Sound Velocity of High-Strength Polymer with Negative Thermal Expansion Coefficient

R. Nomura [a,1], M. Ueno [a,2], Y. Okuda [a], S. Burmistrov [a,3] and A. Yamanaka [b]

[a] *Department of Condensed Matter Physics, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro, Tokyo 152-8551, Japan*

[b] *Research Center, Toyobo Co., Ltd, 2-1-1, Katata, Ohtsu, Shiga 520-0292, Japan*

Abstract

Sound velocities of fiber reinforced plastics (FRPs) were measured along the fiber axis at temperatures between 360K and 77K. We used two kinds of the high-strength crystalline polymer fibers, polyethylene (Dyneema) and polybenzobisoxazole (Zylon), which have negative thermal expansion coefficients. They also have high thermal conductivities and high resistances for flash over voltage, and are expected as new materials for coil bobbins or spacers at cryogenic temperatures. They have very large sound velocities of about 9000 (m/s) at 77K, which are 4.5 times larger than that of the ordinary polyethylene fiber.

Key words: polymer, fiber reinforced plastic, sound velocity

1. Introduction

New high-strength crystalline polymer fibers have been developed recently and their fiber reinforced plastics (FRPs) are expected for cryogenic applications. We measured sound velocities of two kinds of FRPs, Dyneema-FRP and Zylon-FRP, along the fiber. Dyneema is a trademark of TOYOBO in Japan, which is highly crystalline polyethylene fiber (crystallinity of about 80%) and has ultra-high molecular weight ($> 10^6$), ultra-high molecular chain orientation and excellent mechanical strength. Dyneema have negative thermal expansion coefficient[1], low frictional coefficient[2], high thermal conductivity[3] and high resistance for flash over voltage[4]. It is suitable for superconducting coil bobbins[5] or spacers[6] by these properties. High field superconducting magnets sometimes quench by wire motion induced by the electromagnetic force. If the coil bobbins are made from the FRP, it is expected that wire motions are 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[7] and smaller negative thermal expansion coefficient than Dyneema. Figure 1 is the molecular structures of Dyneema and Zylon. In FRP many mono-filaments of these high strength polymer are aligned and immersed in epoxy resin. Diameters of the mono-filaments were about 10 μm. Fiber volume fraction was 0.6 for both FRPs in this measurement. Sound velocity measurement will shed light on the physics of the high mechanical properties, negative thermal expansion and high thermal conductivities of these FRPs.

2. Results and Discussion

FRP samples were fabricated to the rectangular shapes ($10 \times 10 \times 20$ mm^3) and fibers were aligned to

[1] Corresponding author. E-mail: nomura@ap.titech.ac.jp , Fax: +81-3-5734-2751

[2] Present address: Department of Physics, University of Tokyo, 7-3-1, Hongo, Bunkyou, Tokyo 113-0033, Jpan

[3] Permanent address: Department of Superconductivity and Solid State Physics, Kurchatov Institute, Moscow 123182, Russia

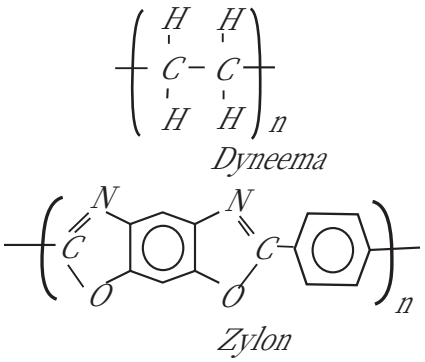

Fig. 1. Molecular structures of Dyneema and Zylon.

the 20 mm direction. We also prepared an epoxy sample, which is the same material for the FRP matrix, and measured sound velocity. Two transducers were glued to the flat surfaces by silicon rubber and sound direction was parallel to the fiber. Measurements were performed in the sound pulse transmission method. Sound were longitudinal and its frequency was about 5MHz.

Figure 2 shows temperature dependences of sound velocities for Dyneema-FRP ($\bullet, v_D$), Zylon-FRP ($\circ, v_Z$) and epoxy ($\triangle, v_E$). Because $v_D, v_Z >> v_E$, most of the elastic properties of FRPs are determined by the fibers. At room temperature $v_D \approx 6800$ (m/sec) and it increased by cooling and almost saturated at about 8900 (m/sec) below 100 K. For Zylon-FRP temperature dependence was weaker, $v_Z \approx 8700$ (m/sec) at room temperature and $v_Z \approx 9200$ (m/sec) below nitrogen temperature. These values are surprisingly large for organic polymers. For example sound velocity of iron is 5950 (m/sec) and that of silicon is 8433 (m/sec). Sound velocity of the ordinary polyethylene fiber is about 1950 (m/sec). v_D is 3 times larger at room temperature and 4.5 times at nitrogen temperature than that of the ordinary polyethylene fiber. Note that these two fibers are chemically identical, but high crystallinity, high molecular weight and high molecular chain orientation of Dyneema resulted in this big difference of sound velocities.

Thermal conduction of these fibers are due to phonons, and thus these large values of sound velocities and high crystallinity will explain the high thermal conductivities of these materials along the fiber[3]. Thermal conductivity perpendicular to the fibers in FRPs were also measured in ref. [3] and it was about 80 times smaller than that in fiber direction. These large anisotropies of thermal conductivities are very interesting and we tried to measure sound velocity perpendicular to the fiber. We used the same FRP samples with shorter sound path length of 10 mm, but

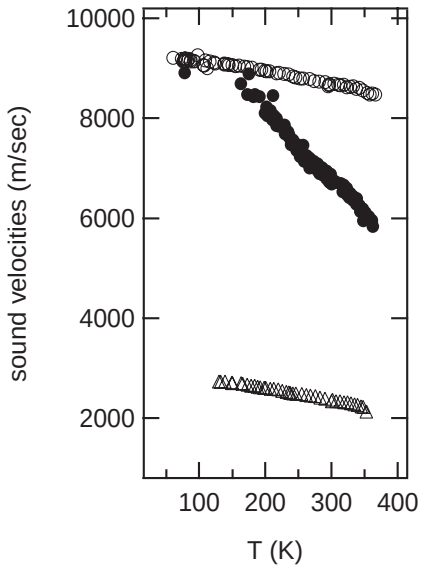

Fig. 2. Temperature dependences of sound velocities for Dyneema-FRP (•), Zylon-FRP (○) and epoxy (△)

no transmission signal was observed because of large attenuation of ultrasound.

3. Summary

Sound velocities of Dyneema-FRP and Zylon-FRP were measured along the fiber direction between 360K and 77K. They have very large sound velocities for the organic polymers, which explain the origin of the high thermal conductivities.

Acknowledgements

We acknowledge K. Fujimoto for his assistance in the early stage of this experiment.

References

[1] T. Kashima *et al.*, Adv. Cryog. Eng. **42** (1996) 147.

[2] T. Takao *et al.*, Proc. of ICEC16/ICMC, (1997) 1993.

[3] H. Fujishiro *et al.*, Jpn. J. Appl. Phys., **36** (1997) 5633.

[4] T. Nitta *et al.*, Proc. of MT-15, (1997).

[5] T. Kashima *et al.*, Adv. Cryog. Eng. **41** (1996) 441.

[6] A. Yamanaka *et al.*, Cryog. Eng. **32** (1997) 330.

[7] S.J. Krause *et al.*, Polymer **29** (1988) 1354.