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Advanced materials are being implemented in many Army systems. These systems require new non-destructive techniques for assessing in service degradation. Secondly, techniques are required to assess material integrity during manufacturing. IAP Research proposes a NDE technique based on Brillouin Scattering that is capable of determining changes in elastic constants of polymer based composite materials and monolithic composite materials. The change in elastic constants can then be used to predict component mechanical property degradation caused by thermal or low velocity impact damage. In the case of processing feed back the technique will allow for the in-situ evaluation of the effect of processing variables on mechanical properties.

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## SECTION 1

### INTRODUCTION & EXPERIMENTAL DETAILS

In a Brillouin experiment, a laser beam interacts with a sample - the composite in our case - and the energy of the inelastically scattered photons are measured relative to the incident beam. The resulting spectrum is a record of the intensity of the scattered light corresponding to specific shifts in energy. These energy shifts are related to the structural and molecular characteristics of the composite and reveal acoustic excitations in the medium.

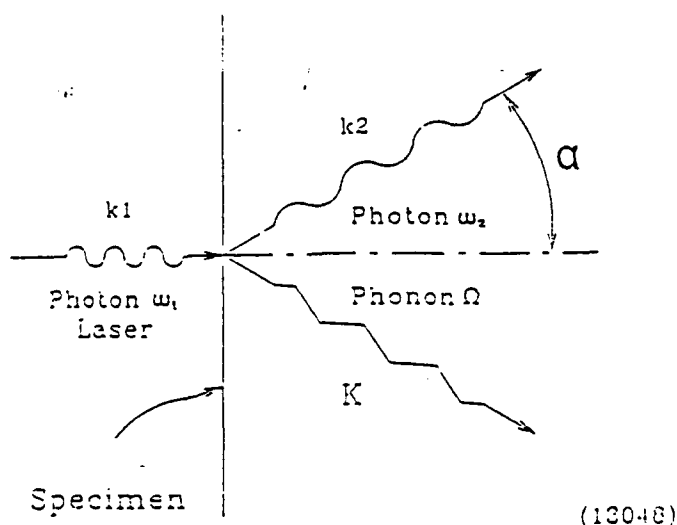
Brillouin scattering has been used in the laboratory for several years to study basic acoustic properties of various material systems such as semiconductor films, superconductors, dielectrics and metals. The motivation behind this project has been to demonstrate the utility of this technique for commercial applications. This includes identification of commercial applications and adaptation of the instrument to industrial environment. In Phase II proposal we detail some of the potential commercial applications and issues involved in the industrialization.

#### 1.1 BACKGROUND

This process can be described in three steps as shown in Figure 1. In step 1, an incident photon of wave vector  $k_1$ , frequency  $\omega_1$ , is incident on the material under study. Step 2 involves the interaction between this photon and the material in which sound waves of frequency  $\Omega$  and wave vector  $K$  are created or destroyed. In step 3, the photon is scattered into a new state with wave vector  $k_2$  and frequency  $\omega_2$ . The requirement of conservation of momentum and energy for this three step process yields following relationships:

$$k_1 - k_2 = K \quad \text{and} \quad \omega_1 - \omega_2 = \Omega$$

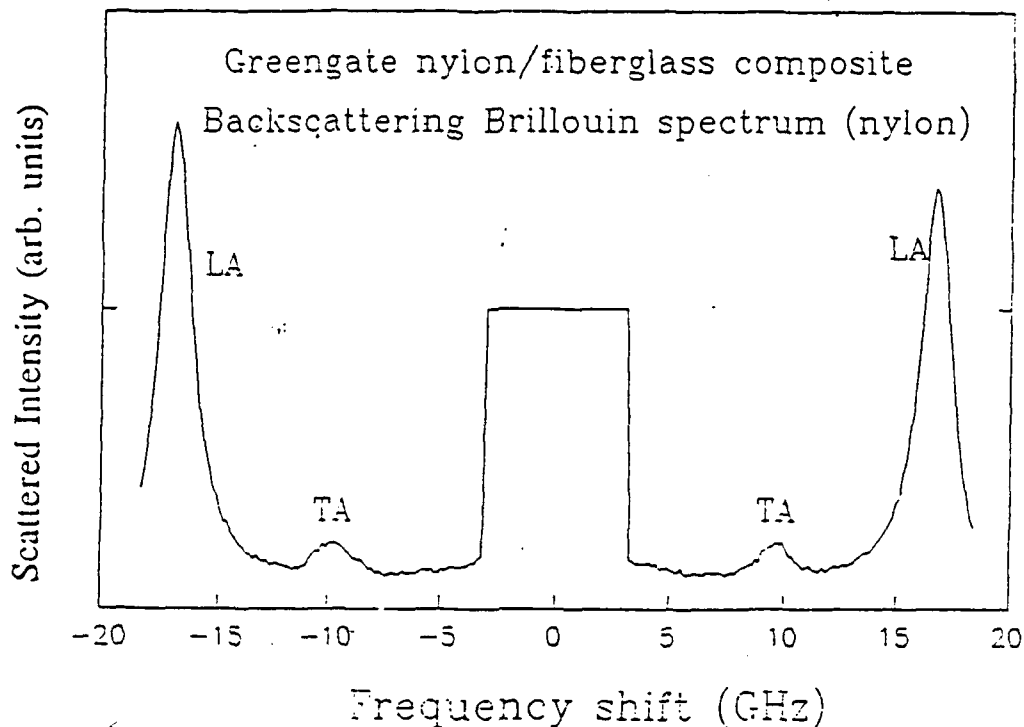
The choice of laser and the scattering angle completely determines  $K$  for the sound waves under study.  $\Omega$ , the frequency of the sound wave, can be directly determined by measuring the frequency shift  $\omega_1 - \omega_2$ . For acoustic waves  $\Omega = VK$  where  $V$  is the transverse or longitudinal acoustic velocity. In Brillouin experiments from the composite,  $\Omega$  has an upper limit of  $\sim 30$  GHz for incident radiation in the visible.



**Figure 1. Our technique is based on inelastic light scattering.**

To a good approximation sound waves are pressure (density) fluctuations thereby enabling photons to couple directly to these acoustic excitations. The scattering spectrum thus consists of a Brillouin doublet symmetrically located about the unshifted laser line and separated from it by a frequency  $\Omega$  equal to that of a compressional sound wave propagating through the composite. The doublet, also known as Stokes and Anti-Stokes peaks, arises since the incident photon can destroy or create an acoustic excitation in the medium and thus its frequency can be upshifted or downshifted from the incident value. A typical spectrum from the nylon segment of the composite showing these spectral features is illustrated in Figure 2. The peaks identified as LA and TA are respectively the longitudinal and transverse acoustic phonons while the suppressed peak centered at zero frequency shift corresponds to the unshifted laser beam.

Since density fluctuations in an isotropic solid, like the nylon segment of the composite, can produce only diagonal elements in the polarizability tensor, the polarization of the scattered light is in the same direction as the incident light. Moreover, as the wavelength of the laser light is  $\sim 0.5$  microns, and thus large compared to the molecular spacings, the results can be analyzed on the basis of elastic continuum theory. From the measured Brillouin frequency shifts and the scattering geometry that provides for the wave vector of the acoustic excitation, the velocity of sound along a specific direction in the solid can be obtained. The elastic properties i.e., the different elastic constants and moduli, of the solid can then be deduced from knowledge of the density.



**Figure 2. Light scattering spectrum from the nylon segment of the composite.**

Brillouin scattering is a sensitive non-destructive method to determine the elastic constants of solids. With the availability of lasers providing monochromatic radiation, these constants can be determined to an accuracy of about 1%. The largest error arises from measuring the frequency of the Brillouin excitation and thus a high resolution and high contrast spectrometer must be utilized to detect the extremely small frequency shifts ( $\sim$ GHz) with sufficient accuracy.

As discussed below this is realized by use of Fabry-Perot cavities for the dispersion of scattered radiation. Since the laser beam can be focussed to spot sizes of the order of 50 microns, the measurements can probe elastic properties averaged over such dimensions.

The technique can be applied to transparent materials as well as opaque samples. In the case of transparent systems as the nylon composite investigated in this study, the scattering is from bulk excitations. These include the longitudinal (LA) and transverse (TA) acoustic phonons. The observation of these phonons provide sufficient information to determine the different elastic constants of such solids. In a very few instances phonons localized on the surface of transparent materials are also observed through Brillouin scattering. The associated scattering cross-sections are generally weak as the light is not localized near the surface. In the event that surface vibrations are observed, these modes provide an additional cross-check on the elastic constants derived from the bulk modes.

Surface excitations were not observed in our study of the composites. In transparent materials the scattering geometry can vary from back scattering to forward scattering with the light incident at different angles to the surface of the sample. The largest wave vector transfer is provided in a back-scattering geometry and was thus utilized in our study. Of course, it is a straight forward extension of our measurements to disperse the transmitted beam instead, although no new information would be gained.

On the other hand, in the case of opaque materials such as metals the surface mode, also called the Rayleigh mode, dominates the Brillouin spectrum since the light is strongly localized in this region. In this case one is restricted to probing only the reflected radiation. The dispersion of the Rayleigh mode along different directions provides for the elastic constants of the material in the vicinity of the surface.

## 1.2 DESCRIPTION OF TEST SPECIMEN

The sample investigated in this study, Greengate nylon-fiberglass composite, was provided by the US Army Chemical Research Development and Engineering Center. This polymer composite consisted of laminated nylon with bundles of fiberglass running at right angles to each other and embedded within the nylon. The composite was thus divided into approximately 3 mm x 3 mm square segments of transparent nylon, with each segment separated by the fiberglass. The fiberglass in turn were made of bundles of glass filaments. Each filament was about 20 microns wide and there were about 50 filaments per bundle. The overall size of each fiberglass bundle was thus about 1 mm in diameter. This nylon/fiberglass Greengate composite was transparent to the wavelength of the exciting laser radiation used.

## 1.3 EXPERIMENTAL SETUP

The experimental set-up used during the course of this Phase I study is shown in Figure 3. It consists of an Argon-ion laser, two Fabry-Perot (F-P) interferometer cavities in tandem, input-output optics consisting of lenses L and pinholes P, a photo-multiplier tube for detecting the signal and the necessary electronics for acquisition and storage of the data. The cavities were electronically controlled to maintain their parallelism during operation. A low dark count, high quantum efficiency, photo-detector (RCA C31034-A02) was utilized during these studies. The pin holes were typically of about 100 microns in size and were utilized to collimate the beam, ensure the passage of a parallel wave front through the cavities, and eliminate optical aberrations. Between 10 and 100 mW power

of the 514.5 nm laser line was used and the beam was focussed to a spot size of about 50 microns. Different segments of the composite were studied by focussing the laser beam to the nylon segment, and separately onto the fiber. The region in the vicinity of the fiber-nylon interface was also probed in an attempt to study any changes in the elastic properties of the nylon caused by interfacial effects. The experiments were carried out in back-scattering and bulk acoustic phonons were detected. The radiation was primarily incident at an angle of  $60^\circ$  to the nylon surface, although other angles were also utilized to vary the wave vector transfer.

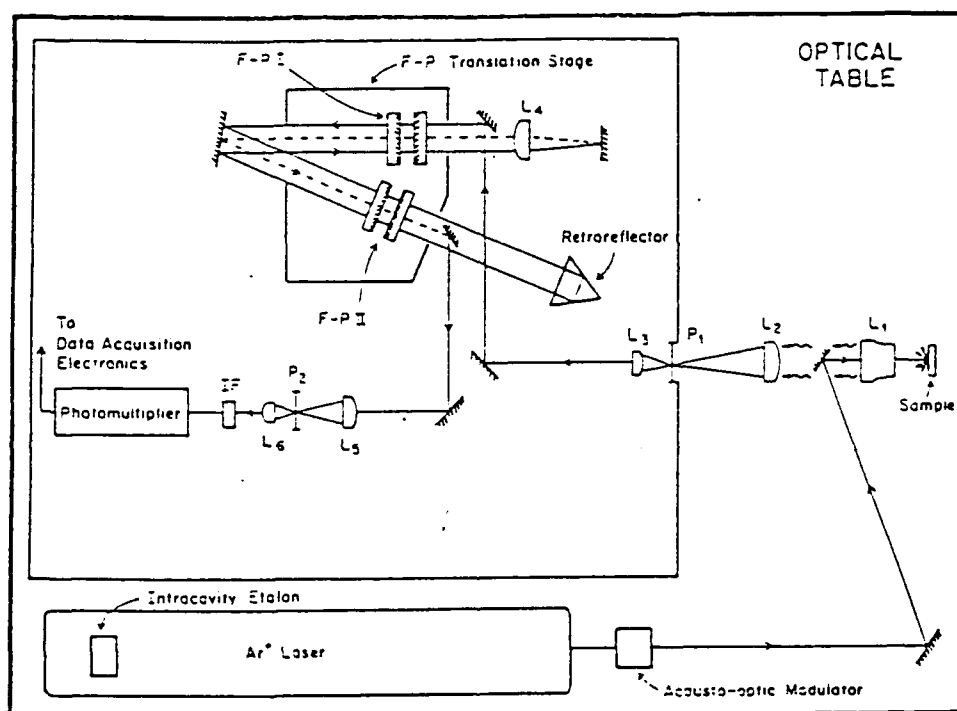


Figure 3. Brillouin experimental setup F-P Fabry Perot interferometer  $L_1$ ,  $L_2$ ,  $L_3$ ,  $L_4$ ,  $L_5$ , and  $L_6$ —lenses  $P_1$  and  $P_2$ —pin holes.

It is noted that two cavities were utilized with multi-passage of the scattered radiation through them. This laboratory system is characterized by high sensitivity for applications on various classes of materials including those displaying low scattering cross sections such as metals. Since the scattering cross-sections from the composites have turned out to be extremely large, the spectra were recorded within three minutes. Due to such enormous cross-sections, a much simpler single pass interferometer can be used for the present composite work. We propose to use such a single pass interferometer during Phase II work of this project. This feature of nylon/fiberglass composites makes Brillouin scattering an especially attractive non-destructive and rapid technique to probe the mechanical properties of these materials.

## SECTION 2

### PHASE I RESULTS

The primary aim of this Phase I study was to demonstrate the potential of the Brillouin scattering method to measure elastic constants of composites and to monitor sensitively the variation of these constants with time after chemical, mechanical or thermal damage. To our knowledge, this is the only non-contact NDE technique which can monitor such changes with high accuracy.

We have chosen the Greengate composite which was of interest to the US Army's Chemical Research and Development Center and investigated the effects of chemical and mechanical damage. We attempted to use chemicals close to model stimulants used by the Army for chemical damage. However, due to the inability to procure such chemicals within the time frame of this Phase I study, we used 40% hydrochloric acid as an example. For mechanical damage, the ASTM D-3885-80 flex/abrasion test was used. We have successfully monitored dramatic changes in the elastic constants of the nylon after exposure to the acid and studied the time evolution of these changes.

While this study is restricted to an investigation of one type of polymeric composite in Phase I, the method can be extended to other similar composites. In addition, the influence of a variety of different chemicals or damage such as mechanical/thermal on the elastic properties of these class of systems can be monitored.

In this section, we present results of our Brillouin scattering studies on Greengate flexible nylon/fiberglass composite and briefly discuss them. In order to demonstrate the versatility of the technique as an excellent non-destructive probe, we have separately measured the Brillouin spectrum of the nylon and fiberglass segment of the composite in the as-received state. The composite was then exposed to 40% reagent grade hydrochloric acid for 10 minutes. The subsequent time evolution of the elastic parameters of the composite was determined over a period of 20 hours after removal from the acid solution. This effort clearly reveals time dependent changes in the elastic moduli and detrimental reductions greater than 70% in the bulk modulus of the nylon immediately after exposure to the diluted acid. In addition, effects of mechanical damage caused by flexing and abrasion tests will also be presented.

## 2.1 PHASE I STUDY OBJECTIVES AND ACCOMPLISHMENTS

We have clearly demonstrated in our Phase I study, the feasibility of Brillouin scattering as an excellent technique for measuring the elastic properties of polymer composites. This was done by fulfilling the objectives listed in the Phase I proposal. All of the following key questions of the Phase I objectives were successfully demonstrated. These are listed below with the answers obtained from the Phase I study.

1. *Can the proposed light scattering technique clearly detect changes in the elastic constants of the polymer composite, in particular, the matrix and fiber elastic constants?*

We have done Brillouin scattering individually on the nylon matrix and fiber segments of green gate nylon/fiberglass composite. We have measured the elastic constants and moduli of nylon segment. These moduli determined by our method agree with the reported results of tensile tests. We have recorded Brillouin spectra of the fiber part of the composite and demonstrated its tubular nature. We have also measured the elastic nature of nylon/fiber interface using Brillouin scattering. Subsequently, the composite was mechanically and chemically damaged. The changes in the elastic constants due to such damage were monitored and measured as a function of time. A summary the results and discussion follow at the end of this section.

2. *What are the optics and laser requirements for the proposed system?*

This objective of Phase I was also successfully completed. The signals from the composite in our measurements were very strong. The laser power used for the measurements was only 30 mW. The presently used mirror spacings in the interferometer (5 mm) provided an excellent resolution of 0.2 GHz (1 micro electron volt). From our Phase I results, we have demonstrated that GaAs semiconductor lasers would be sufficient in terms of power and wavelength requirements. However, in Phase II we will demonstrate the actual use of these lasers focussing on their stability and emission linewidths. The signal to noise ratio, as seen from the spectra from the composite, is excellent. As a result, we propose to demonstrate the adequacy of using a simpler single pass interferometer in Phase II.

3. *What are the critical design issues that effect the packaging of the system in a factory or field environment?*

From the results in Phase I, we have identified key issues and solutions for achieving the

required industrialization of Brillouin scattering.

The laboratory interferometer system used in the Phase I effort has many features that are not critical to many industrial NDE applications. Two interferometers were used in tandem to provide multi-passing of the scattered radiation. This is critical in a sensitive laboratory system when a broad range of materials are characterized. We identified the usage of a single interferometer operating in a single pass mode. This will result in a significant reduction in alignment.

Industrial environments can be harsh, with respect to operating conditions such as dust, vibrations and temperatures. We recommend approach for illuminating and collecting scattered signals from specimens using commercially available fiber optic coupling systems. This will enable the laser and system optics to be located remotely from the test specimen. Another critical issue for a commercial Brillouin system is to reduce the sampling time to achieve quasi-continuous operation. Typical scanning times in Phase I were 2-3 minutes. For even faster data acquisition, we identified two approaches. The first will be to sample only one of the segments of the Brillouin spectra (Stokes or Anti-Stokes) and thus reduce the time by a further factor of two. The second approach will be to use higher laser power levels within the damage tolerance of the samples. This will provide for higher scattered intensity and will enable further reduction of measurement times. In order to reduce cost and to make the system compact, we recommend the approach of using semiconductor lasers in place of the gas ion laser currently used. This is because semiconductor lasers are cheaper, do not require large power inputs, and are miniature in size.

This is the concept design for the components for the commercial Brillouin system that evolved as a result of our Phase I work. In Phase II we will actually demonstrate the feasibility of using these components and do a preliminary system design for the commercial Brillouin scattering system. Thus from the Phase I study, we clearly demonstrated the technical feasibility of the Brillouin scattering to measure elastic constants of composites and to monitor sensitively the variation of these constants with time after damage (chemical or mechanical or thermal). To our knowledge, this is the only non-contact NDE technique which can monitor such changes with high accuracy. We have also identified the optics and laser requirements for the proposed work. We have completed concept design for commercial Brillouin scattering system in terms of identifying issues and solutions.

While this Phase I study is restricted to an investigation of one type of polymeric composite, the method can be extended to other similar composites in Phase II. In addition, the influence of a variety of different chemicals or damage such as mechanical/thermal on the elastic properties of these class of systems can be monitored.

## 2.2 BRILLOUIN RESULTS FROM THE AS-RECEIVED NYLON PART OF THE COMPOSITE

In this section, Brillouin scattering results from the nylon part of the composite will be elaborated. This includes identification of the peaks in the spectrum, calculation of  $C_{11}$  and  $C_{44}$  elastic constants, the Young's modulus  $Y$ , and  $B$  the bulk modulus of the undamaged specimen.

As shown in Figure 2, the Brillouin spectra from the nylon segment, contains two pairs of peaks labelled LA and TA each occur on the Stokes and anti-Stokes segments. We identify the strong peak at 16.8 GHz to be scattering associated with the longitudinal acoustic (LA) compressional phonon and the weaker peak with the transverse acoustic (TA) shear vibration at 9.6 GHz. These modes have frequencies  $\omega_{LA}$  and  $\omega_{TA}$ , respectively. Due to the isotropic nature of the nylon, the two transverse vibrations that characterize a solid are degenerate, and thus occur at the same frequency  $\omega_{TA}$ . The weakness of the peak associated with the TA modes is typical for the case back-scattering. The recording of this spectrum was done in only two minutes with a few milli-watts laser power.

The LA and TA phonon frequencies  $\omega_{LA}$  and  $\omega_{TA}$  that we measure from our Brillouin spectra are related to the longitudinal and transverse sound velocities  $V_L$  and  $V_T$  in the isotropic nylon through  $V_L = \omega_{LA}\lambda_0/(4\pi n)$  and  $V_T = \omega_{TA}\lambda_0/(4\pi n)$  respectively. Here  $\lambda_0$  is the wavelength of the incident radiation (514.5 nm) and  $n$  the refractive index of the composite at this wavelength that is known to be 1.52. From these measured velocities it is then possible to directly evaluate  $C_{11}$  and  $C_{44}$  via  $C_{11} = \rho V_L^2$  and  $C_{44} = \rho V_T^2$ , where  $\rho$  ( $= 1.14$  gm/cc) is the density of the medium. It is therefore directly possible to evaluate these elastic constants for the nylon from our measured frequency shifts. Moreover, the nylon can be treated as an isotropic material and therefore its bulk modulus  $B$  and Young's modulus  $Y$  are given by

$$B = C_{11} - (4/3) C_{44}$$

$$Y = C_{44} [ 3C_{11} - 4C_{44} ] / [ C_{11} - C_{44} ]$$

Hence,  $B$  and  $Y$  can be directly deduced from the measured  $C_{ij}$ 's for the undamaged and exposed samples. From our measurement on the undamaged material we derive  $C_{11} = 11$  GPa and  $C_{44} = 3.2$  GPa. The corresponding Young's modulus and Bulk modulus are  $Y = 8.5$  GPa and  $B = 6.5$  GPa, respectively. These values are in good agreement with published results from nylon

as measured through conventional stress-strain methods.<sup>1</sup>

### 2.3 BRILLOUIN RESULTS FROM THE AS-RECEIVED FIBER PART OF THE COMPOSITE

Results from the fiber were obtained and, unlike the nylon, is anisotropic. This anisotropic nature is demonstrated through polarization dependent scattering from acoustic excitations propagating within the quasi-one dimensional filament.

Figure 4 shows the spectra recorded from the fiber for different polarization of the incident radiation with respect to the filament. The energy range shown covers the transverse vibrations with the longitudinal wave lying outside the chosen spectral range. The exciting power utilized was about 100 mW and is thus an order of magnitude larger than that used on the nylon segment. The increased power was utilized to enhance the weaker scattering from TA phonons. The measurements were carried out in backscattering normal to length of fiber. Thus the phonons detected in this configuration propagate radially in the fiber. The three spectra shown in Figure 4 correspond to polarizations (a) normal to the filament  $\Theta = 90^\circ$ , (b) inclined at  $\Theta = 45^\circ$  to the fiber and (c) parallel to the fiber,  $\Theta = 0^\circ$ . These geometries are illustrated in the inset to Figure 4.

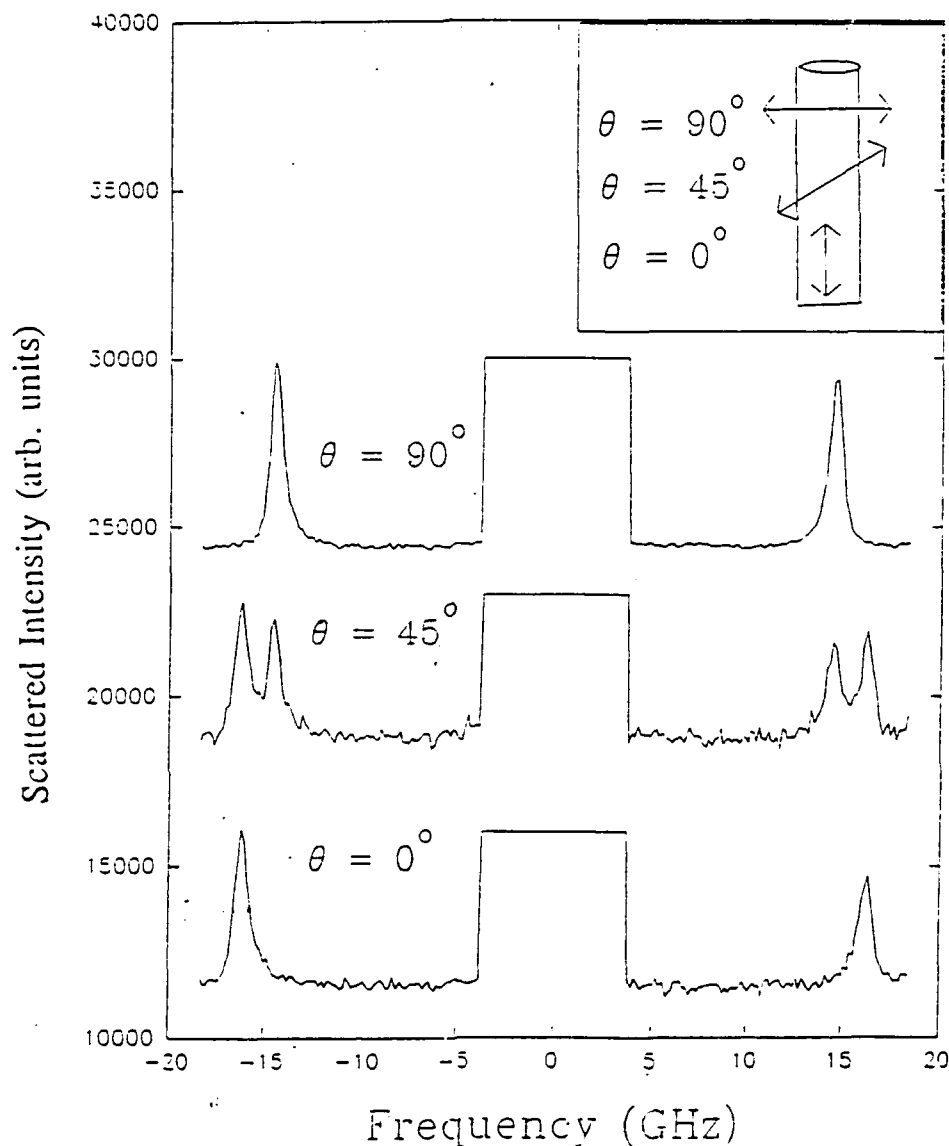
For  $\Theta = 90^\circ$ , the acoustic phonon is detected at 14.5 GHz while for  $\Theta = 0^\circ$  a corresponding mode occurs at an increased frequency of 16.2 GHz. The differences in these frequencies is a direct result of the filament nature of the scatterer. In one case,  $\Theta = 0^\circ$ , the incident photons couple to atomic displacements that are along the filament, while for  $\Theta = 90^\circ$  the displacements lie in a radial direction. Since, unlike the nylon, the filament is not isotropic, the two quasi-transverse vibrations we observe are not degenerate and thus occur at different frequencies. In this case one transverse vibration involves the vibration of atoms along the length of the filament while the other mode is characterized by atomic displacements in a radial direction. The propagation direction of the phonons in both cases are along the direction of the incident laser beam which is normal to these displacements.

This is further confirmed from the spectrum recorded at  $\Theta = 45^\circ$ , when the incident radiation can couple to both these quasi-transverse phonons. Therefore, for this polarization setting both shear vibrations are observed concurrently. This polarization dependence of the Brillouin spectra is thus a direct manifestation of the tubular nature of the fiber and, together with the higher lying LA

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1. W.E. Morton, and J.W.S. Hearle, Physical properties of textile fibers; John Wiley, New York, 1975.

phonon, provides for the elastic properties of the fiber.



**Figure 4. Light scattering spectrum from the fiber segment of the composite.**

The determination of the elastic constants of the fiber segment is complicated by its highly anisotropic nature. The cylindrical symmetry of the filament reduces the number independent elastic constants to five namely  $C_{11}$ ,  $C_{22}$ ,  $C_{44}$ ,  $C_{12}$ , and  $C_{13}$ . A complete determination of the elastic properties of the fiber thus requires a knowledge of all five elastic constants. Moreover, the phonon velocities along any specific direction will depend on different combinations of these constants. It therefore becomes necessary to monitor phonon propagation along several carefully chosen directions along the fiber and then deduce the individual elastic constants from these measurements. Only the most symmetric phonon directions of propagation, normal to and along length of fiber, were studied in this

Phase I effort. The other directions would have required a much more stringent selection of mode propagation directions in the fiber as well as a careful measure of the anisotropic refractive indices in these fibers to identify the exact photon refraction direction within the fiber. We hence did not pursue this effort in this feasibility study. We note that this complication related to measurement of individual elastic constants in anisotropic materials is not restricted to light scattering methods but also transcends to other techniques such as ultrasonic methods.

## 2.4 BRILLOUIN RESULTS FROM FIBER/NYLON INTERFACE

Attempts were made to investigate the fiber/nylon interface segment of the composite. The laser beam spot was focussed to dimensions of the order 50-100 microns and thus was about the diameter of two-five fiber filaments. Figure 5 shows several spectra recorded in the vicinity of the fiber/nylon interface. As the beam was focussed on the nylon segment of the composite with the laser spot almost touching the fiber bundles (curves A, B, F and G, Figure 5) no significant changes were observed in the Brillouin features originating from the nylon. When the beam was focussed with the laser beam overlapping the fiber bundles scattering from the fiberglass were observed. The spectra show the case when the light was polarized at an angle of  $45^\circ$  to the fibers and the resulting scattering peaks were at the same values as obtained from fiber bundles separately (See Figure 4). We thus conclude that within the 50-100 micron spatial resolution offered by the technique, there is no significant changes detected in the elastic constants of composite at the interface.

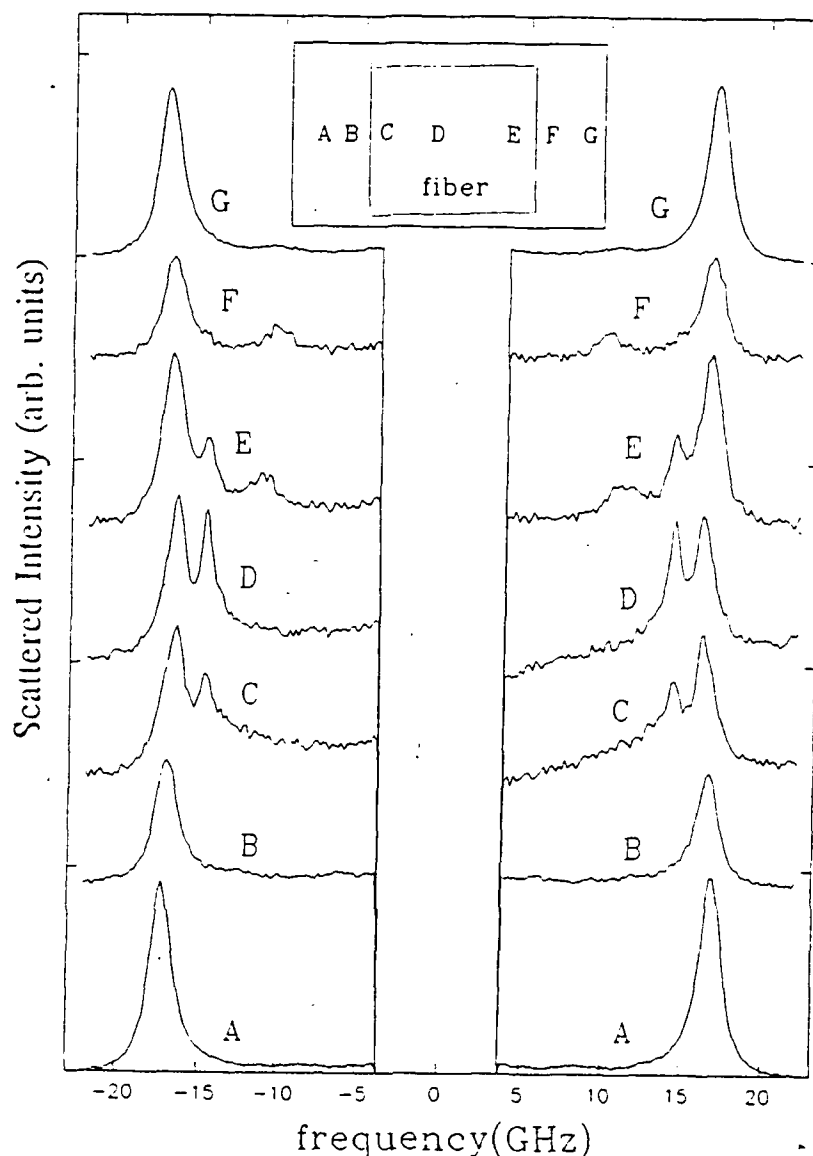
## 2.5 BRILLOUIN RESULTS AFTER EXPOSURE TO 40% HYDROCHLORIC ACID

The composite was exposed to 40% HCl acid for 10 minutes for chemical damage. Figure 6 shows the Brillouin spectra of the composite after exposure.

Our results show that there is a dramatic change in the elastic properties of nylon after sorption of HCl and these changes can be reversed by complete desorption. These results agree with the published work of L.H. Reyerson and L.E. Peterson<sup>2</sup>, who's studied the sorption of HCl gas on nylon using manometric pressure and X-ray methods.

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2. L.H. Reyerson and L.E. Peterson, "The Sorption of Gases by Solid Polymers. 1. The Sorption of Ammonia and Hydrogen Chloride by Nylon," J. Phys. Chem., Vol. 60, 1956, p. 1172, and Vol. 64, 1960, p. 1959.

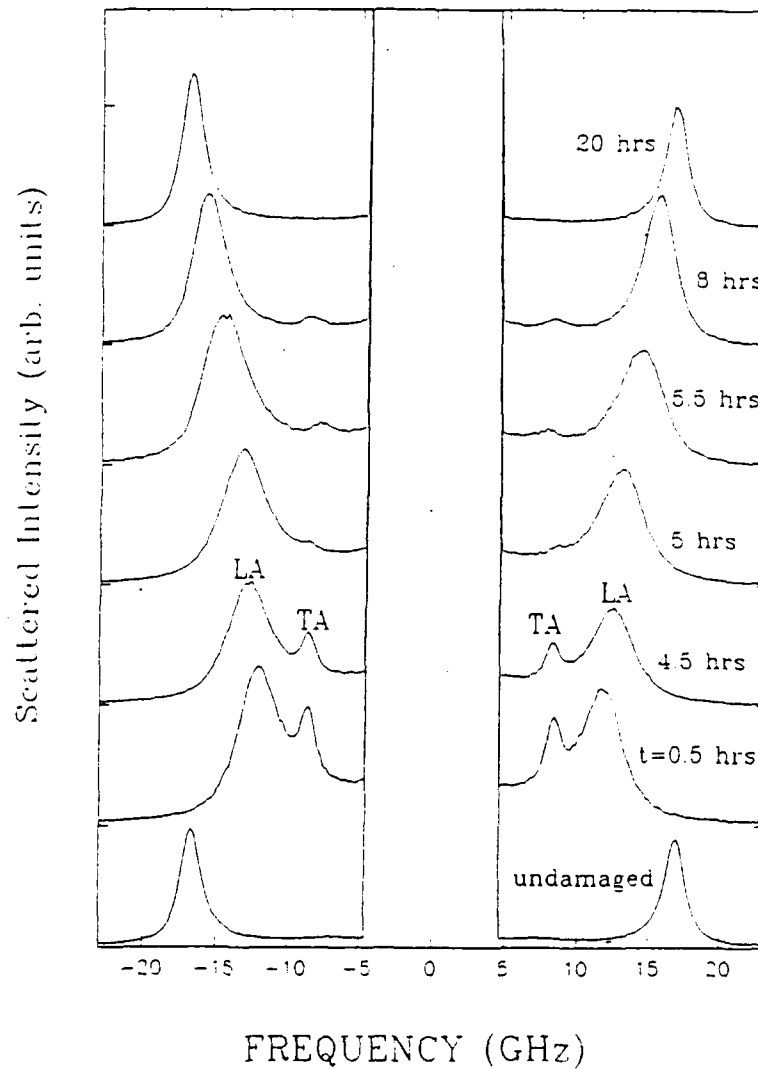


**Figure 5. Brillouin spectra of nylon/fiber interface.**

Although we recorded an entire time evolution sequence of spectra that were used in the analysis presented below, only a few representative spectra are shown in Figure 6. These data were measured with 10 mW power and each curve recorded in three minutes.

It is clear that the effects of exposure on the nylon to the 40% acid are dramatic. The lowest spectrum shows the result, similar to Figure 2, from the undamaged sample. The weaker TA mode is not clearly evident in the spectra of the undamaged sample due to the suppressed scale. The spectra recorded 0.5 hours after exposure to acid shows the LA mode frequency  $\omega_{LA}$  has softened from 16.8 GHz to about 12 GHz and the line width has broaden. In addition, the TA mode  $\omega_{TA}$  appears at a slightly lower frequency from that in the undamaged sample and appears to have gained spectral intensity. As time evolves, the LA mode remains broad and hardens by approximately 1

GHz per hour for about 5.5 hours, while at the same time the TA mode slowly loses intensity. Beyond about 6 hours, the LA mode begins to sharpen and gradually regains the frequency of the unexposed specimen. Finally after 20 hours from treatment, the spectrum appears to have fully recovered to the normal state.



**Figure 6. Effects of exposure (immersion) of the composite to a 40% HCl for 10 minutes.**

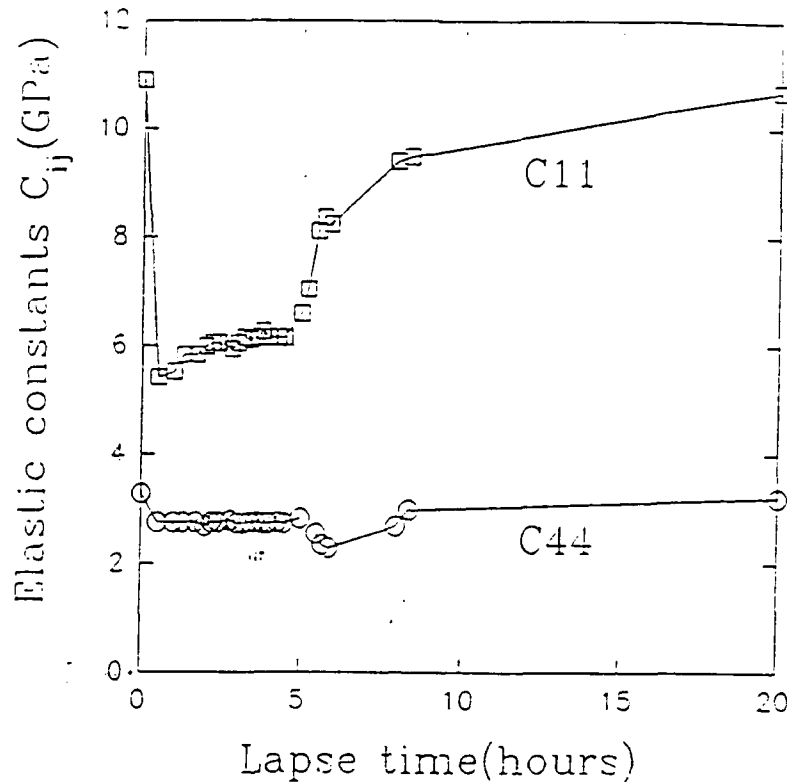
It is evident from Figure 6 that upon exposure to the 40% HCl, the acoustic, and hence elastic properties of the nylon are affected in a significant manner. The softening of the LA mode is clearly tied to reductions in the  $C_{11}$  elastic constant while the very minor changes to the shear TA mode shows that not only does the  $C_{44}$  constant not vary in any significant manner but that the density of the composite is also not modified to within about 1%. The broadening of the LA mode soon after

exposure reveals that there is some non-uniformity to the degree damage as the acid percolates into the material. In addition, some of this inhomogeneity may arise from scattering from the HCl solution which was found to have a Brillouin mode at 7 GHz. The increased spectral intensity of the TA mode in this case is somewhat surprising and may reflect contributions directly from unreacted acid. The virtually complete recovery of the Brillouin spectra with time illustrates that the modifications to the relevant elastic constants upon exposure to the acid are not permanent. This is due to the complete desorption of HCl from the specimen at room temperature as has also been reported in Reference 2.

In evaluating the elastic parameters after exposure, we need to know the changes, if any, to the density and refractive index. The changes to the density of nylon upon exposure to moisture is documented to be minimal since changes to the mass are accompanied by corresponding changes to the volume via swelling. While no direct measure of the refractive index  $n$  of the nylon after exposure to the acid was made, we anticipate no dramatic changes to have taken place since no permanent chemical modifications appear to be induced on the system by the exposure. We thus retain the pristine values for the density and refractive index after exposure to the diluted acid.

Figure 7 summarizes the results for the two elastic constants before and after exposure. It is evident that soon after removal from the acid,  $C_{11}$  undergoes a huge softening to 5.8 GPa while the  $C_{44}$  shear constant reveals only a minimal change. With time  $C_{11}$  initially recovers slowly until about 5 hours at which point there is a rapid increase from ~6 GPa to about 9 GPa which then slowly approaches the undamaged value after approximately 20 hours. The changes to  $C_{44}$  are much less dramatic and show minimal changes that also completely recover with time.

The Young's and bulk moduli were derived as discussed above for the undamaged sample. The results are summarized in Figure 8. Again, dramatic changes are evident soon after exposure to these elastic quantities on time scales of the order minutes. The biggest change is in the bulk modulus that softens by over 70% while  $Y$  is reduced by about 35% during the very early stages after immersion in the 40% acid. The system is then observed to recover, slowly until about 5 hours at which point it reveals a substantial increase within about an hour and then more gradual retrieval towards the value of the unexposed sample.



**Figure 7. Time dependent variation of elastic constants of nylon before and after exposure to 40% dilute HCl.**

Our results agree with previous work<sup>2</sup> on the effects of exposure of nylon to HCl gas, where it was observed that the acid sorbed nylon lost its tensile strength. Further, the specimen appeared to regain its original elastic behavior upon desorption at ambient and elevated temperatures. These observations are in full agreement with our quantitative results where we are also able to monitor the time dependence of the losses in strength arising from individual components of the elastic moduli. Brillouin scattering is the only known technique that offers such resolution and capability.

We carried out supplementary tests of mass measurements and scanning electron microscopy to further our understanding of the behavior of nylon upon sorption and desorption of HCl.

## 2.6 MASS MEASUREMENT TESTS

In these tests the mass of a piece of composite was measured. It was then immersed in water for 6 hours and the mass of the specimen was then measured. The relative mass gain of the composite due to regain was about 7%. There was relatively no swelling or color change in the transparency due to immersion in water.

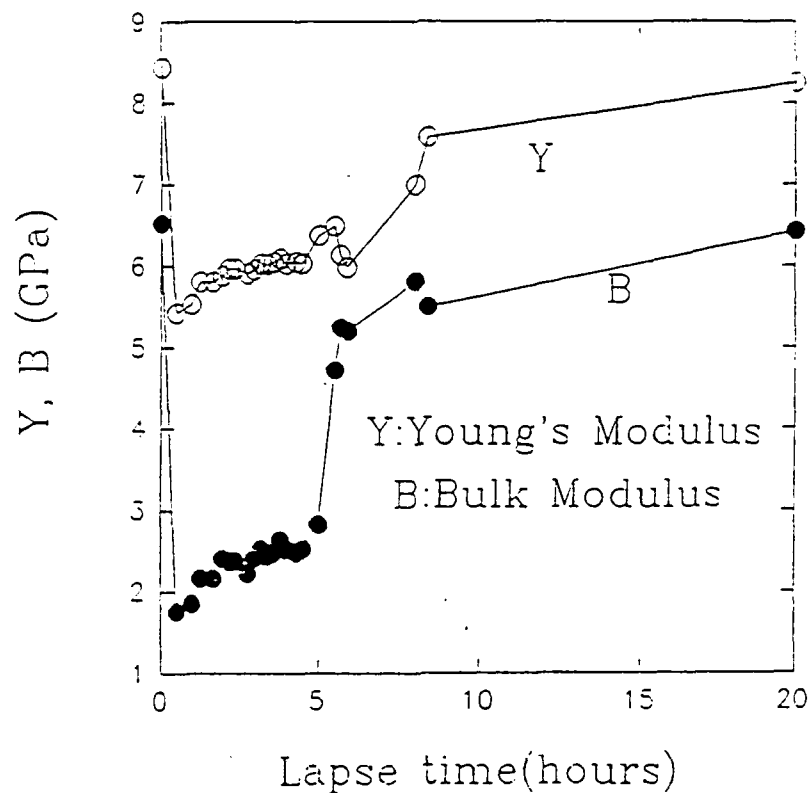


Figure 8. Time dependent behavior of Young's and bulk moduli of nylon before and after exposure to 50% dilute HCl.

A similar composite specimen was also immersed in 40% HCl for 3 hours. The gain in mass due to this limited exposure to acid was much greater being almost 105%. It is thus clear that the regain from HCl is much larger than that arising from water alone. Upon drying with a blow dryer, the nylon regained its original untreated weight. This agrees with our Brillouin scattering results, implying that the overall modifications of the elastic properties due to HCl can be reversed by the desorption of HCl.

Similar results were reported in Reference 2, where when the HCl absorbed nylon came in contact with water it gained weight and lost its tensile strength. Upon desorption of HCl, regain in tensile strength, mass and color to that of the untreated nylon were noticed.

## 2.7 SCANNING ELECTRON MICROSCOPY RESULTS ON COMPOSITE

We attempted to observe any related structural changes before and after exposure to the acid using scanning electron microscopy.

Figure 9 shows the image at low magnification where bundles of fiberglass filaments were embedded in the nylon matrix for the composite. The individual fibers of ~20 micron diameter are

shown in Figure 10. These dimensions for the fibers are consistent with their associated polarization dependent Brillouin spectra shown in Figure 4, that illustrates the anisotropy rendered by their tubular nature. Figure 11 is a cross-sectional image of the nylon sheet and clearly illustrates its laminated crystalline and non-crystalline segments. Upon exposure to HCl, the moisture absorption readily takes place via such exposed segments of the non-crystalline regions.

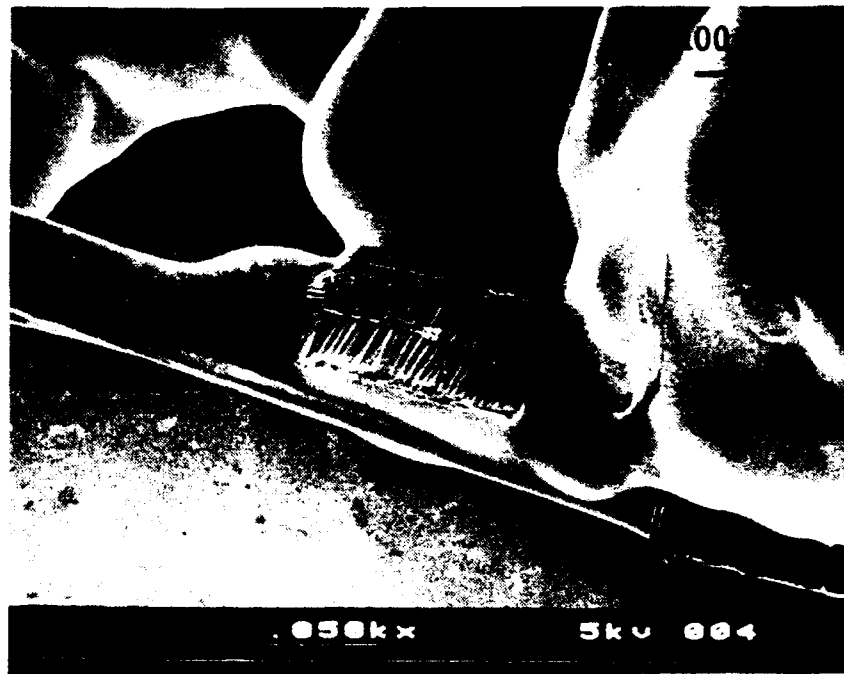


Figure 9. Scanning electron microscopy (SEM) pictures of fiberglass bundles embedded in the nylon matrix of the green gate composite.

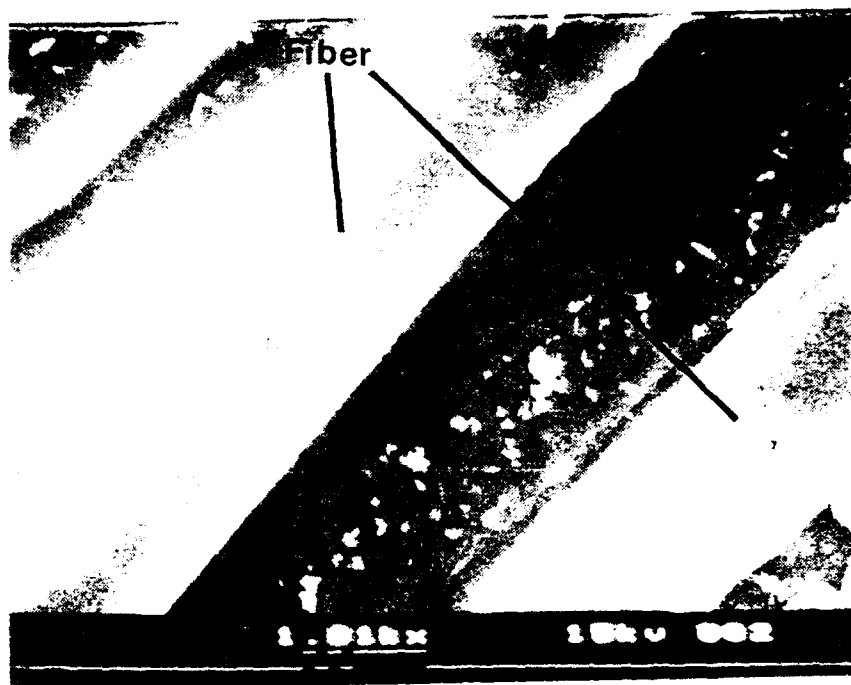


Figure 10. SEM of individual fibers in the fiber bundle of the composite.

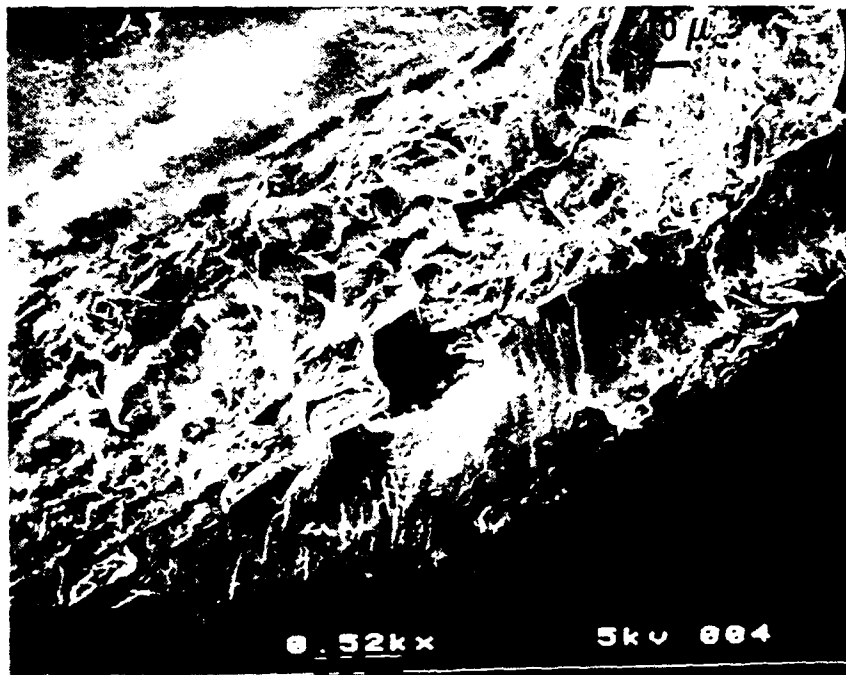


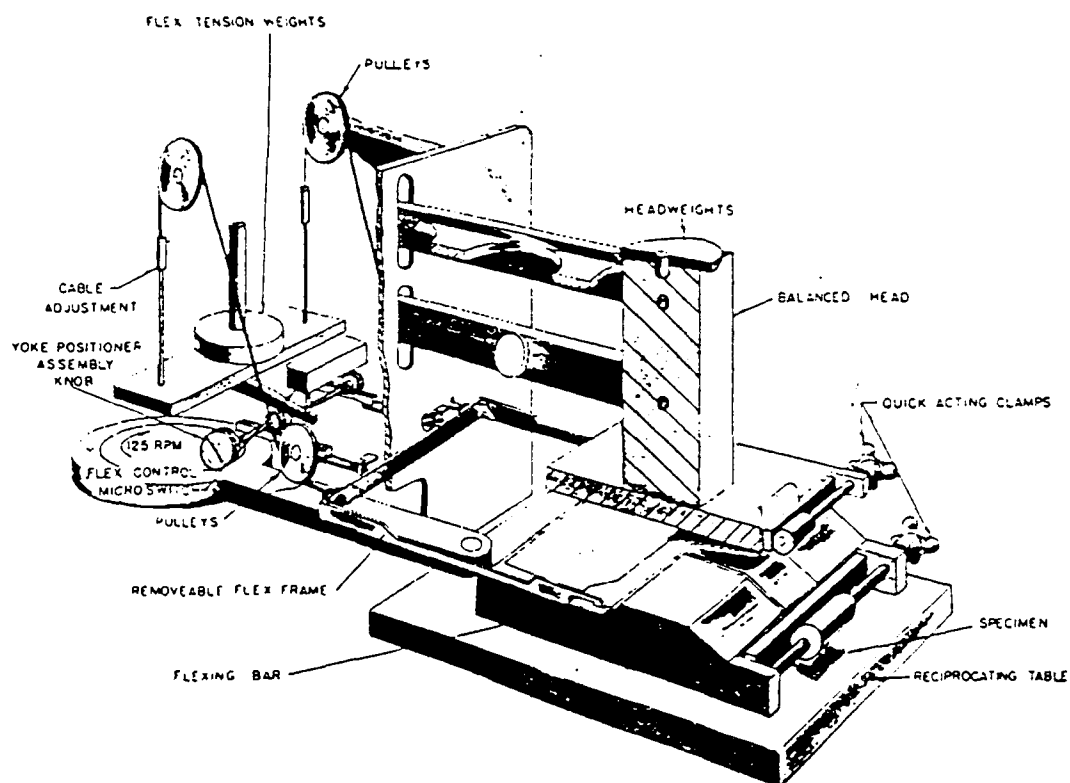
Figure 11. SEM of the cross section of the nylon matrix in the composite. Lamellar pattern of the crystalline and amorphous regions can be seen.

SEM images of the exposed sample could not be obtained. This was due to the inability to reach vacuum levels needed with the moist sample for operation of the SEM.

## 2.8 MECHANICAL DAMAGE TESTS

In order to demonstrate the use of Brillouin scattering for evaluating the mechanical damage due to wear, the following damage test was performed on the Greengate nylon/fiberglass composite.

The test is an ASTM D3885-80 test for determining the abrasion resistance of textile fabrics. This method covers the determination of the resistance of woven fabrics to flexing and abrasion using the flexing and abrasion tester. A schematic diagram of the latter is shown in Figure 12.



**Figure 12.** Schematic diagram of flexing and abrasion tester.

In this method, a specimen is subjected to unidirectional reciprocal folding and rubbing over a bar having specified characteristics, under known conditions of pressure and tension. Resistance to flexing and abrasion is evaluated by the following methods:

1. Failure: specimen abraded till rupture.
2. Percentage loss in breaking load: Abrade the specimen a specified number of times and determine the loss in breaking load % as  $= 100(A-B)/A$  where A is the breaking load

before abrasion and B the breaking load after abrasion.

3. Visual rating: Abrade the specimen a specified number of cycles and then evaluate visually for the effect of abrasion on the luster, thickness etc..

We utilized a commercial flexing and abrasion tester located at the department of Textile and Fabrics at Ohio State University. In mounting the composite we used 1 lb. of top pressure and 5 lbs. of back tension. We initially used 500 cycles and checked for damage visually and with an electron microscope. No evidence of damage was detected. A second piece was ruptured after 815 cycles. The damage occurred in a drastic manner with breakage of the fabric. There was no visually evident damage to the nylon matrix. On carrying out Brillouin scattering measurements from this damage segment, no changes in the elastic constants were found.

We hence concluded that for this particular composite damage occurs by brittle fracture of the fibers with no damage sustained to the nylon matrix.

## SECTION 3

### DISCUSSION

Discussion of the results of this Phase I study will be focussed on two important aspects of this project. The first will be the potential of the Brillouin light scattering as a technique for evaluation of composite damage. The second feature will focus on a discussion of the results on nylon exposed to HCl. In the later will show that our results agree with observations deduced from other destructive techniques and will highlight the additional information and accuracy offered by the light scattering method.

#### 3.1 POTENTIAL OF BRILLOUIN SCATTERING TECHNIQUE FOR COMPOSITE DAMAGE EVALUATION

In the results presented above we have measured the elastic constants of the composite and determined how they varied with time after immersion in HCl acid. We were able to monitor quasicontinuously the variations in elastic properties to within 1% accuracy. In addition, reversible changes in elastic moduli due to the desorption of HCl were tracked. Such measurements are, if possible, tedious to perform by regular tensile strength methods. In general, by regular method it is difficult to isolate the behavior of individual elastic constants and monitor changes on short time scales. Our method also offers detailed results on the fiber and matrix parts of the composite via non-contact methods. In specific applications, the elastic properties along various directions can be measured with relative ease by merely choosing the scattering geometries. To our knowledge this is the only non-contact NDE method which can provide such detailed information on the elastic properties of polymer composites.

In the following section we present our understandings of the results from nylon exposed to HCl acid.

#### 3.2 UNDERSTANDING OF RESULTS OF NYLON EXPOSED TO 40% HCl

We have also identified the optics and laser requirements for the proposed work. We have completed concept design for commercial Brillouin scattering system in terms of identifying issues and solutions.

### 3.2.1 Structure of Nylon

Nylon 66 is an aliphatic polyamide<sup>3,4,5,6</sup> with the structure as illustrated in Figure 13. The structure is composed of a mixture of crystalline and amorphous regions. The structure is probably micellar, with most deformation concentrated in the amorphous regions. The properties of specific nylons could vary over a range depending on inherent characteristics of the polymer, which each manufacturer controls by varying processing details. However, in general owing to the alternation of  $-CH_2-$  sequences and  $-CO.NH-$  groups, structure must act as a rubber with the equivalent of two or three random links between network points. In crystalline regions that compose about 50-60% of the whole, the molecules are closely packed together in a regular pattern. Many important properties derive from this structure and from the fact that the hydrogen bonds between the  $-CO.NH-$  groups are rather easily ruptured. The active groups form cross-links between molecules, for example, by hydrogen bonding. The material most likely accessible and thus reactive to external chemicals will be the non-crystalline regions.

### 3.2.2 Reactivity of Nylon to HCl and Water

Our results suggest that the effect of immersion in 40% HCl is to enable the solution to enter the nylon, and that in penetrating the polymer the HCl broke the existing hydrogen bonds at the amide groups. This allows the water and HCl components to be absorbed by the composite. Similar results were previously deduced by Reyerson and Peterson<sup>2</sup> via HCl gas absorption studies in conjunction with X-ray work. For the specific Greengate composite studied the drop in the modulus is substantial (see Figure 8) due to direct penetration of the water and HCl molecules to the interior of the nylon. These conclusions are in good agreement with published reports of the effects of sorption of hydrogen chloride gas by nylon. In these studies it was concluded that at room temperature one molecule of HCl was taken up by each amide group in the nylon and that the nylon would swell in cross-section during the early part of sorption. Consistent with our Brillouin results a large loss of strength was found upon exposure of the nylon to HCl gas. The results are reversible

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3. W.H. Howard and M.L. Williams, "Viscoelastic Properties of Oriented Nylon 66 Fibers, Part II Moisture Dependence of Creep," - *Tex. Res. J.* 36, 1966, p. 691.
  4. International Conference on Fiber Science - held at Arad, Israel, February 29 - March 5, 1976.
  5. J.W.S. Hearle, B. Lomas, D. Cooke, and I.J. Duerden, "Fiber Failure and Wear of Materials," Ellis Horwood Series in Polymer Science and Technology.
  6. H.H. Yank. "Aromatic High Strength Fibers," John Wiley and Sons, Inc., 1989.

when HCl is desorbed with regain in tensile strength. The most significant structural changes during sorption-desorption could be in the reorientation of long chain molecules as suggested in Reference 2. The time dependence of our data is consistent with the desorption of moisture and HCl from the system and the complete recovery of the elastic properties of the original structure. This result is similar to the effects of HCl gas on the nylon discussed above. From Figures 7 and 8, we deduce that rapid desorption of moisture takes place around 5 hours after removal from the diluted acid. The acoustic measurements do not reveal any permanent damage to the nylon from the dilute hydrochloric acid by itself. We conjecture that this may be due to the fact that once the HCl is removed from the nylon, the molecules could hydrogen bond. Simple dipole-dipole interactions between HCl and the polar groups of the polymer may also play a role in regard to the apparent reversibility of the intake of HCl acid. These conclusions drawn from our Brillouin results are consistent with reports that subsequent to removal of HCl molecules there is a more perfect alignment achieved via reorientation of long chain molecules within the nylon.

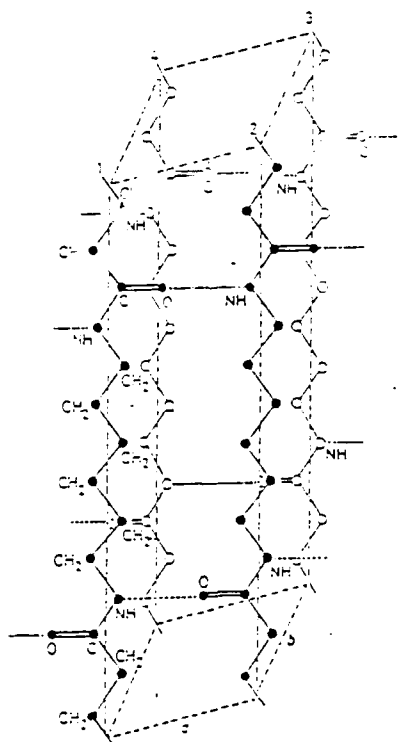


Figure 13. Crystal structure of  $\alpha$ -nylon 6.6.

## SECTION 4

### SUMMARY AND CONCLUSIONS

In summary we have demonstrated that Brillouin scattering does work as an excellent probe to measure elastic constants and moduli of polymeric composite materials. The significant highlights that have emerged from this feasibility study are (a) quantitative values for the elastic constants and Young's and Bulk moduli which are easily measured for the matrix and fiber segments of the composite, (b) the measurement times for determining these constants were very small with the potential for reducing it by a further order of magnitude, (c) the signal strengths were extremely large for these polymeric composites, (d) changes due to chemical treatment in the elastic properties of the composite were determined quantitatively, and (e) the time dependence of these changes in the elastic constants were determined.

In our measurements we have been able to probe the elastic constants within a time period of two minutes. These times scales could be further shortened by an order of magnitude through scanning only one segment (Stokes or anti-Stokes) of the Brillouin spectrum, optimizing the laser power and detection system. Thus we envision usage of this method as a quasi-continuous process control technique for curing of composites, evaluation of effects arising from permeation of chemicals through composite materials and quality control of polymer layers deposited for protection of electronic devices.

In general the technique of Brillouin scattering can be used for monitoring the mechanical property changes due to various deformations. These deformations could arise from mechanical, thermal or chemical processes. The advantages of this technique over existing ultrasonic methods are (a) it is non-destructive and non-contact, (b) since the acoustic excitations probed by light scattering are inherently present in the system, no external transducers and detectors for their generation or observation need be attached to the test piece, (c) as demonstrated, the data acquisition is rapid with the capability to probe local areas of micron dimensions and (d) the ability to monitor separately changes on different segments such as the fiber and matrix. We foresee this as a potential NDE technique applicable to a wide range of applications.