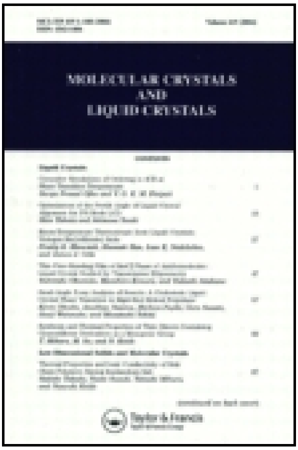

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Jacketing of Optical Fibers with Ordered Thermotropic Liquid Crystal Polyesters

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JACKETING OF OPTICAL FIBERS WITH ORDERED THERMOTROPIC LIQUID CRYSTAL POLYESTERS

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Abstract Thermotropic liquid crystal polyesters (LCPs), based on improved polyethylene terephthalate (PET) and para-hydroxybenzoic acid (PHB), are investigated as a secondary jacketing material for enclosing optical fibers. Because of shear- and deformation-induced molecular orientations produced during extrusion, the newly developed LCPs exhibit low thermal expansion coefficients and high Young's moduli. As a result, the LCP-jacketed optical fibers show small loss increases in the -60°C to 80°C temperature range and high lateral load resistance, compared with conventional nylon-jacketed optical fibers. Furthermore, the low melt viscosity and significantly low thermal shrinkage allow us to coat the LCPs on the optical fibers at high speeds above 300 m/min.

INTRODUCTION

Resent increase in the public use of optical communication systems and growing expectations for new media services make it necessary to develop high performance and low cost optical fiber cables. Today, many kinds of polymers are used as supporting materials for optical fibers. In particular, polymer jackets are essential for fiber support because optical fibers are made of hair thin glass with a diameter of 125 μm and the mechanical strength of bare fibers is extremely sensitive to surface flaws or imperfections.

In order to mechanically isolate optical fibers from their surroundings, they should be tightly jacketed with soft polymers (primary coating) during the fiber drawing process, and then tightly or loosely jacketed with hard polymers (secondary coating) (Fig. 1). However, because of the significant difference in thermal expansion coefficients (α) between optical fibers ($\alpha \simeq 6 \times 10^{-7}/°C$) and the

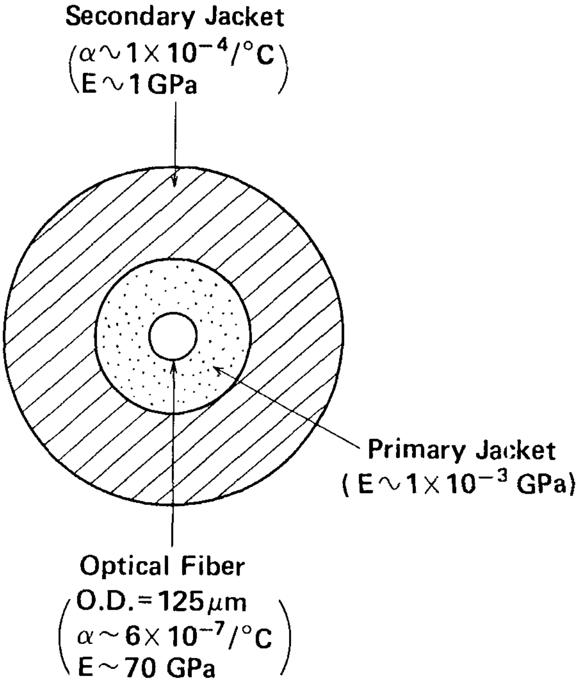


FIGURE 1. Cross-section of tightly jacketed optical fibers.

secondary coating materials ($\alpha \simeq 1 \times 10^{-4}$/°C), jacketed optical fibers without low α supporting materials such as steel exhibit increase in microbending transmission loss due to jacket contraction at low temperatures.

Furthermore, low Young's moduli ($E \simeq 1$ GPa) of ordinary secondary jacketing materials make it necessary to use fairly intricate cable structures to avoid both fracture of optical fibers due to tension and increase in distortion loss due to lateral load. Thus, high E, low α jacketing materials have been investigated for the development of simple, high performance optical fiber cables.[1]

It is well known that thermotropic liquid crystal polyesters (LCPs) can easily order in the liquid crystal state under shear or elongational stress, and the ordered LCPs exhibit significantly high E and low α, compared with ordinary polymer materials. These facts indicate that ordered LCPs have potential advantages as a new optical fiber jacketing material.[2] However, they have some serious disadvantages such as brittleness arising from molecular orientation.

Material properties of LCPs depend significantly on molecular structure and processing conditions. Thus, different properties may be developed from one LCP material. For the application of LCPs, however, the desired properties have to be obtained stably under a given processing condition that is predetermined in many cases.

In this paper, LCP is applied to optical fiber secondary jackets in order to develop novel high E and low α jackets. The use of LCP in optical fiber jacketing and in the extrusion-coating method is investigated. The orientation properties of the newly developed LCP and the optical characteristics of the LCP-jacketed optical fibers are then discussed.

REQUIREMENTS FOR SECONDARY JACKETING MATERIALS

In order to avoid fiber fracture and transmission loss increase, it is necessary to reduce optical fiber elongation and bending due to external forces. The primary requirements for simple (low cost), highly reliable, high density optical fiber cables, and the requirements for secondary jackets are shown in Table I. High E is necessary for the secondary jacket to resist tension due to external force. Low α is needed to prevent micro- and macro-bending loss increases due to jacket contraction at low temperature. Low thermal shrinkage does not cause loss change in long-term use. Flexibility is for good handling of cables during installation, and low melt viscosity is one of the requirements for high speed coating. It is difficult to

TABLE I Requirements for jacketed optical fibers and properties of jacketing polymer.

Requirements for tightly jacketed optical fiber	Requirements for jacket polymer	Nylon properties	LCP properties
High load resistance	High Young's modulus	1 GPa	10 GPa
No loss increase at low temperature	Low thermal expansion coefficient	1×10^{-4}/°C	$\leq 10^{-5}$/°C
No loss increase in use	Low thermal shrinkage, 130°C	0.7%	0.1%
Flexibility for good handling	Small bending radius	$\leq$ 2mm	$\leq$ 2 mm
High speed coating	Low melt viscosity	10^3 poise	10^3 poise

find traditional jacketing materials which fulfill all these requirements. For instance, nylon 12 jacketing material exhibits low E, high α, and unless it is cooled gradually during the extrusion coating, it shrinks during long-term use because of recrystallization or molecular orientation release.

LCP MATERIAL PROPERTIES

LCP Materials

A series of investigations applying high E, low α LCP materials to optical fiber jackets were made. Among many LCPs which have been proposed from all over the world, a nematic LCP[3] consisiting of polyethylene terephthalate (PET) and para-hydroxybenzoic acid (PHB) was selected as a standard material for the following reasons:

(1) Relatively low liquid crystal transition temperatures and resulting capability of extrusion using a conventional extruder (processing temperature $\leq$ 340°C).

(2) Possibility of the reductions in brittleness because of flexible chains in the molecular structure.

(3) Expectations of LCP material cost reduction because of low monomer costs and ease of the synthetic procedure.

PET/PHB Copolymer Composition

The copolymer composition dependence of the liquid crystal transition temperature (T_m) and the isotropic transition temperature (T_i) for 20/80 to 80/20 PET/PHB copolymers is shown in Fig. 2. When the PHB content is $\geq$ 50 mole%, a clear liquid crystaliine state is observed at temperatures above 220 °C[4]. T_m increases with increases in PHB content,

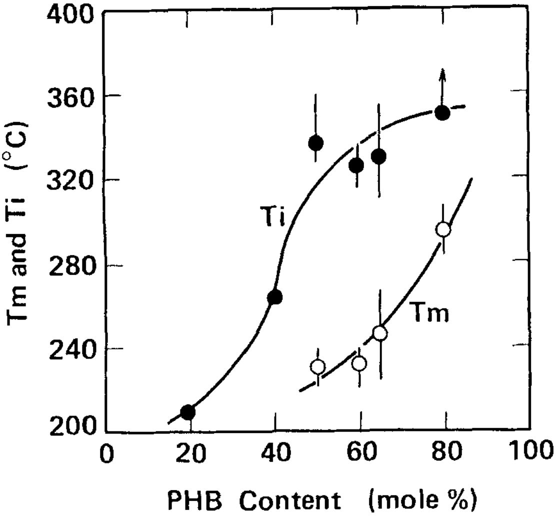


FIGURE 2. Effects of PHB content on liquid crystalline transition temperature (T_m) and isotropic transition temperature (T_i).

while T_i remains constant. It is preferred that extrusion-coating of optical fibers occur at jacketing temperatures that are as low as possible. This is because of processing ease and no thermal degradation. Therefore, PET/PHB copolymers having PHB $\leq$ 70 mole% are suitable for the jacketing material.

A Low thermal expansion coefficient (α) is one of the most outstanding characteristics of LCP. The relationship between α and the copolymer composition ratio for 0.5-mm PET/PHB rods prepared at a 240°C extrusion temperature, a shear rate of 1 x 10^3 sec^{-1} and an elongational draw ratio of 1 is shown in Fig. 3. α decreases abruptly with increases in the PHB content, and becomes less than 1 x

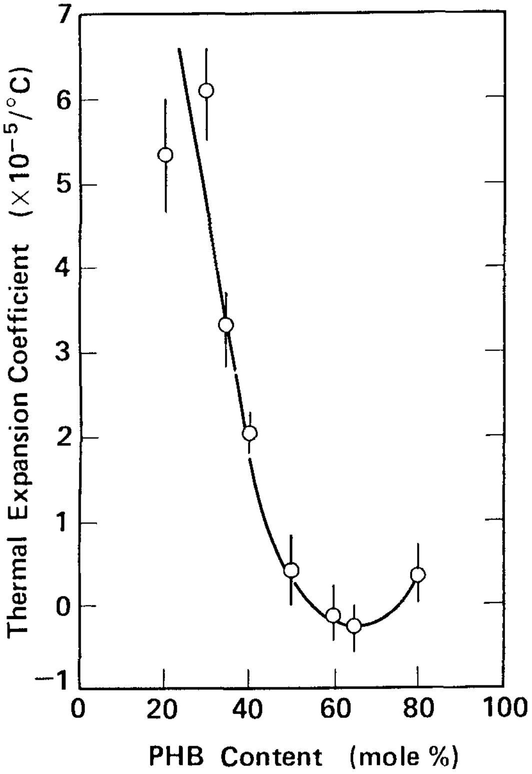


FIGURE 3. Relationship between linear expansion coefficient and copolymer composition ratio. Rod diameter is 0.5 mm, extrusion temperature is 240°C, shear rate is 1 x 10^3 /sec and elongational deformation ratio is 1.

10^{-5}/°C when PHB = 45 mole%. Apparently, the LCPs exhibit low α values when they are extruded in a liquid crystalline state. From these results, it has been shown that PET/PHB copolymers exhibiting low processing temperatures and low α are attained in the 50 to 70 mole% PHB content range.

PET/PHB COPOLYMERS ORIENTATION PROPERTIES

Young's Modulus Increase in Molecular Orientation

The molecular orientation of LCP is induced by shear and/or elongational forces in the liquid crystal state. Orientation properties change significantly with the degree of molecular orientation.[5] The well-defined orientation function (f_L) is related to Young's modulus (E) in the molecular orientation direction by the following:[6]

$$f_L = 1 - E_0/E, \tag{1}$$

where E_0 is Young's modulus for isotropic material without molecular order. Therefore, E can be used as a parameter for the degree of molecular orientation.

The increase in Young's modulus (E) of 1.0-mm rods extruded at various shear rates without elongational deformation[7] is shown in Fig. 4. Here, thermal and mechanical properties in the molecular orientation direction are discussed. Young's modulus increases linearly with the logarithm of the increasing shear rate. In spite of the three order increase in shear rate, the highest value of 11 GPa is still small. The low maximum Young's modulus at a high shear rate can be explained by considering molecular orientation distribution (birefringence distribution) in extruded rods (Fig. 5). Here, birefringences (Δn) were determined based on the optical retardation, which was measured by a beam with a diameter of 100 μ m. Molecular orientation occurs in the 150 μ m thick surface skin layer. On the other hand, the inner part is not affected by shear force. Since the overall Young's modulus is the average of those of the two regions, Young's modulus remained as low as

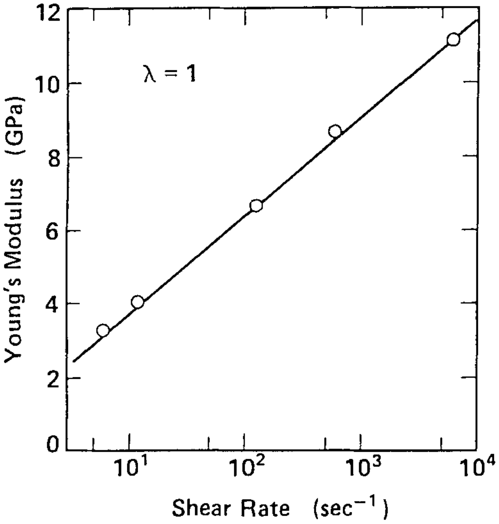


FIGURE 4. Change in Young's modulus with shear rate for extruded rods without elongational deformation.

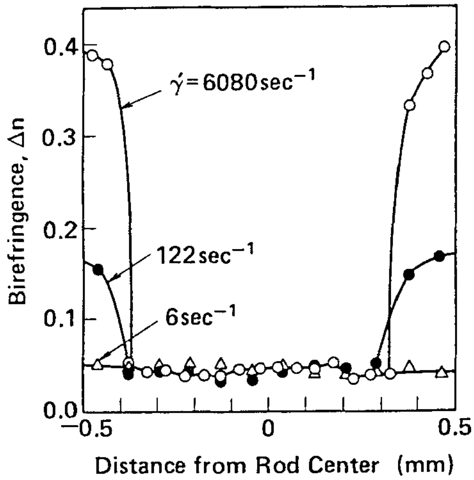


FIGURE 5. Change in birefringence distribution in the radial direction with shear rate.

11 GPa even at high shear rates.

Young's modulus of LCP increases significantly with increasing elongational force (Fig. 6). With a draw ratio of 50, Young's modulus is about 35 GPa.[8] This value is more than three times the highest value obtained by shear orientation. This significant increase in Young's modulus due to elongational deformation can also be explained in terms of molecular orientation distribution (Fig. 7). When the draw ratio λ is almost 1, that is, when elongational deformation does not occur, only the rod surface layer

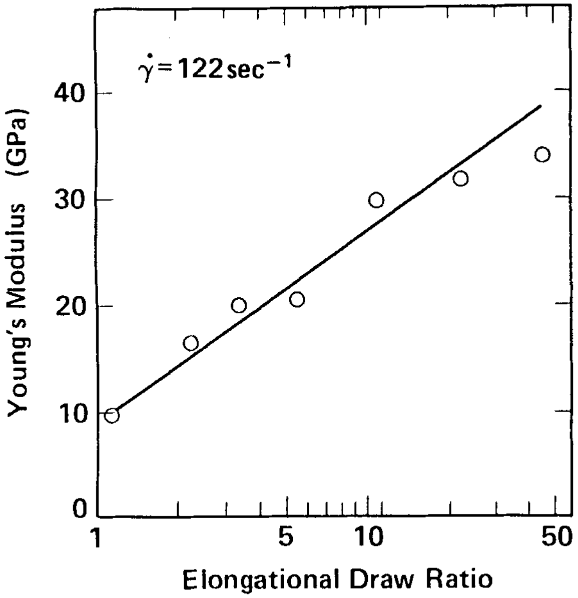


FIGURE 6. Change in Young's modulus with elongational deformation ratio. Shear rate is 122/sec.

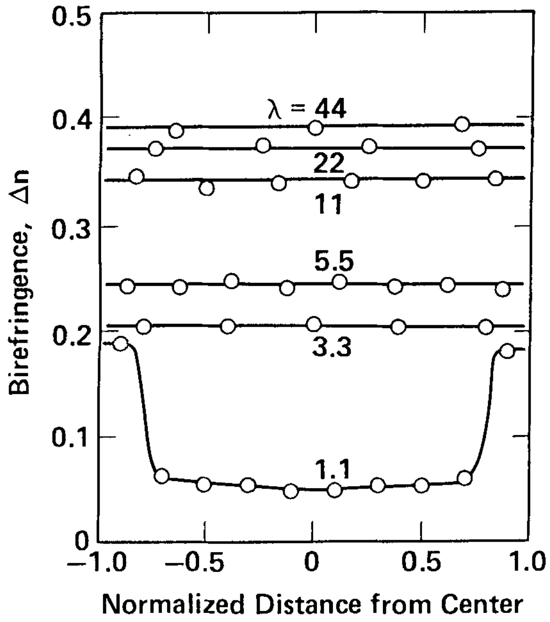


FIGURE 7. Change in birefringence distribution in the radial direction deformation ratio (λ).

orders by shear stress. However, with a draw-down ratio of as low as 3.3, the shear stress influence is wiped out. The inner part of the rod shows the same molecular orientation as the surface. The Δn distribution is small. With high-draw down ratios, therefore, high Young's moduli are easily attained.

Jacketing-Related Properties

The relationship between α and E_s for oriented PET/PHB copolymers with 30 to 65 mole% PHB contents is shown in Fig. 8. These were prepared under various extrusion or orientation conditions.[9] E_s is the sonic modulus measured at a 10 kHz pulse frequency. α decreases abruptly with

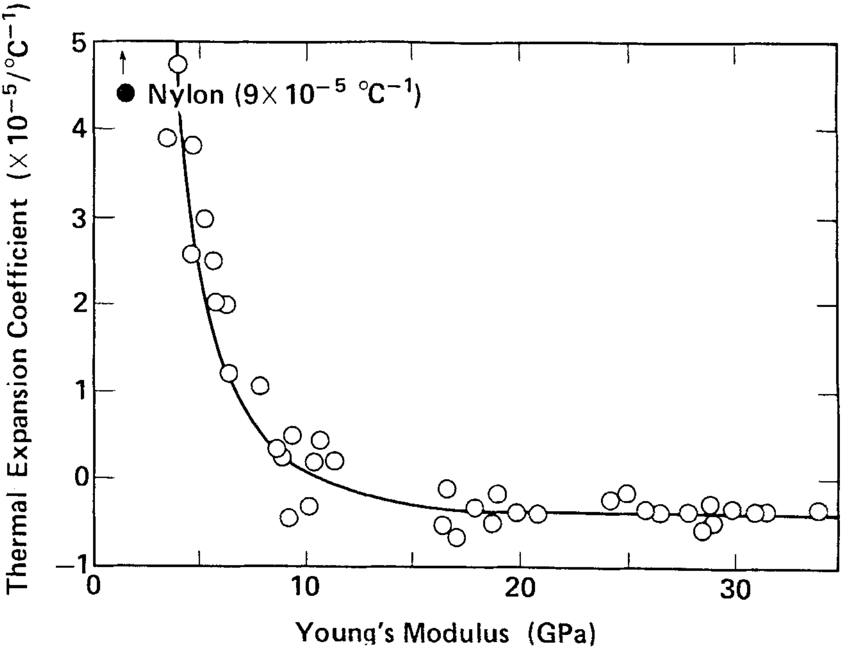


Figure 8. Relationship between linear expansion coefficient and Young's modulus for LCP (○) and Nylon (●).

increases in E_s, and levels off at 10^{-6}/°C when E_s = 8 GPa. E_s of 8 GPa corresponds to f_L = 0.56, since $E_{s,o}$ is estimated to be 3.5 GPa (see Fig. 13). The extremely low α values are ca. one-hundredth that of a conventional nylon 12 jacket.

The relationship between thermal shrinkage (δ) parallel to the molecular orientation and E_s for oriented PET/PHB copolymers is shown in Fig. 9. δ decreases with increases in E_s and levels off at a constant value of less than 0.1 % when E_s = 8 GPa. This decrease in δ is consistent with the decrease in α. The low α and δ values of PET/PHB copolymers are because of high molecular orientation and no orientation release. On the other hand,

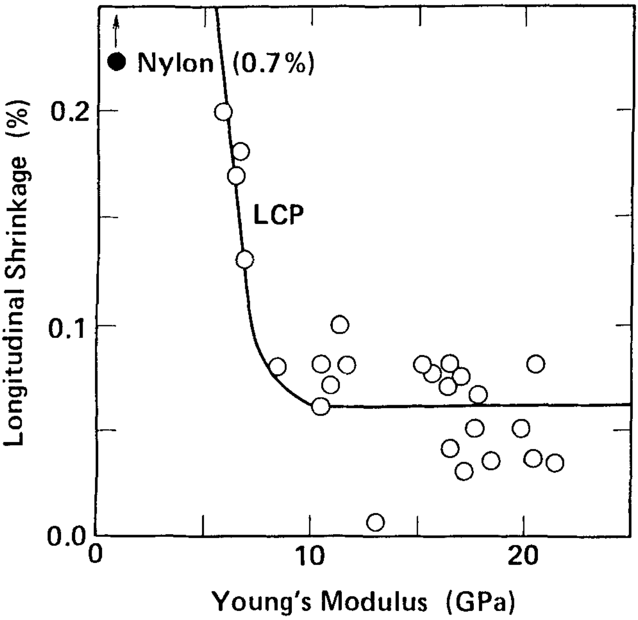


FIGURE 9. Relationship between thermal longitudinal shrinkage at 130°C and Young's modulus for LCP (○) and nylon (●).

a nylon 12 jacket had a δ of ca. 0.7 % at 130 °C.

The relationship between breaking strain (ε_b) and E_s for oriented PET/PHB copolymers, together with the relationship for improved copolymers, which will be discussed later, is shown in Fig. 10. ε_b decreases with increases in E_s and levels off at ca. 2 % when E_s = 10 GPa. ε_b of ca. 2 % for highly oriented PET/PHB copolymers with high PHB contents is approximately equal to that of PHB homopolymers. It seems that the fracture of PET/PHB copolymers is governed by the breaking strain of the continuous PHB-rich region.[10] From these results, it is evident that although oriented PET/PHB copolymers exhibit

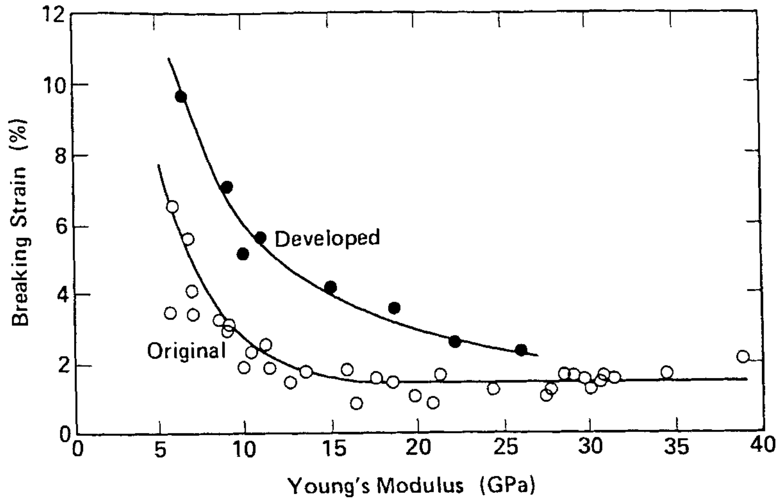


FIGURE 10. Relationship between breaking strain and Young's modulus for original (○) and improved (●) LCPs.

low α and δ when E_s = 8 GPa, they become very brittle.

Orientation Properties of Developed LCPs

In LCPs, brittleness arises from intense molecular orientation due to shear or elongational stress. In order to improve the molecular orientation of PET/PHB copolymers, the following was done:

(1) Liquid crystallinity was reduced by decreasing the PHB content.

(2) A third component with a large molecular volume was introduced.

(3) Randomness of PET and PHB components was increased by using a new synthetic method.

(4) Molecular entanglement was increased by increasing molecular weight.

The developed LCPs showed the same α and δ characteristics for E_s as the original LCPs, however, ε_b was different (Fig. 10). In LCP rods with orientaton distributions in the cross section, although α and δ are obtained as average values over cross sections, overall ε_b values are determined by the minimum at the highest oriented part. Δn distributions in rod cross sections for original and developed LCPs are shown in Fig. 11. When E_s = 10 GPa,

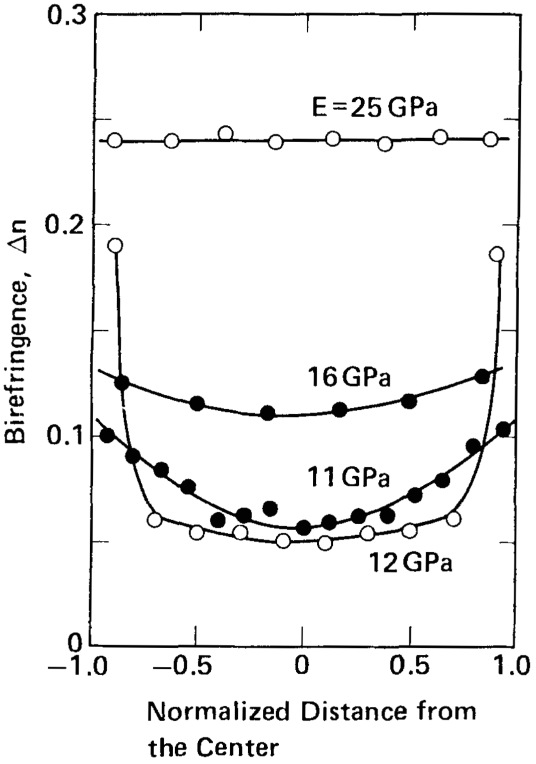


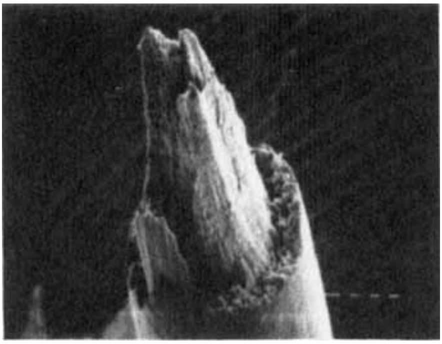
FIGURE 11. Birefringence distribution in radial direction of original (○) and improved (●) LCPs.

the original LCP rod (PET/PHB = 40/60) consists of both surface (skin) and inner (core) layers with extremely high and low degrees of molecular orientation, respectively. Consequently, ε_b of the rod is determined by that of the skin layer. On the other hand, the developed LCP rod is almost flat and, as a result, the highest Δn value at the rod surface is smaller than that of the original LCP rod. The difference in molecular orientation distribution of the two LCP rods can be determined by observation of the fractured surfaces (Fig. 12), i.e., the skin-core morphology is clearly recognized at the fractured surface of the original LCP rod, but not at that of the developed LCP rod. Reduction in Δn at the surface layer leads to considerably high ε_b values for the developed LCP (Fig. 10).

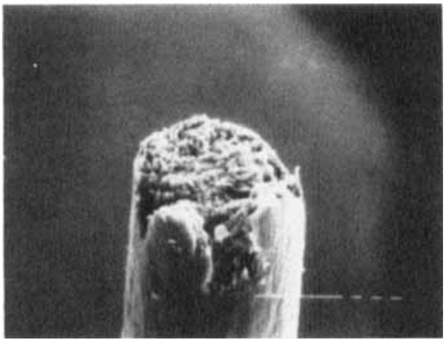
The relationship between $E_{s//}$ and $E_{s\perp}$ is shown in Fig. 13. $E_{s//}$ is parallel to the extrusion orientation direction and $E_{s\perp}$ is perpendicular to the molecular orientation direction of the developed LCP. $E_{s//}$ is important for resistance to tention and $E_{s\perp}$ is important for lateral forces which are applied to the jacketed optical fibers. Although $E_{s\perp}$ decreases with increases in $E_{s//}$, it remains at 3 GPa even when $E_{s//}$ = 10 GPa. $E_{s//}$ is seven times that of the ordinary jacketing material nylon 12, and $E_{s\perp}$ is twice as much, respectively. Thus, it is apparent that the developed LCP exhibits high E and ε_b, and low α and δ in the wide range of the molecular orientation state.

PROPERTIES OF LCP-JACKETED OPTICAL FIBERS

The developed LCP was applied as a secondary-coat on a primary-coated optical fiber using a conventional



Original



Developed

FIGURE 12. Fractured surfaces of original and developed LCP rods.

extrusion-coating line (Fig. 14). The primary-coated fiber from the pay-off drum was subjected to a constant back-tension of less than 100 g and was then fed into the cross-head die of the extruder. The jacketed optical fiber was then quenched to room temperature in a water bath located at a distance of ca. 70 cm from the die lip, and was

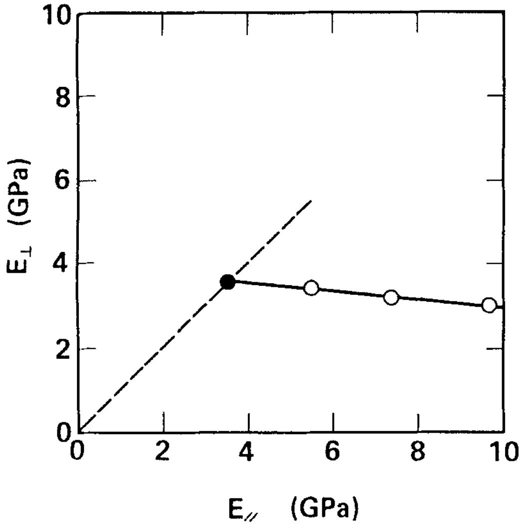


FIGURE 13. Relationship between Young's moduli in the direction of molecular orientation and in the perpendicular direction for LCP sheet.

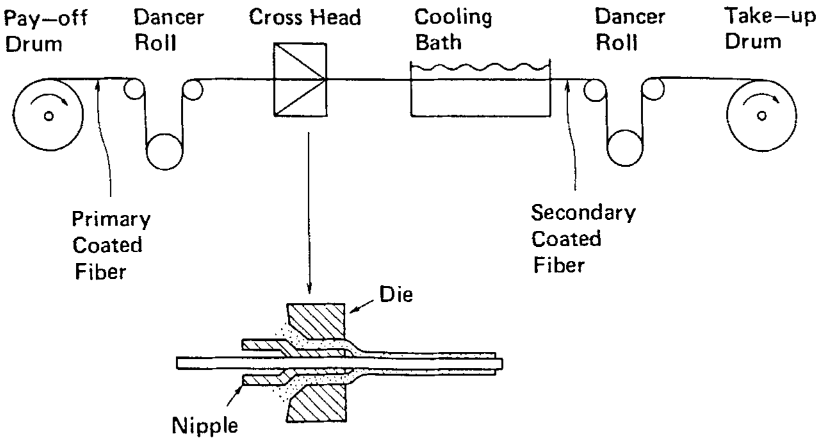


FIGURE 14. LCP extrusion-coating line.

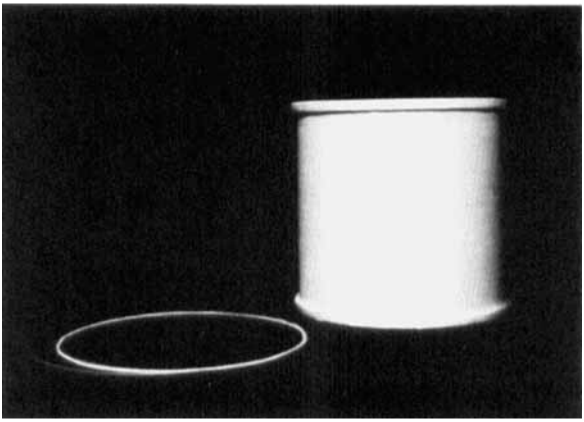


FIGURE 15. LCP-jacketed optical fiber wound on a drum.

then wound on the take-up drum (Fig. 15). No special technique, including control of the cooling rate from the LCP-melt, was required. In this line, molecular orientation of LCPs was induced by both shear stress at the die and nipple walls and elongational draw-down stress at the die lip. The molecular orientation was fixed at the cooling bath.

A graded-index multimode fiber was used, with a 50/125 μm core/cladding diameter and a 1-percent relative refractive-index difference between the core and the cladding. The optical fiber was coated with ca. 400-μm diameter primary silicone rubber and with ca. 900-μm diameter secondary nylon 12 or with 700 ∿ 900-μm diameter secondary LCP.

In general, optical fibers have been jacketed with nylon 12 at a rate of 100 m/min or less. Optical fibers can be jacketed with LCPs at much higher jacketing speeds because of no molding shrinkage and molecular orientation stability. Changes in E_s of an LCP-jacket with increases in jacketing speed are shown in Fig. 16. In the 50 to 300 m/min range, E_s is at 7 to 10 GPa, which offers excellent jacket properties, as already described. Here, the mechanical and optical properties of a LCP-jacketed optical fiber produced at a jacketing speed 300 m/min are shown.

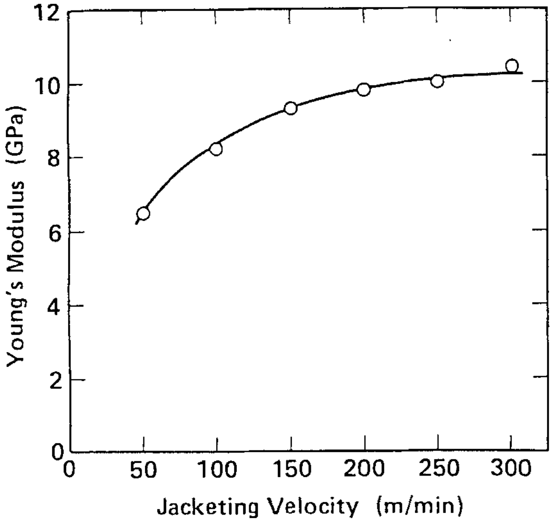


FIGURE 16. Change in Young's modulus with jacketing velocity for LCP jackets.

Transmission loss spectra before and after LCP jacketing are shown in Fig. 17. Processing incremental loss (jacketing loss) does not occur in the 0.7 to 1.7 μm wavelength within an experimental uncertainty of ± 0.1 dB/km. On the other hand, the jacketing loss of a nylon-jacketed optical fiber produced under the same

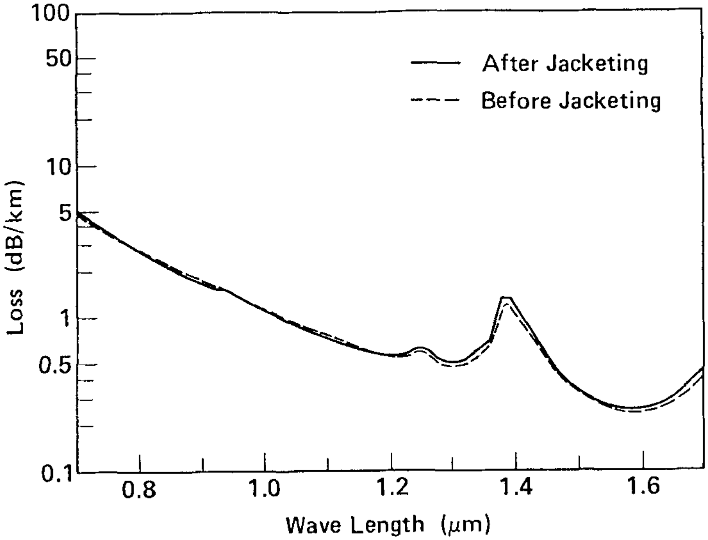


FIGURE 17. Loss spectra of optical fibers before and after LCP jacketing.

condition was at least 0.3 dB/km. The difference depends on whether jacket shrinkage (mold shrinkage), which induces micro- and macro-bending of the inner optical fiber, occurs during extrusion-coating.

Strength-strain curves on the initial state at a 0.05 min^{-1} strain rate at 25 °C for LCP- and nylon-jacketed optical fibers are shown in Fig. 18. The 900-μm diameter LCP-jacketed fiber strength is 450 g at a 0.1 % strain, although that of the nylon-jacketed fiber is 160 g. Since optical fibers should be kept at low tensile strains to avoid fracture, high resistance to tension of LCP-jacketed fibers makes it easy to design, produce and install.

The behavior of loss increase with decreases in temperature for the LCP- and nylon-jacketed fibers is shown

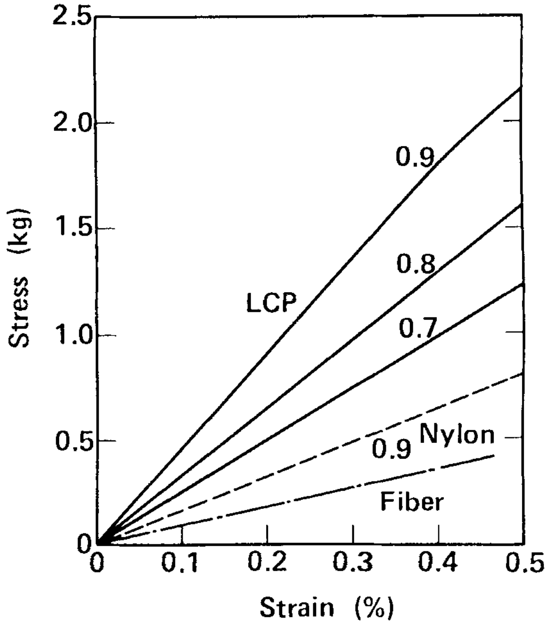


FIGURE 18. Stress-strain curves for optical fibers. Outer diameters of jacketed fibers (mm): (A) 0.9-LCP, (B) 0.8-LCP, (C) 0.7-LCP, (D) 0.9-nylon, (E) 0.4-silicone rubber without a secondary jacket.

in Fig. 19. No loss increase is observed in the LCP-jacketed fiber. Very stable optical transmission characteristics are attained. Fiber strains induced by decreases in temperature for the LCP- and nylon-jacketed fibers are shown in Fig. 20.[11] The change in fiber strain for the LCP-jacketed fiber is less than 0.1 % in the -60 °C to 80 °C temperature range because of the low α of the LCP jacket. Consequently, fiber-microbending and loss increase do not occur at low temperatures. On the other hand, the nylon-jacketed fiber exhibits a marked change in fiber

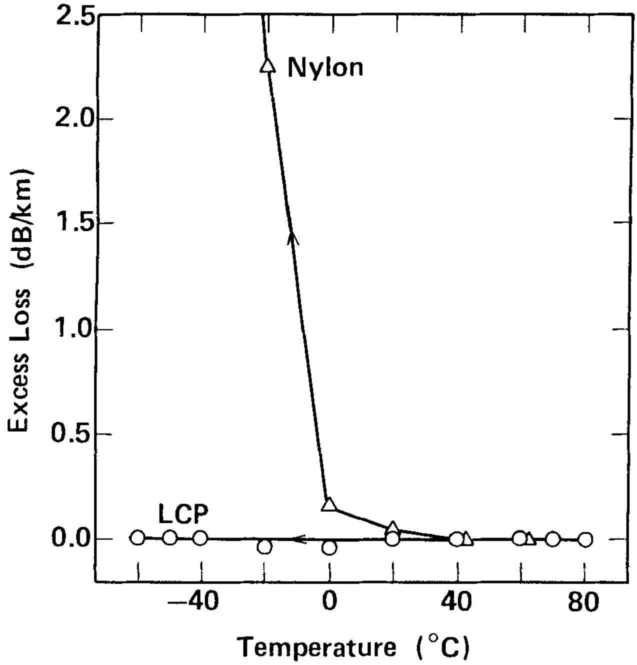


FIGURE 19. Change in excess loss with temperature for 0.9-mm LCP- and nylon-jacketed fibers.

strain of more than 0.2 % in the -60°C to to 60 °C temperature range. This induces fiber-microbending loss due to large compressive strain even at 0 °C.

Furthermore, LCP-jacketed fibers exhibit excellent loss properties even below -60°C, especially at liquid nitrogen temperature.[12] The nylon-jacketed fiber exhibits a significant loss increase over 1000 dB/km, while in the LCP-jacketed fiber, loss increase is less than 20 dB/km (Table II). This difference can be explained in terms of the magnitude of the heat shock due to immersion in liquid

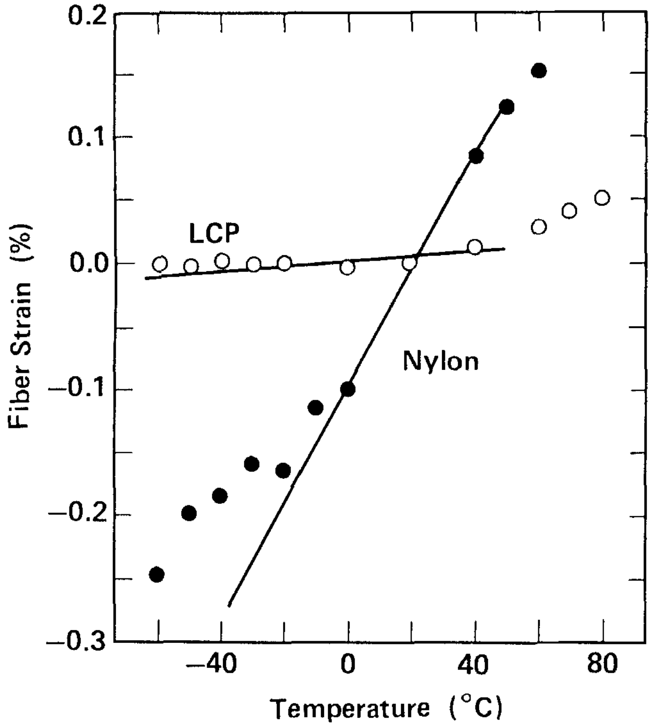


FIGURE 20. Change in fiber strain with temperature for 0.9-mm LCP- and nylon-jacketed fibers.

TABLE II Loss increase for jacketed fibers at -196°C.

Coating Material	Outer Diameter (mm)	Loss increase at −196°C* (dB/km)
Silicone/Nylon	0.9	1562 ± 480
Silicone/LCP	0.9	18 ± 3
Silicone	0.4	1168 ± 111

* Sample number = 11.

nitrogen. That is, the heat shock, which results in irregular fiber bending, is enhanced by the overcoated temperature-sensitive nylon but reduced by temperature-insensitive LCP.

Transmission loss change with increases in lateral load for LCP- and nylon-jacketed fibers is shown in Fig. 21. Here, the change in the transmission loss of the jacketed fibers under lateral load was measured by using the cross rod method[13]. The test fiber was placed between a flat metal board and 1-mm diameter-steel rods, which were placed

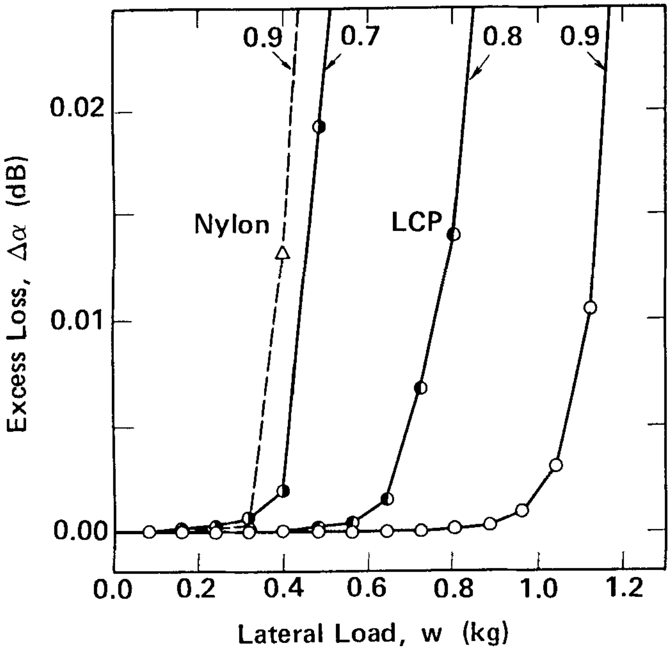


FIGURE 21. Increase in excess loss with lateral load for LCP- and nylon-jacketed fibers.

10 mm apart, perpendicular to the test fiber. The LCP-jacketed optical fiber starts to show loss increase at about 1.0 kg, although it occurs at 0.3 kg in the nylon-jacketed fiber. Thus, the critical load for the LCP-jacketed fiber is three times that of the nylon-jacketed fiber. This excellent lateral load resistance is due to both high E_s and low creep of the LCP jacket.[13]

OTHER APPLICATIONS

LCPs show significant variation in material properties due to differences in both molecular structure and degree of molecular orientation. This makes it possible to use them for other purposes in optical communications. For example, the combination of stability in molecular orientation with low melt viscosity of high shear rates has enabled a new thermotropic rubber/liquid crystal polyester dual-coextrusion coating[14] for an in-line high speed coating system for optical fiber drawing. A tape material covered with "ribboned" fibers which are packed in linear arrays has been developed as a result of the ease of making high E, low α thin films ($\sim$10 μm). Furthermore, high Young's modulus, high strength and high heat resistance properties attained using wholly aromatic LCPs are suitable for optical fiber strength members and jacketing for use at temperatures as high as 200°C.[15]

CONCLUSION

It has been shown that a novel optical fiber jacket exhibiting a high modulus (E) an a low thermal linear expansion coefficient (α) can be obtained when thermotropic liquid crystal polyesters based on improved polyethylene terephthalate (PET) and para-hydroxybenzoic acid (PHB) are ordered by shear- and elongational deformation- stresses. The E and α values of the newly developed LCPs are ca. 10 GPa and less than 1×10^{-5}/°C under given extrusion-coating conditions, respectively. They exhibit outstanding characteristics, compared with ordinary optical fiber jacketing materials such as nylon 12. Furthermore, the breaking strain is about twice that of a original PET/PHB (=40/60) copolymer. They provides sufficient flexibility for the ordered LCP jacket.

When the developed LCP is used as an optical fiber jacket, loss increase due to fiber microbending in the -60°C to 80°C temperature range does not occur. LCP jackets may also be used at liquid nitrogen temperature with high-quality-transmission lines of security sensors that are located in liquiefied fuel storage facilities. They also exhibit superior mechanical properties including resistance to tension and lateral load. On the other hand, additional improvements are necessary in reliability and high speed coating techniques for LCP jackets. It is expected that LCP materials will contribute to the development of high performance cables and their extended application in harsh environments.

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