MODIFICATION OF THE PPTA FIBER SURFACES BY ULTRASONIC WAVES

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Introduction

Recent studies have shown that poly(p-phenylene terephthalamide) (PPTA) fibers exhibit relatively weak bonding to polymer matrices in composites. A difficulty of incorporating the fibers into the matrix and resulting poor interfacial stability arises from a lack of adequate bonding between the fiber and the matrix. In order to improve the interfacial properties it is necessary that we understand the surface functionality and modify the surface in such a way that a greater amount of surface functional groups are available to form environment-stable interface. Using deuterium exchange and studying frequency shifts in the infrared spectra, Chatzi et al. determined that about 70% of the N-H groups of PPTA fibers are unaccessible for bonding as they are part of a highly ordered material. As a result, only 30% is available for reaction with a polymer matrix. Apparently, extensive intramolecular hydrogen bonding on the surface further reduces the number of available bonding sites. Thus, one way to increase the reactivity of the fiber surface is to activate the amide groups by breaking the surface hydrogen bonds. Such bond disruption can be accomplished by the chemical treatment in strong solvents. However, the highly reactive chemical environments may disturb the mechanical integrity of the fiber and therefore, more surface localized treatments are required.

Residual impurities in the PPTA fibers can effect the hydrolytic and oxidative stability of the fiber surface as well as the characteristics of the microvoid and moisture sorption. PPTA fibers contain 15,000-17,000 ppm impurities. 50% of the impurities are Na_2SO_4 located in impurity-rich regions between 60 nm diameter fibrils. These regions are paths for preferential moisture diffusion. The Na_2SO_4 impurities generate osmotic pressures that lead to the formation of 10 nm diameter spherical microvoids during fiber fabrication. The microvoid also contains small amounts of sulfonic acid, sulfate salt, and carboxylic acid groups. Thus, the most desirable treatment would be such that it will activate the surface and, at the same time, will eliminate undesirable surface impurities.

Recently, we have reported the use of ultrasonic waves to modify the surface of polyvinylidine fluoride (PVDF) films. It has been shown that the ultrasonically treated surfaces are highly uniform and provide stable, coherent layers of conjugated chains on the PVDF surface. In this work we utilize the ultrasonic energy to modify the surface of PPTA fibers in the presence of polar liquids.

Experimental

The PPTA (Kevlar) fibers were used as received from Du Pont, and treated in 1M H_2SO_4, 1M NaOH, and water (room temperature). The fibers were soaked in the solvent at room temperature concurrently with another fiber sample being treated in the same solvent in the presence of ultrasonic waves. The samples were removed from the treatment after 45 minutes and allowed to dry for an additional 30 minutes.

The surface treatments were monitored by photoacoustic Fourier transform infrared spectroscopy (PA FT-IR). Photoacoustic FT-IR spectra were recorded on a Digilab FTIR-106 FT-IR spectrometer equipped with a photoacoustic cell (Digilab). 400 scans were coadded and ratioed to a carbon black reference. The spectra were transferred to an AT compatible computer for further spectral manipulations. Spectra Calc software (Galactic Ind.) was utilized to perform the necessary manipulations.

Mechanical testing was conducted on a model TM Instron mechanical tester.

Results

In order to reveal how ultrasonic treatment affects the PPTA fiber surface, it is first necessary to define the origin of the infrared bands
sensitive to such treatment. While the band assignments of the untreated fibers are in agreement with the previously reported results\textsuperscript{16,19}, the ultrasonic treatment of the fiber in water, sodium hydroxide and sulfuric acid yields distinct differences. In order to highlight the surface treatment, the difference spectra were generated. Figure 1, traces A through C, shows the difference spectra (4000-2600 cm\textsuperscript{-1} region), derived from the PA FT-IR spectra of the untreated fibers subtracted from that of the fibers treated with ultrasound in sodium hydroxide, sulfuric acid, and water, respectively. Because the bands in the difference spectra show either positive or negative intensities, new structures will be reflected by positive bands while negative bands represent the loss of original structures. Traces A and C of Figure 1 show positive bands at 3700 cm\textsuperscript{-1} (O-H stretch) indicating an increase of surface adsorbed water caused by the ultrasonic treatment. Trace B of Figure 1 shows neither increase or decrease of the water bands signifying that the ultrasonic treatment in sulfuric acid does not hydrate the polar amide groups. Figure 1 also indicates the decrease of hydrogen bonding at the amide groups, which is demonstrated by the decreasing intensity of the N-H stretching mode at 3300 cm\textsuperscript{-1}. The loss of hydrogen bonded species is indicative of structural changes brought about by the ultrasonic treatment.

Although the use of ultrasound to treat the PPTA fibers is not expected to largely affect the fiber surface, the most sensitive groups for such treatment are the surface amide groups because of their extensive hydrogen bonding with amide groups of the neighboring chains and adsorbed moisture. Figure 2, traces A through C, illustrates the difference spectra derived from the PA FT-IR spectra in the 1700-1350 cm\textsuperscript{-1} region. Increasing intensities are observed for the carbonyl (C=O) stretching vibrations of the carboxylic acid and amide groups, at 1676 cm\textsuperscript{-1} and 1650 cm\textsuperscript{-1}, (traces A and C, respectively). This indicates that possibly two processes occur: first, there is cleavage of the polymer backbone, manifested by the increase of the acid carbonyl band at 1676 cm\textsuperscript{-1} and, secondly, the amide groups become available for bonding, which is indicated by the increase of the amide carbonyl band at 1650 cm\textsuperscript{-1}.

Although, the cleavage of the polymer backbone should be minimized in order to maintain the mechanical integrity of the fiber, the increased amounts of free amides will improve the bonding between the fiber and the polymer matrix. Trace B of Figure 2 shows the increase of the intensity of the acid carbonyl band at 1676 cm\textsuperscript{-1}, which is accompanied by the decrease of the amide carbonyl band at 1650 cm\textsuperscript{-1}. Figure 2 also indicates the increasing intensities in all three traces of the free amide band (N-H bonding mode) at 1535 cm\textsuperscript{-1}. The above observations indicate the cleavage of the polymer backbone of the PPTA fiber surface. The hydrolysis of an amide group yields free carboxylic acid and amine groups at the end of newly separated PPTA chains.

Figure 3, traces A through C, shows the difference spectra derived from the PA FT-IR spectra in the 1425-800 cm\textsuperscript{-1} region. Traces A and C indicate the decrease of intensities of the S=O stretching band at 1010 cm\textsuperscript{-1} due to the sulfate ions. The ultrasonic treatment in the presence of water and sodium hydroxide causes a decrease of the sulfate groups (traces A and C, respectively). On the other hand, trace B shows the increase of the 1010 cm\textsuperscript{-1} band. Apparently, the ultrasonic treatment in sulfuric acid increases the amount of sulfate groups on the fiber surface, whereas water and sodium hydroxide are cleaning the fiber surface.

Discussion

As illustrated in Figure 1, the loss in the hydrogen bonded amide groups upon the treatment with ultrasound can be viewed in two ways: first the loss of hydrogen bonds can be considered as an increase of the accessible for bonding N-H groups and, the second, the loss of hydrogen bonds as a reordering of the structure of the fiber crystallites.\textsuperscript{16} The second view can be ruled out because there is an increase of the water, amide carbonyl band at 1650 cm\textsuperscript{-1}, and amide N-H band at 1550 cm\textsuperscript{-1}, indicating less hydrogen bonded amide groups of neighboring chains and more hydrogen bonding with water. As a result, these amide groups become more available for bonding. The increased availability of the amide groups should cause stronger bonding with the matrix polymer due to a greater amount of the active sites on the PPTA surface.

Figure 2 depicts the increase of carboxylate carbonyl and free amine bands in all three solvents and is attributed to hydrolysis of the amide linkages. However, the sulfuric acid treatment results in more pronounced hydrolysis of the amide groups due to a stronger hydrolyzing ability of the
acid. This is demonstrated in trace B of Figure 2. An increased amount of the carboxyl carbonyl and free amine surface groups is desirable as long as the inner fiber layers are not affected by the treatment. Unfortunately, the ultrasonic treatment in sulfuric acid approaches destruction of the integrity of the fiber. As was indicated earlier inclusion of small quantities of H_2SO_4 in the fiber causes a loss in hydrolytic and oxidative stability.

Before the ultrasonic treatment, strong hydrogen bonding between crystallites of the PPTA fibers prevents the crystallites from moving relative to one another. When a mechanical stress is applied to the fiber, the fiber loses its mechanical strength when the hydrogen bonds begin to break. Another word, the PPTA crystallites are torn apart because there are no hydrogen bonded groups allowing flexibility between the crystallites. Water, which is hydrogen bonded to the amide groups, induces the needed flexibility. When the PPTA fibers are produced they are spun and immersed into water at a low temperature (0-5°C). Such treatment introduces water molecules between PPTA crystallites. As a result, the mechanical stability of the fiber is improved since water molecules diffuse into the fiber to form hydrogen bonds which allow slippage between the crystallites. When methanol or acetone are used as coagulating solvents, the mechanical properties of the fiber are decreased and original hydrogen bonding, brittle failure is observed. These observations support our results utilizing ultrasonic treatment in the presence of water and sodium hydroxide solutions. Essentially, such treatments promote the loss of hydrogen bonding between amide groups and increasing amounts of water. However, the mechanical stability of the PPTA fibers is not improved.

As indicated in the results section, the ultrasonic treatment in water and sodium hydroxide leads to the decrease of the 3300 cm\(^{-1}\) band, due to hydrogen bonded N-H groups, as well as the increased intensity of the 3700 cm\(^{-1}\) band due to adsorbed water. This observation is attributed to the loss of hydrogen bonds between amide groups of neighboring chains during the ultrasonic treatment. Apparently, the water molecules intercept the hydrogen bonds between two neighboring amide groups before they are able to reform after the ultrasonic treatment. Because the ultrasonic treatment is a nonequilibrium process, the hydrogen bonding will reassert itself if water is not present to prevent it. On the other hand, the ultrasonic treatment in the presence of sulfuric acid leads to dehydration of the fiber as well as the disruption of the hydrogen bonded amides which, in turn, cause the decrease of mechanical strength of the fiber. This is shown in Figure 1, the loss of water bands as well as the decrease of intensity of the bands due to hydrogen bonded amides are observed.

Thus, the ultrasonic treatment provides a sufficient amount of energy to break the hydrogen bonds between the polar amide groups and allowing water molecules to diffuse into the fiber. Figure 4 demonstrates how water molecules form new hydrogen bonds with the amide groups preventing them from reforming the original hydrogen bonds. The spectral data indicates that a greater amount of free amide groups are available after the ultrasonic treatment signifying the increase of sites available for bonding with the polymer matrix. The ultrasonic treatment not only allows water molecules to diffuse into the fiber, but also removes sulfate ion impurities from the surface. These impurities result from the neutralization step in the fiber spinning process. Figure 5 illustrates the mechanism of diffusion of sulfate ions from the fiber.

In order to confirm the PA FT-IR results, mechanical testing of the PPTA fibers was carried out. The mechanical stability of the PPTA fibers is similar to that predicted by the PA FT-IR results. The work to break of the sonicated fibers in the presence of sulfuric acid is lower than the work to break of the untreated fibers. Table I lists the mechanical properties upon various treatments. A poor mechanical strength is attributed to hydrolytic chain cleavage during the ultrasonic treatment in acid, as evidenced by the increase of the carboxyl carbonyl band at 1670 cm\(^{-1}\) and free amine band at 1550 cm\(^{-1}\) (Figure 2). The ultrasonic treatment in the presence of water and sodium hydroxide yields a small decrease of the work to break. Even though the mechanical stability slightly decreases, the reactive surface groups become accessible for bonding through sonication in both solvents which, in turn, will enhance the bonding with the polymer matrix.

While the above studies were performed by two independent methods, photoacoustic FT-IR and mechanical testing, it is our goal to monitor the molecular deformations in fibers and composites during stress-strain measurements. For that purpose we have incorporated a mini stress-strain
device into the photoacoustic cell in order to follow the events on a molecular level during fiber stretching. Preliminary results of these novel in-situ stress-strain PA FT-IR measurements will be presented and discussed.

Conclusions

The loss of hydrogen bonding between neighboring amide groups and the increase of the amide carbonyl and amide N-H bands during the ultrasonic treatment in water and sodium hydroxide leads to the increase of accessible for bonding amide groups. Such treatment should lead to improved adhesion in composite matrices and does not affect the mechanical strength of the fiber. Upon sonication in the presence of sulfuric acid, the loss of the hydrogen bonded amide band (3300 cm⁻¹) and the increase of the free amine band (1550 cm⁻¹) is observed. The sulfuric acid treatment promotes the polymer chain cleavage leading to fiber degradation. Moreover, such treatments hydrolyze main chain polymer bonds leading to a smaller work to break.

Acknowledgments

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References


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<tr>
<th>TABLE I</th>
<th>The effect of sonication on the mechanical properties PPTA fibers</th>
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<tr>
<td>Solvent</td>
<td>Work to break [J]</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.069</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.058</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0.013</td>
</tr>
<tr>
<td>Untreated PPTA</td>
<td>0.078</td>
</tr>
</tbody>
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Figure 1. Subtraction spectra of PPTA fibers sonicated in NaOH, H₂SO₄, and H₂O (4000-2600 cm⁻¹).

Figure 2. Subtraction spectra of PPTA fibers sonicated in NaOH, H₂SO₄, and H₂O (1700-1350 cm⁻¹).

Figure 3. Subtraction spectra of PPTA fibers sonicated in NaOH, H₂SO₄, and H₂O (1425-800 cm⁻¹).

Figure 4. The effect of ultrasound and stretching PPTA fibers.

Figure 5. The diffusion of sulfate ion out of the PPTA fiber during sonication.