulating the filler or fiber reinforcement by a band of resin capable of energy
absorption was indicated to be highly desirable.

TABLE 1. Effect of electrodeposited polymer on graphite fiber composite
properties (V_f: 50%)[a] (12)

Electrodeposited Polymer[b]	Interlaminar Shear Strength, MPa	Impact Strength, kJ/m^2	Flexural Strength, MPa × 10^{-1}
SMA 1000	68	57	110
SMA 2000	59	72	110
SMA 3000	62	56	100
PA 6	61	42[e]	100
PA 18	52	44[e]	91
AN 119	48	86	90
AN 139	59	130	95
AN 169	54	140	86
None (CG-3)[c]	34	63	78
None (CG-3)[d]	52	43	96

a) Fortafil fiber, (170 GPa modulus); epoxy matrix (Diglycidyl ether of
    Bisphenol-A cured by metaphenylenediamine)

b) Copolymers of maleic anhydride with styrene (SMA), hexene (PA 6),
    octadecene (PA 18), and methyl vinyl ether (AN); fully described in
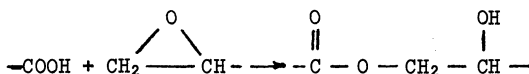   text.

c) Untreated, Fortafil CG-3 fiber.

d) Surface-treated Fortafil CG-3 fiber.

e) Fibers electrocoated in modified apparatus.

The observed improvement in interlaminar shear strength can be taken as a measure of the
increased adhesion between the carbon fiber and the epoxy matrix resin. At least two factors
can be recognized in the electrocoating process that could have contributed to better
adhesion. One is the efficiency of deposition of charged polymers on the fiber surface to
produce a uniform coating that adheres well. Scanning electron micrographs do attest to the
uniformity of the polymer coating obtained. As the polymer layer is formed, the increased
electrical resistance of the coating directs further coating to uncoated areas which are
more conducting. A uniform coating free of pin holes also indicates that the washing process
did not materially alter the uniformity or completeness of the polymer coating.

The polymer coating on the surface of carbon fibers makes the fibers compatible with the
organic polymer matrix. In the present case, where an epoxy resin is used, the possibility
of chemical interaction between the carboxyl functional groups on the copolymer coating and
the epoxy functional group of matrix resin must be taken into account. At the temperatures
used in preparing the composite specimens, the esterification of -COOH by the epoxy group
is a facile reaction:

$$-COOH + CH_2 \overline{} \overset{\displaystyle O}{\overset{\displaystyle /\backslash}{CH}} - \longrightarrow -\overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - O - CH_2 - \overset{\displaystyle OH}{\overset{\displaystyle |}{CH}} -$$

The carbon fiber-epoxy matrix interface is thus bridged by a well-adhering copolymer layer
which is also chemically bonded to the epoxy matrix. Improved adhesion and increased inter-
laminar shear strength are the consequences of electrodeposition.

The basic mechanism described here suggests the possibility of using polymers with appropri-
ate functional groups which can interact with the matrix polymer after electrodeposition.
Amino functional groups, for example, can be reacted with epoxy polymers. Electrodeposition

of cationic amino polymers on carbon fiber cathodes can produce such coatings. Or, anodic electrodeposition of a butadiene-maleic anhydride copolymer can leave the unsaturation on the backbone of the copolymer to react with a polyester matrix. Such extensions of the electrocoating process are part of our continuing investigations.

The polymers used for electrodeposition were a series of copolymers of maleic anhydride. Styrene-maleic anhydride copolymers, SMA-1000, SMA-2000, SMA-3000 of average molecular weight about 1600 were obtained from ARCO. The ratio of styrene to maleic anhydride in these copolymers was 1:1, 2:1, and 3:1 respectively. Other copolymers used were PA-6, PA-10 and PA-18 (Gulf) which are 1:1 low molecular weight copolymers of maleic anhydride with hexene, decene and octadecene respectively, and Gantrez AN 119, AN 139 and AN 169 (GAF) which are similar 1:1 copolymers of maleic anhydride and methyl vinyl ether, with increasing molecular weights, 500,000, 750,000 and 1,250,000, respectively.

For polymers of the same chemical composition, a number of molecular features of the inter-phase polymers seem to have varying effects on composite properties. Undoubtedly these variations are related in turn to the physical and mechanical properties of the polymer interlayer. In the SMA copolymer series, the ratio of styrene to maleic anhydride is varied from 1:1 to 2:1 to 3:1 in SMA 1000, SMA 2000 and SMA 3000 respectively. The comonomers in PA 6 and PA 18 are hexene-1 and octadecene-1 respectively; thus while the backbone has the same structural unit in both the α-olefin copolymers of maleic anhydride, the side chains are much longer in PA 18 than in PA 6. In the case of the methyl vinyl ether-maleic anhydride copolymers, the molecular weights increase progressively from 500,000 in AN 119 to 750,000 in AN 139 to 1,250,000 in AN 169. A wide range of controlling parameters is thus available in modifying the electrodeposited polymer film properties. It is conceivable that an independent evaluation of the properties of the polymer film on graphite fiber can be conducted which could then be correlated with corresponding changes observed in composite properties.

Electropolymerization on graphite fibers (11)

A variety of monomer-solvent-electrolyte systems were studied to determine the conditions necessary for forming a polymer coating on graphite fibers by electropolymerization. Using commercially available graphite fibers having different mechanical properties (Thornel, Fortafil and Hercules) as electrodes, it became apparent that graphite fibers were a very good substrate for electropolymerization. Polymer coatings, many visually observable, formed quickly within seconds after application of voltage with no apparent differences observed between different fibers.

Polymer presence was observed by weight increases of the fibers after polymerization, scanning electron micrographs of the polymer coatings, and, where possible, infrared spectral analysis of polymer extracted from the fibers. In conducting these polymerizations it is necessary to select a solvent-electrolyte system which is capable of forming a solution with the monomer and which has sufficient current conducting properties. Dimethylformamide and dimethyl sulfoxide proved very useful in this respect as solvents. Both homopolymerization and copolymerization in aqueous and nonaqueous solvent systems were observed to form coatings. Monomer containing a variety of functional groups – terminal vinyl, carboxylic acid, anhydride, epoxy, and aziridinyl – were observed to form coatings. It is interesting that even a liquid copolymer, VTBN (vinyl-terminated butadiene-co-acrylonitrile), could be further polymerized by this technique.

While the electroinitiated polymerization of vinyl monomers in solution is well established (23-26), the polymerization observed here of monomers containing cyclic functional groups such as epoxy and aziridinyl groups is novel and is similar to the electroinitiated polyester synthesis from the reaction of propylene oxide with phthalic anhydride (27). Detailed studies of this new electroinitiated polymerization of aziridines (28) have yielded interesting results regarding the mechanisms of initiation and propagation, and are reported elsewhere. It has also been found that the polymerization of acetylenic and nitrile groups can be initiated electrochemically. For example, phenylacetylene and benzonitrile are polymerized to yield linear polymers with a conjugated backbone, $\{(C_6H_5)C = CH\}_n$ and $\{(C_6H_5)C = N\}_n$ respectively (29,30).

Electroinitiated polymers are formed on graphite fiber both when it is used as anode or as cathode. The mechanisms of polymerization would be dependent on the locus of polymerization. It should be noted that the relevant properties of the polymer coating could be altered by the mechanism of polymerization. Therefore, in addition to the available choice of monomers and comonomers of varying chemical structure and reactivity, and the solvent media, the use of graphite fibers as anode or cathode is important as a controlling parameter in modifying the properties of the electroinitiated polymer formed on the fibers. Polymerizations conducted so far have produced polymer coatings with a wide range of chemical and mechanical properties which could be used to modify the carbon fiber-polymer matrix interphase of composites prepared from fibers treated by electropolymerization.

Chemical bonding of the matrix resin to the electroinitiated polymer interphase could be achieved by residual epoxy, carboxylic acid or aziridinyl functional groups present in the coating after electropolymerization. Acrylic acid, EPON 828, or glycidyl methacrylate are

examples of monomers that could be used for this purpose. Such a possibility is particularly interesting if the polymer coating formed initially in electropolymerization is chemically bonded, i.e., grafted to the graphite fiber surface.

Polymer Grafting

Chemical bonding of the polymer to the fiber was investigated by weight increase of fibers after an electropolymerization treatment and extraction in a known solvent, followed by scanning electron microscopy. Fortafil 3T and 5T untreated carbon fibers were subjected to electropolymerization followed by continuous extraction for a period of 120 h to ensure removal of all the unbonded polymer which would be soluble. Observed weight increases were used as preliminary evidence of the presence of a grafted polymer. Scanning electron micrographs of the extracted fibers confirmed the presence of unextractable polymer. In the case of monomers such as methyl methacrylate which would be expected to yield linear, soluble polymers, the retention of insoluble polymer on the fiber surface can be taken as strong evidence of grafting, though it cannot be useful as evidence for grafting in the case of polyfunctional monomers that would lead to network polymers. In this manner, it was found that diacetone acrylamide, methyl methacrylate and styrene did form graft polymers on graphite fibers. When grafting occurred, it was observed with both high modulus, 5T, and low modulus, 3T graphite fibers.

It is not unexpected that grafting should occur on graphite fiber, exposed as it is to the electropolymerization medium containing monomer during the generation of reactive species by electron transfer at the electrode surface. The mechanism of grafting was not investigated. Organic functional groups such as -COOH and -OH, even if only in traces, are present on carbon fibers. These groups are capable of forming free radical sites, for example, by chain transfer. Initiation of free radical polymerization or termination by combination of growing polymer radicals at these sites could lead to the observed polymer grafting.

The formation of grafted polymer on the graphite fiber assumes added significance in the possible effects it can have on composite properties. For example, Brie and co-workers increased the shear strength of polyester and epoxy resin composites containing graphite fibers by grafting to the fiber a carboxylated polymer compatible with the matrix resin or an elastomeric polymer (31,32). In their experiments, the fibers were treated with ozone to form surface carboxyl groups prior to the grafting reaction with monomers under gamma radiation.

Polymer Stereoregularity

Apart from the variations in the electron transfer properties of the electrodes, a significant factor in the role of the electrode in electrosynthesis is the adsorption of reactants and products (26). It is conceivable that stereoregularity in the polymer could be introduced by polymerization of monomer adsorbed on graphite fibers or if the monomer were oriented on approaching the field of the electrode. Methyl methacrylate monomer was selected to examine the occurrence of stereoregulation because its NMR spectra are well defined and it is known that α-methyl resonances for isotactic (I), syndiotactic (S), and heterotactic (H) triads appear at $\tau = 8.67$, 8.90 and 8.79 respectively. Using this technique on poly(methyl methacrylate) extracted after 5 second polymerization on graphite fibers, it was found that the polymer contained about 40% isotactic and 10% syndiotactic triads (11). The polymer formed in solution, on the other hand, had 25% each of isotactic and syndiotactic and 50% of heterotactic triads, as would be expected for a completely atactic polymer.

It is relevant to draw attention to a related observation of Bogenschütz in studies of electropolymerization of diacetone acrylamide (19). In this study, the electropolymerized layer of polymer on metal electrodes was examined by X-ray diffraction. It was observed that the diffuse halo of the polymer changed to sharp lines on annealing the polymer above the melting point at 200°C, indicating that stereoregular polymer was formed in electropolymerization.

Composites of Coated Fibers

The principal effect of electropolymerization of monomers on graphite fibers is expected to be in altering the interfacial bond strength of the coated fibers when incorporated in a composite. The single-fiber pull-out test was unsuccessful in determining the changes in fiber-matrix adhesion in these systems. This was apparently so because in these tests, failure occurred, partly at least, in the matrix when interfacial bonding was strong (33). Therefore, the interlaminar shear strengths of composites prepared from Hercules type AU carbon fibers coated by electropolymerization of a series of different monomer systems were measured. Systems were selected to include representatives of the various types of monomers in both aqueous and nonaqueous solvent-electrolyte systems encountered during the screening process. Composites prepared from Hercules type AU, untreated, and type AS, commercially surface treated, graphite fibers without further treatment were also tested for comparison. It could be seen from these results, that incorporation of a polymer interlayer on graphite fibers prior to embedding them in a polymer matrix has significantly affected the interlaminar shear strength of the composite. Although further detailed studies are needed to

standardize the electropolymerization technique in order to obtain optimum results. The resulting composite mechanical properties were found to be a function of the monomer, solvent, polymerization time, fiber content, and post-electropolymerization treatment of the coated carbon fibers (11).

The results of impact tests on notched specimens, provided further evidence that the carbon fiber-polymer matrix interface could be modified by electropolymerization. As was observed in the shear tests, significant differences occur in the impact strength as well as in strength variations with volume fraction of fibers that had undergone different treatments.

It should prove extremely valuable to standarize electropolymerization conditions to control polymer film properties. Considering the importance of high temperature resistant graphite composites, it is also desirable to study the electropolymerization of vinyl-terminated phenyl quinoxaline oligomers, acetylene-terminated polyimide oligomers, aminophthalic acids, and similar other intermediates for the synthesis of temperature resistant polymers on graphite fibers. Investigations along these lines of polyimide intermediates have confirmed the expectations outlined above (34).

Fiber release from composites

This program of research, initiated with emphasis on improvements in mechanical properties, has also been extended to minimize the hazards of release of electrically conductive fiber fragments from graphite composites (34,15). As mentioned in the introduction, precursor coatings were formed on graphite fibers by electropolymerization/deposition of organophosphorus compounds and polyimide intermediates. The thermal oxidative behavior of composites incorporating the coated fibers was then studied by thermogravimetric analysis.

The data for weight loss in a Perkin TGS-1 thermobalance in flowing dry air (25ml/min), at a heating rate of 10°C/min are presented in Fig. 1.
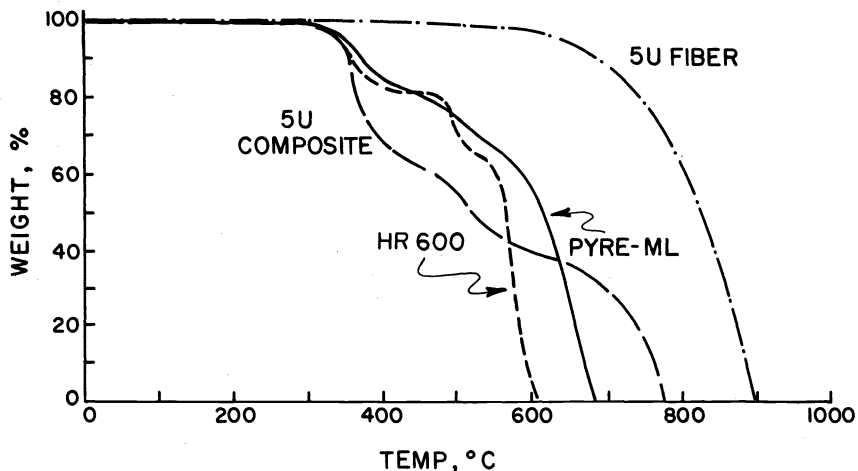

Fig. 1. Dynamic TGA of graphite-epoxy composites prepared from untreated and treated Fortafil 5u fibers. The TGA curve for the bare 5u fiber is also shown for comparison.

Several interesting observations can be made. The fiber decomposition in both polyimide (Pyre-ML and HR-600) coated fiber composites occur at temperatures about 100°-200°C lower than is observed in the untreated fiber composite. This suggests that the decomposition of the polyimides in some manner catalyzes the oxidation of the fiber. The thermal stability of the graphite fiber is thus reduced, and with it, the potential for its survival and release during combustion of the composite.

A similar behavior is observed with fibers electrocoated with ammonium polyphosphate (Phoschek 30/P, Monsanto) (13,15). On the other hand, a coating of tetrakis(hydroxymethyl) phosphonium sulfate (THPS-75, Hooker) results in the formation of a significant amount of char on the fiber after the matrix resin is decomposed. This has the effect of binding fiber fragments into clumps and thus reduces their susceptibility to be released as floating fine fragments. Titanium di(dioctyl pyrophosphate) oxyacetate (KR138-S, Kendrich) also leads to the formation of char on the fiber. Furthermore, a residual, noncombustible, electrically insulating layer of titanium dioxide is also left on the fiber. The electrical hazards of fibers covered thus are minimal.

All of the effects described above could be seen as either preventing the release of carbon fibers into the environment, or resulting in a fiber having reduced conductivity, thereby preventing electrical contact once released.

It is obvious that a great deal of further study will be necessary to answer questions raised by this investigation. Future research should be directed toward determining the effect these coatings have on the electrical conductivity of the fiber, both before and after thermal decomposition of the matrix resin. Also, since the coated fibers are to be used in composites, a study of the composite mechanical properties would be essential. Further study of the mechanical and thermal oxidative properties of carbon fibers treated by electrochemical means would be very useful in gaining an understanding of the behavior of the fiber in the composite.

CONCLUSIONS

The introduction of a polymer interphase by electrodeposition of ionizable polymers on graphite fibers results in significant improvements in composite strength and toughness when the coated fibers are incorporated in an epoxy matrix. The molecular features of the interphase polymer offer a range of controlling parameters that influence the extent of improvement achieved. This novel technique can be extended to boron fibers. Similar results are observed by electropolymerization of monomers on graphite fibers. The concept of interphase modification can be expanded to deal with other properties of composites. Thus, the thermal oxidative behavior of the graphite fiber in the composite can be modified by formation of appropriate precursor coatings by electrodic processes. Consequently, the potential electrical hazards of conductive fiber fragment release can be minimized.

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