Temperature Dependence of Sound Velocity in High-Strength Fiber-Reinforced Plastics

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Longitudinal sound velocity in unidirectional hybrid composites or high-strength fiber-reinforced plastics (FRPs) was measured along the fiber axis over a wide temperature range (from 77 K to 420 K). We investigated two kinds of high-strength crystalline polymer fibers, polyethylene (Dyneema) and polybenzobisoxazole (Zylon), which are known to have negative thermal expansion coefficients and high thermal conductivities along the fiber axis. Both FRPs had very high sound velocities of about 9000 m/s at low temperatures and their temperature dependences were very strong. Sound velocity monotonically decreased with increasing temperature. The temperature dependence of sound velocity was much stronger in Dyneema-FRP than in Zylon-FRP. [DOI: 10.1143/JJAP.42.5205]

KEYWORDS: high-strength polymer, fiber-reinforced plastic, hybrid composite, sound velocity

1. Introduction

New high-strength crystalline polymer fibers have recently been developed and are used in hybrid composites or fiber-reinforced plastics (FRPs). Unidirectional hybrid composites are fabricated by aligning the fibers in an epoxy matrix, and they are expected to have many applications because of their superior mechanical and thermal properties.

Dyneema, which is a trademark of TOYOBO in Japan, is a polyethylene fiber that has a high mechanical performance. Its good mechanical strength results from its high crystallinity\textsuperscript{1} (about 95%), ultrahigh molecular weight (\( > 10^{6} \)), and ultrahigh molecular chain orientation. Dyneema has a negative thermal expansion coefficient (\(-9 \times 10^{-6}/\text{K}\)),\textsuperscript{2} low frictional coefficient,\textsuperscript{3} high thermal conductivity (typically 0.1 W/cmK at 100 K)\textsuperscript{4} and high resistance to flash over voltage.\textsuperscript{5} One example of Dyneema-FRP applications is in cryogenics. Its properties make it suitable for superconducting coil bobbins\textsuperscript{5,7} or spacers.\textsuperscript{8} High-field superconducting magnets are sometimes quenched by wire motion induced by an electromagnetic force. If the coil bobbins are made of FRP, it is anticipated that the wire motion will be decreased by the expansion of FRP at low temperatures.

Polybenzobisoxazole (Zylon, which is also a trademark of TOYOBO in Japan) is a rigid-rod lyotropic liquid crystal fiber. Zylon has better mechanical strength\textsuperscript{9} and a smaller negative thermal expansion coefficient\textsuperscript{10} than Dyneema. It also has better heat and flame resistance, and thus is expected to be useful in a high-temperature environment.

Figure 1 shows the molecular structures of Dyneema and Zylon fibers. Both crystals have a one-dimensional characteristic because the intrachain covalent bond is much stronger than the interchain van der Waals interaction in both systems. In FRP, many mono-filaments of high-strength polymer, whose diameters are about 10 \( \mu \text{m} \), are aligned and immersed in an epoxy matrix. The fiber volume fraction was 0.6 for both FRPs.

Due to the high mechanical strength of the above FRPs, they are expected to have a very high sound velocity. Heat is transported by phonons in the FRPs and their high thermal conductivities must also be a result of this high sound velocity. Information on sound velocity is important in understanding the mechanical properties, thermal conductivities, and negative thermal expansion of these FRPs. It also provides insight into the FRP structural properties, such as glass transition in the noncrystalline portion and melting transition in the crystalline portion. A high sound velocity also opens new applications of these materials. We report here for the first time the sound velocities in Dyneema-FRP and Zylon-FRP along the fiber over a wide temperature range.

2. Experimental

We fabricated FRP samples to a rectangular shape (\( 10 \times 10 \times 20 \text{mm}^3 \)). Fibers were aligned in the 20 mm direction and sound velocity was measured along them. A sample of epoxy resin, which was the same material as the FRP matrix, was prepared in the same way for comparison. Two transducers for longitudinal sound were glued on the flat surface of the samples facing each other. We used several types of silicon rubber and silicon grease to glue the sound transducer to the samples. Measurements were carried out by the sound pulse transmission method. Transmitted signals were phase sensitively detected and absolute value of sound velocity \( v \) was determined from phase \( \theta \) by sweeping the frequency \( f \):

\begin{equation}
  v = \frac{C}{f} \sin \theta
\end{equation}

\begin{equation}
  C = \frac{2d}{\tan \theta}
\end{equation}

Fig. 1. Molecular structures of Dyneema and Zylon fibers.

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\[ v = 2\pi L \frac{df}{d\theta}. \]  

(2.1)

where \( L \) is the sample length. We used sound frequencies from 4 to 9 MHz. The duration of a sound pulse was 0.5 \( \mu \)s to avoid cross talk and overlapping with the reflected signals. Two types of LiNbO\(_3\) transducer, which had different resonance frequencies, were used for measurements. No systematic dependence on the type of transducer, glue, or resonant frequency was observed. We had a relatively large uncertainty of about 4% in the absolute values of \( v \) obtained by this method. We could not use a time-of-flight method to measure the absolute values of \( v \) with better accuracy, because of the high sound velocity and the large sound attenuation in these FRPs, as will be shown later. However, the absolute values were consistent with those measured by the time-of-flight method within this accuracy. In order to check our sound spectrometer, we applied the same type of method for the materials, such as water and liquid helium, which have well-known sound velocities. They agreed with the reported values of sound velocities within this accuracy. A relative change in \( v \) with sweeping temperature could be measured with a much better accuracy within about 1% because the phase of sound was very sensitive to the relative change in \( v \). FRP samples were set in a cryostat or an oven to sweep temperatures. A Pt resistance thermometer was used for temperature measurement.

We were able to see at most two echo signals at our sample length. Attenuation of sound in our sound frequency was relatively large, more than 0.27 (1/cm). However, we had a problem in bonding the transducer to the samples because of a large thermal contraction, and sound signals sometimes disappeared by sweeping temperature. This is the reason we used several kinds of glue. No systematic measurement of sound attenuation was possible because we were unable to separate the intrinsic and extrinsic attenuations.

3. Results and Discussion

The temperature dependences of sound velocity in all samples, Dyneema-FRP (\( v_D \), ○), Zylon-FRP (\( v_Z \), ●) and epoxy (\( v_e \), △), are shown in Fig. 2. Because \( v_e \) was much smaller than \( v_D \) and \( v_Z \), we can say that the elastic properties of the FRPs are dominated by the fibers. At low temperatures, both \( v_D \) and \( v_Z \) saturated at about 9000 m/s, which is surprisingly large, for example, larger than those of iron (5950 m/s) and silicon (8433 m/s). With increasing temperature, \( v_D \) and \( v_Z \) decreased monotonically. The temperature dependence of sound velocity in Dyneema-FPR was much stronger than that in Zylon-FRP, as shown in Fig. 2.

The temperature dependences of \( v_D \) and \( v_Z \) are expanded in Figs. 3 and 4, respectively. The data taken in the cryostat are represented by dots (●) and those in the oven by circles (○) in these figures. Data in the oven are shifted to connect smoothly to data in the cryostat in the overlapping temperature regions. The amount of the shifts is less than 4%, which is within the accuracy of the absolute values of \( v \).

We lost the sound signal in Dyneema-FRP below 150 K, probably due to a bonding problem with the transducers. We tried to measure \( v_D \) in this temperature range using different types of glue but were unsuccessful. When Dyneema-FRP was dipped in liquid nitrogen directly, we detected the sound signal; this is why we have one data point of \( v_D \) at 77 K. We were able to detect the sound signal in Zylon-FRP in the lower temperature range, down to 60 K, presumably because of its smaller thermal expansion coefficient.

At room temperature, \( v_D \approx 6800 \text{ m/s} \), which is much higher than that of conventional polyethylene fibers (about 1950 m/s). These two fibers, Dyneema and polyethylene, have chemically identical formulas, but the high crystallinity, high molecular weight and high molecular chain orientation of Dyneema enhanced the sound velocity compared with polyethylene. The temperature dependence of \( v_D \) in Fig. 3 has two steep decreases at approximately 230 K and above 400 K. Dyneema contains a noncrystalline portion of about 5%\(^{11}\) which has a glass transition temperature of approximately 170 K.\(^{11}\) In FRP, this glass transition
temperature is thought to be shifted, although this has not been confirmed experimentally. The decrease in $v_D$ at approximately 230 K, which is not so sharp, could be related to this transition. It is also known that Dyneema has a melting transition temperature of approximately 450 K.\(^\text{12}\) We speculate that $v_D$ decreases as it approaches this temperature, which is consistent with the measured behavior.

Zylon has a noncrystalline portion of 14%.\(^\text{13}\) Its glass transition temperature is much higher than room temperature, although the exact value is not known. It is possible that this glass transition temperature is above 420 K because we saw no significant change in $v_D$ in our measurement. The decomposition temperature of the crystalline portion of Zylon is high, at 920 K\(^\text{10}\) which is much higher than our decomposition temperature of the crystalline portion of FRPs, however, a high sound velocity was compatible with large sound attenuation, probably due to the hybrid nature of the two materials.

Let us compare the measured values of sound velocities with those estimated based on the reported elastic constant $K$ and density $\rho$ by assuming a simple model:

$$v = \sqrt{\frac{K}{\rho}},$$

$$K = \alpha K_f + (1 - \alpha) K_e,$$

$$\rho = \alpha \rho_f + (1 - \alpha) \rho_e.$$  

Here, $K_f$ and $K_e$ are the elastic constants of fiber and epoxy, respectively, $\rho_f$ and $\rho_e$ are their densities and $\alpha$ is the volume fraction of the fibers. For Dyneema at room temperature, if we use the values: $K_f = 85$ (GPa), $K_e = 4$ (GPs), $\rho_f = 0.97$ (g/cm$^3$), $\rho_e = 1.05$ (g/cm$^3$)\(^\text{14}\) and $\alpha = 0.6$, we estimate $v$ to be $7.2 \times 10^3$ (m/s). For Zylon, using the values, $K_f = 280$ (GPa), $\rho_f = 1.56$ (g/cm$^3$), \(^9\) we estimate $v$ to be $1.1 \times 10^4$ (m/s). Thus, these estimates are 8% larger than the measured values for Dyneema-FRP and 26% larger than those for Zylon-FRP. The acoustic properties of these materials are tend to be very sensitive to the production process for FRPs. It is not easy to make a realistic prediction of the acoustic properties of the composites beyond this simple estimation, and thus it is worth conducting a practical acoustic measurement of FRPs.

It will be very interesting to investigate the anisotropy of acoustic properties in these kinds of highly unidirectional materials. The anisotropy of thermal conductivity of these FRPs was measured by Fujishiro et al.\(^\text{4}\) These authors found that thermal conductivity perpendicular to the fibers was about 80 times less than that in the fiber direction. We also tried to measure sound velocity perpendicular to the fibers in Dyneema-FRP and Zylon-FRP with a shorter path length, $L = 10$ mm, at room temperature. The same setups for measurement were used but we detected no sound transmission signal at all, presumably due to the very high attenuation of sound in this direction. As mentioned, sound attenuation even along the fibers was also relatively large; we could detect only two transmission signals in the 20 mm sample length. It is generally true that materials with high sound velocities have small sound attenuation. In these FRPs, however, a high sound velocity was compatible with large sound attenuation, probably due to the hybrid nature of the two materials.

4. Conclusions

We measured the sound velocities in Dyneema-FRP and Zylon-FRP along fibers over a wide temperature range and found them to be very large, about 9000 m/s at low temperatures. Sound velocity decreased with increasing temperature and the temperature dependence of sound velocity in Dyneema-FRP was much stronger than that in Zylon-FRP.

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