^{13}C NMR Analysis of the Effects of Electron Radiation on Graphite/Polyetherimide Composites

FINAL REPORT

NASA Grant NCC1-115

ABSTRACT

Initial investigations have been made into the use of high resolution nuclear magnetic resonance (NMR) for the characterization of radiation effects in graphite and Kevlar fibers, polymers, and the fiber/matrix interface in graphite/polyetherimide composites. Sample preparation techniques were refined. Essential equipment has been procured. A new NMR probe was constructed to increase the proton signal-to-noise ratio. Problem areas have been identified and plans developed to resolve them.

TABLE OF CONTENTS

I. INTRODUCTION

During recent years, there has been considerable interest in fiber-reinforced polymeric matrix composites. The use of composites for aircraft structural components has increased due to their outstanding combination of high strength, high modulus, and low density. In addition, fabrication techniques permit the tailoring of these materials to meet specific load and stiffness requirements. However, if these composites are to be utilized as efficient, high performance materials in aerospace applications, their long-range radiation durability must be established.

Initial performance studies focused on the properties of the fibers and the polymeric matrix, but it was soon realized that the interactions at the fiber/matrix interface were highly significant. Since interfacial bonds transmit stress between the fiber and the matrix, the mechanical properties of the material may ultimately depend on the integrity of the interface. The interface also occupies a prominent role in the determination of the modes of failure and the behavior at failure of the material. (1,2)

In order to understand the modifications to the composite caused by radiation, characterization of the interface in terms of its chemical behavior must be accomplished. High energy electrons interact with the composite by exciting the bonding electrons of the material to higher energy states or by ionizing the atoms. This produces radicals or ionic systems. The subsequent molecular changes caused by the radiation-induced

radicals may alter the mechanical properties of the material.

The focus of this project was to investigate the use of high resolution nuclear magnetic resonance (NMR) measuring techniques to characterize and evaluate the fiber/matrix interface before and after irradiation with 1-MeV electrons. NMR affords the opportunity to identify and relate the electronic and geometric structure of the effected molecules to radiation-generated changes in the properties of the material.

In order to accomplish these long-range goals, the first year research effort described in this report involved optimizing NMR techniques for the study of pulverized graphite and Kevlar 49 fibers, graphite/Ultem composites, and polymers (Ultem, Mylar, Kapton, and Lexan). Baseline characterization studies of these materials were initiated. This work provided the necessary groundwork for further studies.

II. SAMPLE PREPARATION

In determining the sample preparation techniques to be used, the requirements of both the NMR spectrometer and the electron accelerator must be considered. The target area of the accelerator is approximately 15 cm X 20 cm which restricts the amount of sample to be irradiated, yet sufficient quantities of sample must be generated in order to detect an NMR signal.

It has been established that pulverization of the fibers, polymers, and composites is necessary in order to maximize the volume of material packed into the NMR tube and therefore to maximize the NMR signal. Due to the requirements of the accelerator facility, the pulverization must be done after irradiation. The pulverization must also be performed as quickly as possible in order to minimize the time the samples are at room temperature between cessation of irradiation and the NMR measurements. It was found that standard grinding techniques could be used provided that the samples were cut into small pieces and ground with frequent additions of dry ice.

III. EQUIPMENT

Part of this project included the procurement of a new pulse programmer which was essential to the planned crosspolarization-decoupling experiment to observe the ^{13}C spectra. The programmer was delivered seven months late. The company, NOVEX Inc., went out of business soon after delivery. To this date, the programmer fails to operate properly. (NOVEX Inc. had been selected as the supplier because they had manufactured most of the other components of the spectrometer and we were concerned about compatibility.)

The magic angle spinning apparatus which is necessary to accomplish high resolution NMR is operational. However, it is also necessary to attain adequate field stabilization. At this time, the field stabilization equipment still allows a field drift of approximately 3 gauss/10 kilogauss per hour. This degree of drift does not permit the magic angle spinning technique to achieve the needed line narrowing.

Baseline measurements of the proton (hydrogen) spectrum in various polymers (Ultem, Mylar, Kapton, and Lexan) and in Kevlar 49 fibers were attempted using the previous pulse programmer while efforts were being made to resolve difficulties with the new pulse programmer. During these investigations, the existence of a small but discernible proton signal in the probe itself, due to the presence of plastics and epoxy, was discovered. The broad proton lines and relatively low signal-to-noise in the materials to be studied required the use of high powers and long-term averaging. While greatly improving the signal-to-noise level,

this also magnified the normally insignificant background signal from the probe materials. In many cases, the background signal was the same order of magnitude as the desired signal. This problem was solved by the construction of an all-new probe.

Each step in the probe construction was carefully monitored to eliminate all materials containing the hydrogen atom (protons). An etching technique (hydrofluoric acid and coil-shaped wax resist patterns) was used to make glass coil forms. A new circuit was also designed to maximize signal-to-noise by improving impedance matching, with an emphasis on reducing the coil's impedance and any stray capacitance which could reduce efficiency.

The new probe was tested using Ultem and found to have an acceptable signal-to-noise ratio. The new probe design also yielded a nearly ideal resonance frequency response curve and good tuning characteristics.

IV. CONCLUSION

Despite the development of the new probe, the field drift problem mentioned previously (3 gauss/10 kilogauss per hour) smeared out any detail in the proton spectrum. (The entire proton spectrum is only 10 ppm wide or about 0.1 gauss in a 10 kilogauss field.) We were unable to achieve the desired high resolution conditions. With such featureless proton spectra it was not possible to discern any differences between the various samples of the study.

This project was plagued with a series of problems including the late delivery of the pulse programmer which does not yet function, field stabilization difficulties, and the necessity of developing a new probe, which made it impossible to obtain any usable results within the time constraints allowed. With more time and resources the field stabilization problem and pulse programmer problem can be solved and high resolution conditions can be reached.

Our plan is to continue this project without NASA funding and to ultimately achieve the goals outlined in the proposal.

REFERENCES:

1. L.J. Broutman, Interfaces in Composites, ASTM STP 452, American Society for Testing and Materials, 27 (1969)

2. G.A. Cooper and A. Kelly, Interfaces in Composites, ASTM STP 452, American Society for Testing and Materials, 90 (1969)