

High Performance Optical Materials Cyclo Olefin Polymer ZEONEX[®]

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ABSTRACT

ZEON CORPORATION developed innovative optical plastic Cyclo Olefin Polymer (COP), ZEONEX[®] with own technology in 1990 then started commercial production of ZEONEX[®] for optical applications with its very unique properties such as high light transmission, low birefringence, low water absorption, and high glass-transition temperature etc. ZEONEX[®] exhibits outstanding optical performance even under high humidity and temperature conditions. In order to meet increasing requirements of optical market, ZEON CORPORATION newly developed ZEONEX[®]F52R which has high glass-transition temperature 156 deg. C and shows the feature of very low focal length change after high-temperature and high-humidity test.

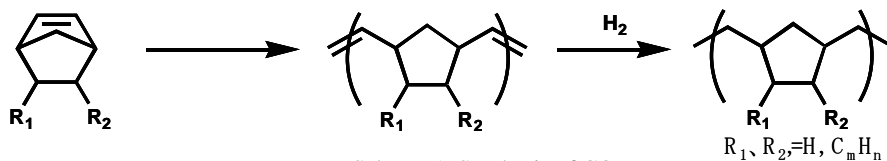
Key words: focal length, refractive index, refractive index distribution, water absorption

1. INTRODUCTION

Digital data transmissions by optical systems have become popular and essential in our lives. There are many kinds of technologies ever developed, for example, transmitting information by optical fibers, imaging display by Flat Panel Displays (FPD), recording and reading from optical disks and printing by laser beam printers, and recording of high-resolution images for digital cameras. The optical devices used in essential parts of the equipments are required high reliability as well as high performance, and the same for optical materials used in the optical devices. There are two classes of optical materials, optical glass and optical grade plastics, each of them has its own particular advantages; that is, glass has high optical performance, durability and reliability, on the other hand, plastics possess good processing ability and sometimes better economies of scale either by injection molding or by extrusion. Especially, for commodity optical parts or systems, optical plastics can provide cost competitive products and are likely to be used. As optical plastics, Polymethylmethacrylate (PMMA) and Polycarbonate (PC) are well known but recently Cyclo Olefin Polymers (COPs) are taking a major position in optical plastics¹⁾⁻⁴⁾.

2. PROPERTIES OF COP AND ITS APPLICATIONS

COP is an amorphous polyolefin with a cyclic structure in the main chain. ZEON CORPORATION, started commercial production under the trade name ZEONEX[®] in 1991. Scheme 1 shows the polymerization scheme and polymer structures. According to it, COP is polymerized by Ring Opening Metathesis Polymerization of norbornene derivatives, followed by hydrogenation of double bonds that provides more stability in terms of heat and weather resistance.



The heat resistance as well as other properties can be changed with chemical design of side chains "Rs". One of the most important things in designing COPs as optical material is combining general optical performance and the minimum birefringence. In general, Polypropylene (PP) and Polyethylene (PE) are popular polyolefins but they do not have sufficient transparency due to light scattering on the interface between their crystalline and amorphous parts in the polymer matrix. Such optical anisotropy results in high birefringence^{5), 6)}. On the other hand, COPs, that are essentially amorphous, have excellent optical properties as a result of incorporating cyclic structures in the polymer chain.

The following properties are generally required for optical materials and COPs are designed to satisfy all of them. That is why they have been widely used as materials for fine optical elements by high-tech user.

- 1) High Light Transmission
- 2) Low Birefringence
- 3) High Heat Resistance
- 4) Low Water Absorption
- 5) High Durability under High Temperature and Humidity
- 6) Good Moldability

For example, the optical resin ZEONEX[®], a brand of COP developed by ZEON CORPORATION, is adopted for various optical lenses; pick-up lenses for optical media (CD and DVD), imaging lenses, finder-prism for digital camera/cell phone and F-theta lens for laser beam printer. And another brand of COP, ZEONOR[®] is being used for optical element of LCD such as optical film, light guide plate and light diffuser plate.

One of the unique properties of COPs is very low water absorption, that is below 0.01% for 24 hrs. As shown in Figure 1, ZEONOR[®]1060R and ZEONEX[®] E48R show very low water absorption compared with PC and PMMA.

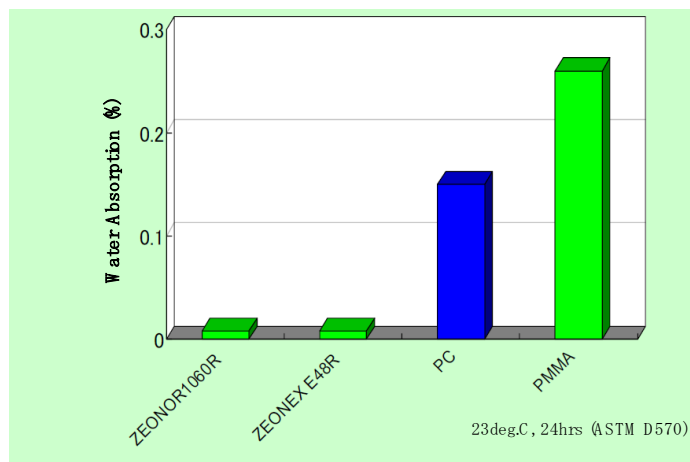


Figure 1. Water absorption of COPs, PC and PMMA (ASTM D570)

This outstanding feature of COP results in high reliability as light guide plates for laptop personal computer. Light guide plate (LGP) of ZEONOR[®]1060R and that of PMMA were put to high-temperature and high-humidity test. Absorption of water by LGP of PMMA resulted in warpage and the change of bright uniformity but LGP of ZEONOR[®]1060R shows no warpage and no change of bright uniformity (Figure 2 and Figure 3).

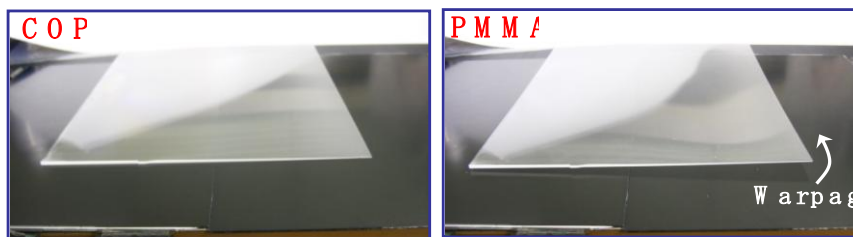


Figure 2. Warpage of 14inch LGP from COP (ZEONOR[®]1060R) and PMMA after high-temperature and high-humidity test. Test condition:50degC, 80%RH, 100hrs

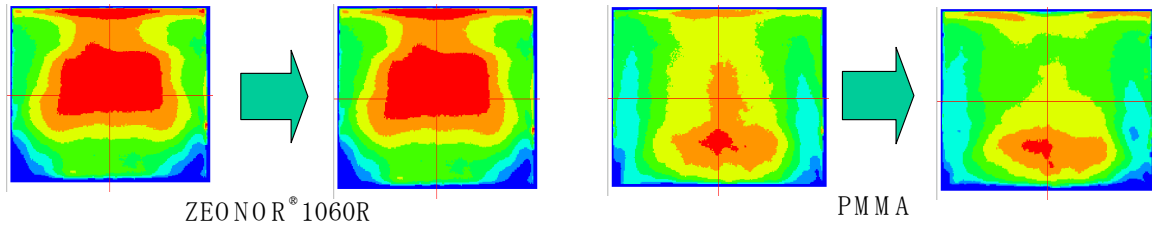


Figure 3. Brightness distribution change of LGP of PMMA and COP(ZEONOR® 1060R) in 14inch Back Light Module before and after high-temperature and high-humidity test
 Test condition: 50degC, 80%RH, 100hrs
 Measurement of Brightness distribution: CA-1000 (MINORUTA)

For optical materials the stability of refractive index value under various environments is one of the most important property in terms of optical design and product management. Fig.4 shows the change in refractive index under 50deg.C and 90%RH and in water absorption with time. PMMA gradually absorbed water and the water absorption came up to 1.2% after 14 days. Furthermore, the refractive index changed from 1.4904 to 1.4918. On the other hand, ZEONEX® E48R of COP didn't absorb water and the refractive-index had no change at 1.5310. That is the reason why ZEONEX® was used for various fine optical lenses.

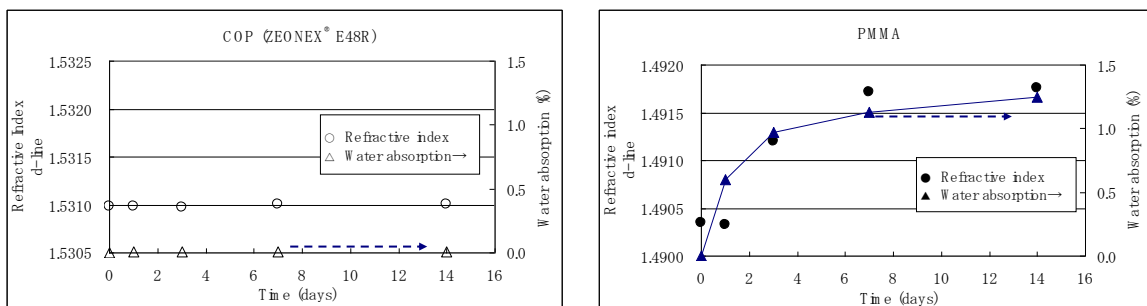


Figure 4. Change in refractive index and water absorption under high-temperature and high-humidity condition with time
 Test condition : 50degC, 90%RH

3. LOW FOCAL LENGTH CHANGE PROPERTY OF COPs

This study focused focal length change between before and after environment testing, one of the most important property in the design of optical lenses. Relationships between humidity and temperature factor and focal length change were examined. Refractive index distribution change under some environment testing conditions were also studied, and the knowledge obtained by these studies finally lead to development of new grade of COP, ZEONEX® F52R, with property of low focal length change.

3.1. EXPERIMENTAL

3.1.1. Preparation of COPs

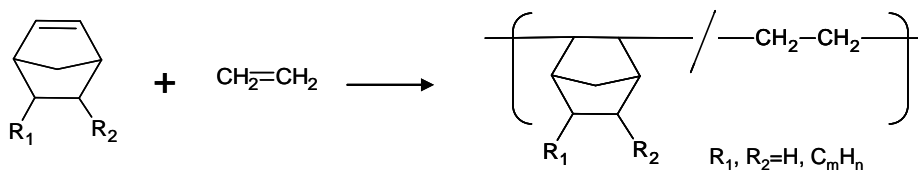
Four COPs were prepared as follows.

COP-1: Ring opening polymer of norbornene derivative with nonpolar group, followed by hydrogenation as shown in Scheme 1 (ZEONEX® E48R : water absorption <0.01%, glass transition temperature 138deg.C)

COP-2: Ring opening polymer of norbornene derivative with polar group, followed by hydrogenation as shown in Scheme 1 (water absorption 0.05%, glass transition temperature 120deg.C)

COP-3: Addition copolymer of norbornene derivative with nonpolar group and ethylene as shown in Scheme 2 (water absorption <0.01%, glass transition temperature 135deg.C)

COP-4: Ring opening polymer of norbornene derivative with nonpolar group, followed by hydrogenation as shown in Scheme 1 (ZEONEX® F52R : water absorption <0.01%, glass transition temperature 156deg.C)



Scheme 2. Synthesis of additive copolymers of norbornene derivative and ethylene.

3.1.2. Comparison of COP-1 with PMMA under high-temperature and high-humidity condition

3.1.2.1. Environment testing condition

Temperature: 50deg.C, relative humidity:90%, 14days

3.1.2.2. Refractive-index change and water absorption under environment testing conditions (Figure 4)

Dimension of test plaque: 65x65x3mm (annealing treatment for 24hrs after injection mold followed by incubation in desiketer with silica gel at 23deg.C for 3 days)

Base material for test plaque : COP-1 and PMMA

Water absorption : weight change (wt%)

Refractive-index measurement: KPR-200 at 25deg.C (SHIMADZU DEVICE)

Measurement light wavelength: d-line

3.1.2.3. Refractive-index distribution change under environment testing conditions (Figure 5)

Dimension of test plaque: 10x10x3mm (V-block)

Preparation of test plaque: test plaque of 65x65x3mm in 3.1.2.2 were finely cut by MC-120 (MARUTO INSTRUMENT) after each environment testing and finely polished by waterproof polishing paper

Base materials for test plaque : COP-1 and PMMA

Refractive-index distribution measurement: KPR-200 at 25deg.C (SHIMADZU DEVICE)

Measurement light wavelength: d-line

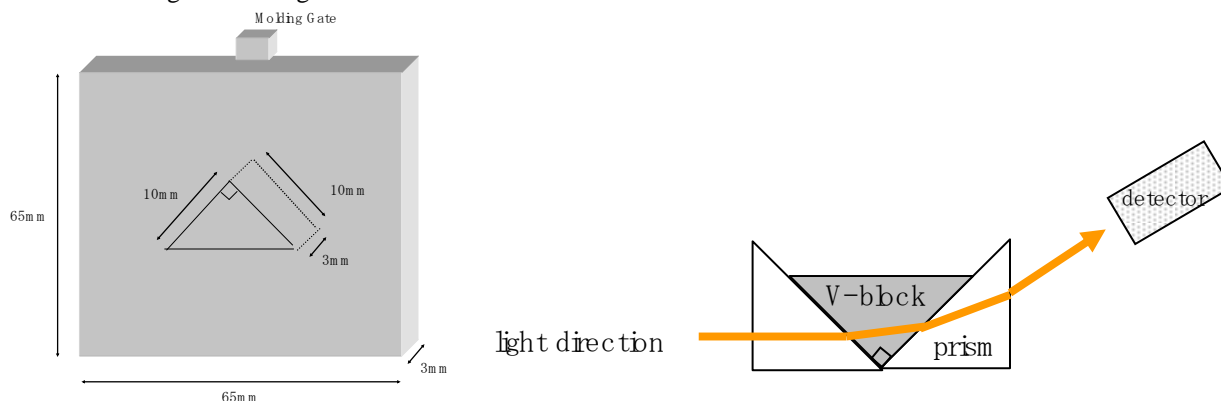


Figure 5. Preparation of V-block and measurement of refractive index and its distribution with it.

3.1.3. Comparison of COP-1 with COP-2 under high-temperature and high-humidity condition

3.1.3.1. Environment testing condition

condition A: temperature: 85deg.C, relative humidity: 85%, 40hrs

condition B: temperature: 25deg.C, relative humidity: 50%, 4days continuously after condition A

3.1.3.2. Focal length change under environment testing conditions (Figure 7)

test plaque: toric lens (annealing treatment for 540hrs after injection mold)

Specifications of toric lens : thickness 7.6mm, focal length designed:40mm,

Base material for test plaque : COP-1 and COP-2

Focal length measurement: special specifications (PEARL OPTICAL INDUSTRY)

Measurement light wavelength: 632nm (coherent light of 2mm Φ diameter)

3.1.3.3. Refractive index distribution change of toric lens under environment testing conditions (Figure 8)

Dimension of test plaque: 13x13x7.6mm (V block)

Preparation of test plaque: toric lens in 3.1.3.2 were finely cut by MC-120 (MARUTO INSTRUMENT) after each environment testing and finely polished by waterproof polishing paper
 Base material for test plaque : COP-1 and COP-2
 Refractive index distribution measurement:KPR-200 at 25degC (SHIMADZU DEVICE)
 Measurement light wavelength: d-line

3.1.4 Comparison of COP-1 with COP-3 and COP-4 under high temperature condition

3.1.4.1 Environment testing condition

Temperature: 85degC, 120hrs

3.1.4.2 Focal length change under environment testing conditions (Table 1 and Table 2)

Test plaque: toric lens (no annealing treatment)

Specifications of toric lens: thickness 7.6mm, focal length designed: 40mm

Base materials for test plaque: COP-1, COP-3 and COP-4

Focal length measurement: special specifications (PEARL OPTICAL INDUSTRY)

Measurement light wavelength: 632nm (coherent light of 2mmΦ diameter)

3.1.4.3 Refractive index distribution change of toric lens under environment testing conditions (Figure 9)

Dimension of test plaque: 13x13x7.6mm (V block)

Preparation of test plaque: toric lens in 3.1.4.2 were finely cut by MC-120 (MARUTO INSTRUMENT) after each environment testing and finely polished by waterproof polishing paper

Base materials for test plaque : COP-1 and COP-3

Refractive-index distribution measurement: KPR-200 (SHIMADZU DEVICE) at 25degC

Measurement light wavelength: d-line

3.2 RESULTS AND DISCUSSION

3.2.1 Impact of water absorption on focal length

The changes in refractive index distribution with time were measured in case of COP-1 (ZEONEX®E48R) and PMMA. Considering the results in Figure 4, a model of water absorption in PMMA was proposed⁷⁾. Then, we focused on COPs, and examined influence of substituent groups, nonpolar or polar, that is relationships between polymer structure and optical stability.

3.2.1.1 Comparison of COP-1 with PMMA

As already noted in Figure 4, COP-1 shows very low absorption, very stable refractive index and its dispersion even after high-humidity and high-temperature test. However, PMMA absorbed water gradually and its refractive index also suffered a change under the same condition. Figure 5 shows Refractive index dispersion change of COP-1 and PMMA under the same condition as in Figure 4. COP-1 shows less change of its refractive index and dispersion but refractive index of PMMA varied greatly with the change of its dispersion. The dispersion of PMMA was widest at 1day and then gradually changed its shape according to water absorption and finally became narrow again after 7days.

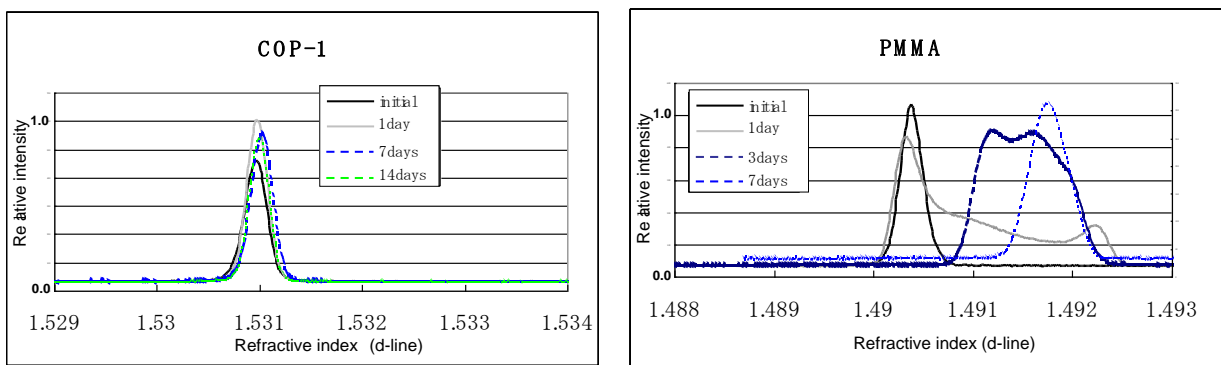


Figure 5. Refractive index change of COP-1 and PMMA
 Test condition : 50degC, 90%RH

According to the results noted above, we speculated the following model of water absorption in PMMA plaque (Figure 6). At first, water is absorbed from the surface of plaque, it causes increase of refractive index only in surficial region. The central portion of the plaque maintains initial refractive index still at this stage. So the refractive index distribution becomes very wide. Water absorption undergoes gradually, and finally the amount of absorbed water comes up to saturation. At this stage, the inside of plaque becomes consistent again, and refractive index distribution becomes narrow as initial distribution. The adsorption-desorption process of water reversibly progress according to its external humidity environment. Therefore changes of refractive index distribution in the plaque may occur according to environmental variation. It can be concluded that the materials absorbing water such as PMMA are inadequate for the fine optical lens, because the values of their focal length and aberration depend largely on its external environment.

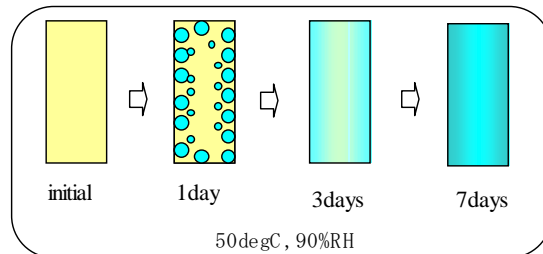


Figure 6. The model of water absorption in PMMA plaque

3.2.1.2 Comparison of COP-1 with COP-2 having polar group

COP-1 shows very low water absorption, below 0.01% but that of COP-2 was larger, 0.05%. That is because COP-2 has polar group partially in polymer backbone.

Figure 7 shows the change in focal length of injection molding toric lens of COP-1 and COP-2 with time. Lenses are initially disposed under high-temperature and high-humidity condition followed by room temperature. The lens of COP-1 shows no change of focal length in all trial period but that of COP-2 shows major change under both of conditions, and especially the magnitude of the change from the beginning of room temperature condition is larger than that of the former condition A.

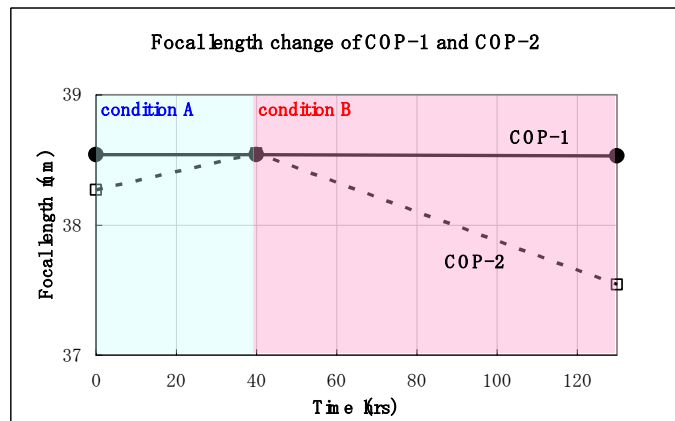


Figure 7. Focal length change of COP-1 and COP-2 under environment test condition. Test condition A :85degC, 85%RH, 40hrs, Test condition B :23degC, 50%RH, 60hrs

As shown in Figure 8, COP-1 has no change of refractive index and its distribution in all trial period but COP-2 shows major changes. In case of COP-2, the refractive index slightly increases under the condition A but its distribution remains at the same level. However, under the condition B following the condition A, the refractive index distribution is getting wider. This phenomenon can be explained by the following assumption. That is, water started to desorb from the surface of the plaque under the condition B, and then, difference of water concentration between the surface and center portion of the plaque occurred, resulted in wide refractive index distribution.

Relatively low water absorbing material such as COP-2 still shows large focal length changes that are critical in reliability of fine optical unit.

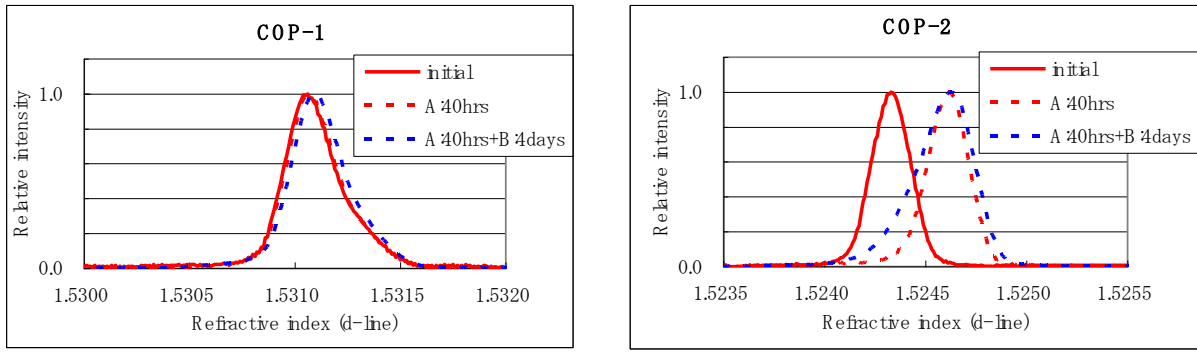


Figure 8. Refractive index distribution change of COP-1 and COP-2
 Test condition A :85degC, 85%RH, 40hrs, Test condition B :23degC, 50%RH, 60hrs

3.2.2 Relationships between polymer structure and focal length change

As mentioned in the previous chapter, water absorption is a critical problem for optical materials, which cause instability of optical properties. Then, we focused on COPs with nonpolar group, and examined relationships between polymer structure and optical stability. Table 1 shows focal length of injection molding toric lens of COP-1 and COP-3 before and after heat test. Variation of COP-1 is smaller than that of COP-3.

Table 1. Focal length change of COP-1 and COP-3 at 85 deg. C

	COP-1	COP-3
Initial / mm	40.2	39.0
After test (120hrs) / mm	39.5	37.9
Focal length change / mm	-0.7	-1.1

Figure10 shows changes of refractive index and its distribution of COP-1 and COP-3. The refractive index peak of COP-1 slightly shifted higher, but its shape and width, that is, distribution was almost the same before and after the test. Meanwhile, in case of COP-3, the refractive index peak shifted higher and additionally, its distribution got narrow. The geometry of tested lenses, measured by 3D geometry measuring equipment, showed no change and the variation of focal length calculated from actual measurement value of refractive index is negligible change. Therefore, it is supposed that variation of refractive index distribution causes change of focal length and it depends upon the polymer structure. We are trying to learn about the influence of physical properties and structures of the polymer in detail.

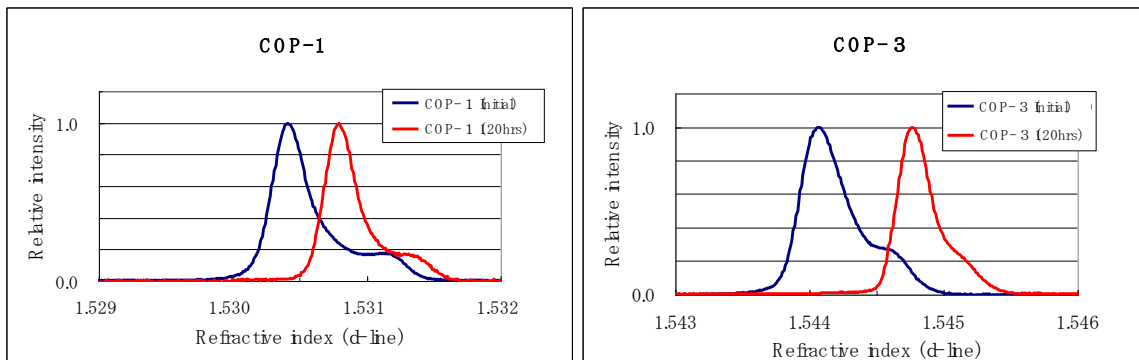


Figure 9. Refractive index distribution change of COP-1 and COP-3
 Test condition : 85degC, 120hrs

4. IMPROVEMENT OF FOCAL LENGTH CHANGE IN COP

4.1 Development of new optical grade COP (ZEONEX® F52R)

According to scientific knowledge described above, improvement of COP was conducted. Finally, by optimizing the polymer structure, that is, the structure of side chains “Rs”, COP-4 was developed. Table 2 shows the focal length change of COP-1 and COP-4 at 85 deg. C. COP-4 succeeded to minimize the change of focal length.

Table 2. Focal length change of COP-1 and COP-4 at 85 deg. C

	COP-1	COP-4
Initial / mm	40.2	41.9
After test (120hrs) / mm	39.5	41.6
Focal length change / mm	-0.7	-0.3

4.2. Typical Properties of ZEONEX® F52R

As mentioned above, ZEONEX® F52R has excellent reliability under high temperature. Table 3 shows other key properties of ZEONEX® F52R. ZEONEX® F52R maintains basic properties such as low water absorption, high light transmittance and impact strength, and on the other hand, it has improved high heat resistance (Tg 156 deg. C). Additionally, it is striking that the birefringence of ZEONEX® F52R is lower than that of ZEONEX® E48R (Figure 9).

Table 3. Typical Properties of ZEONEX® F52R

Properties	Unit	Measurement method	Conditions	ZEONEX® F52R	ZEONEX® E48R
Gravity		ASTM D792		1.02	1.01
Water absorption	%	ASTM D570		<0.01	<0.01
Refractive index	nd	ASTM D542		1.535	1.531
Transmittance	%	ASTM D1003	thickness: 2 mm	91	92
Tg	°C	JIS K7121		156	139
Liner expansion coefficient	cm/cm°C	ASTM E821		6.1×10 ⁻⁵	6.3×10 ⁻⁵
Flexural strength	MPa	ISO 178		100	120
Flexural modulus	MPa	ISO 178		2700	2400
Impact strength	kJ/m ²	ASTM D256	2mm with notch	1.8	2.4

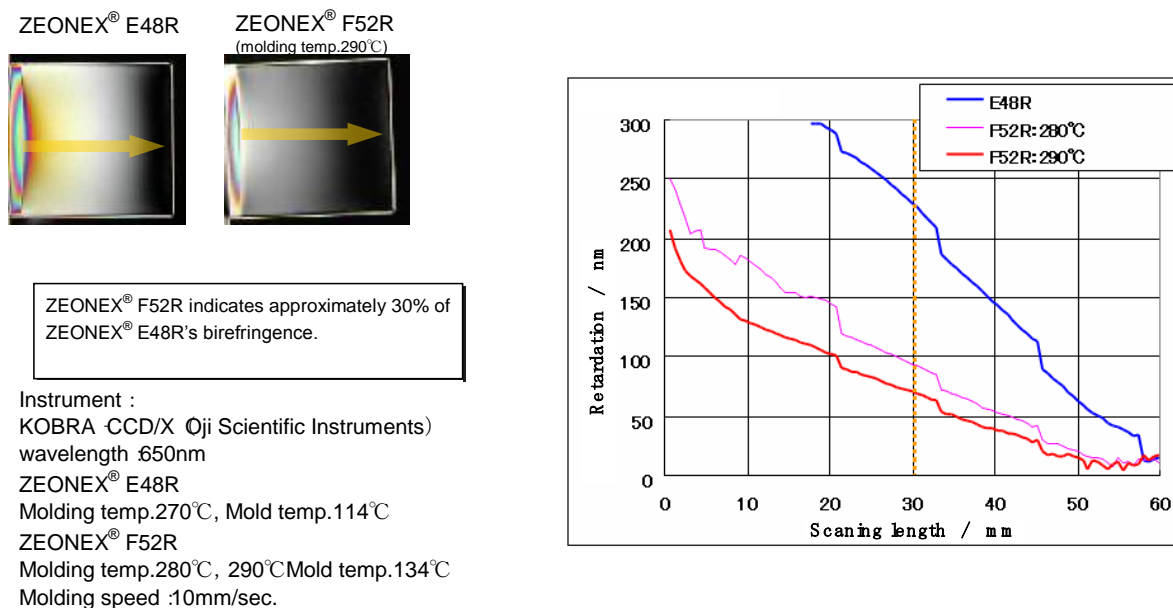


Figure 10. Birefringence of ZEONEX® F52R and ZEONEX® E48R

5. CONCLUSION

COP (ZEONEX®) has very low water absorption, low birefringence, high light transmission and other key properties required for optical plastics. With these excellent properties, COP has been used for many kinds of optical parts such as F-theta lenses for laser beam printers, phone lenses, digital still camera and pick-up lenses and so on. In order to meet the ever-increasing demands for high performance of optical devices, we tried to improve COP in optical stability under harsh environment. Relationships between polymer structures and optical stability were examined, and then we succeeded in development of new COP grade, ZEONEX® F52R. We believe that ZEONEX® F52R will contribute to the growth of the fine optical device industries.

REFERENCES

1. T. Kohara, Kaigaikoubunshikenkyu, 40, 117 (1994)
2. T. Natsuume, T. Kohara, M. Ohshima, T. Nishijima, D. Kakei, Chemical society of Japan gakkaiishi, 1998 (2), 81
3. H. Shinohara, Kagakusousetu, 39, 140 (1998)
4. Y. Yamamoto, Plastics, 47(2), 26 (1996)
5. H. Nakanishi, Plastics-age, 41(2), 100 (1995)
6. Y. Ohtsuka, Koubunshi, 43, 266 (1994)
7. M.Komatsu, T.Kohara, K.Minami, Plastics for precessing, 167 (2006), Kogyo Chosakai Publishing