

Development of Thermoplastic Nanocomposite Optical Materials

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Abstract

Thermoplastic nanocomposite optical materials that include ZrO₂ nanoparticles in high concentration have been developed. Even after undergoing the melt-molding processing, homogeneous dispersion of nanoparticles in the resin was maintained and the molded articles showed good transparency. The refractive index of the resin rose from 1.59 to 1.65 by the addition of 12.5 vol% ZrO₂ nanoparticles. It was found that the kinds and number of functional groups in polymer, the length of linkers between the functional groups and the main chain of the polymer were very important to achieve the homogeneous dispersion of particles and the moldability of the nanocomposite. This material was molded into convex and concave lenses.

1. Introduction

The refractive index is one of the most important fundamental properties of optical components such as lenses. Refractive index control is an essential technique for processing light by manipulating its speed and passage, and materials studies for pursuit of high/low refractive index, Abbe's number (wavelength dependence of the refractive index) control and birefringence (anisotropy of the refractive index) control, etc. have actively been continued.

Lenses made of materials with a high refractive index can refract the passage of light more significantly with a small curvature, which enables making thinner lenses with higher resolution.

Conventionally, the use of inorganic materials, such as glass and ceramics, has been dominant in optical components because they have a wider controllable refractive index range. In recent years, however, needs for lighter and less expensive materials have increased, so that replacement of inorganic materials with resins in various applications has been expedited. On the other hand, resins have a disadvantage of narrower controllable refractive index ranges when compared with inorganic materials, hindering their use in many applications.

To increase the refractive index of materials, it is necessary to increase polarizability or density. In that regard, resins have a critical weakness, as increasing their density is more difficult than that of inorganic materials.

A general way to increase the refractive index of a resin is to design molecules so that its polarizability is increased by introducing halogens (Cl, Br and I), sulfur, heavy metal atoms and aromatic rings^{1), 2)}. However, applying such

methods elongates absorption wavelength, which limits the design of transparent materials. In addition, it needs caution because there is correlation with other issues such as the decrease of resistance to stain by oxidative degradation and the increase of water absorbency.

Resins alone cannot achieve the intended refractive index. Therefore, another means has been investigated, in which inorganic materials with a high refractive index are compounded with resins^{3) to 6)}. As shown in Table 1, compared with organic materials, inorganic materials are known to cover a wider range of refractive indexes. Some materials, such as ZrO₂ and TiO₂, are transparent in the visible range while achieving very high refractive indexes.

Table 1 Refractive index at 589nm of typical optical materials.

Typical optical resin materials	Refractive index	Transparent inorganic materials	Refractive index
Amorphous fluoropolymer	1.34	TiO ₂ (Rutile)	2.72
PMMA	1.49	TiO ₂ (Anatase)	2.52
COP	1.53	Diamond	2.42
Polystyrene	1.59	ZrO ₂	2.10
Optical polycarbonate	1.59 to 1.63	Al ₂ O ₃	1.62
Fluorene-based polyester	1.60 to 1.64	SiO ₂	1.45
Polyethersulfone	1.64	MgF ₂	1.37

It is easily predictable that the refractive index of composites can be controlled by the volume fraction of additional inorganic particles. Organic-inorganic composite technology has already been used widely for thin films such as anti-reflection coatings.

However, there is an issue when applying this technology into thick molded materials such as lenses. The difference in refractive index between resins and high-refractive index

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inorganic particles is significant, and the consequent light scattering greatly affects the transparency of the lenses. It is difficult to realize a high refractive index compatible with high transparency.

To apply cost-effective molding methods, resins need to be melted, flowed and solidified without using solvents, which is also difficult because of the decrease in fluidity originating from particle interaction and because of particle aggregation during the melting process. To achieve the required refractive index while maintaining high transparency, it is necessary to disperse small particles homogeneously at a high concentration. However, when that is done, melt-moldability is generally impaired. There is a strong need for thermoplastic nanocomposite materials with a high refractive index but, as far as we know, such a highly demanding technology has not yet been realized at a practical level.

This paper describes thermoplastic nanocomposite optical materials that we have developed aiming at realization of a high refractive index compatible with melt-moldability by using organic-inorganic composites.

2. Thermoplastic nanocomposite optical materials

2.1 Simulation

If ZrO₂ nanoparticles (refractive index: 2.10) are dispersed homogeneously into a resin (refractive index: 1.60), the refractive index of the composite is expected to change with the volume fraction of the nanoparticles as shown in Fig. 1.

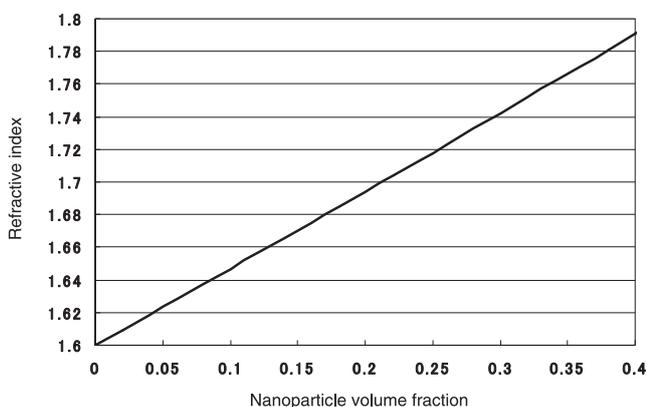


Fig. 1 Refractive index of the nanocomposite calculated according to the volume fraction of the nanoparticle.

According to the calculation, to achieve nanocomposites with a refractive index of 1.70, 21.2 vol% ZrO₂ nanoparticles need to be added. Fig. 2 shows the simulation results for the relationship between nanoparticle diameters and transparency when the thickness of the molded material is 1 mm.

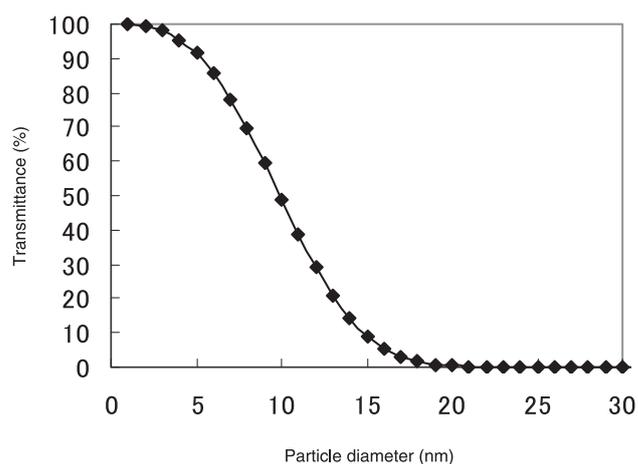


Fig. 2 Transparency of the nanocomposite calculated as a function of the particle diameter.

To achieve a high internal light transmittance of at least 90%, nanoparticles whose average diameter is not larger than 5 nm should be dispersed evenly without aggregation. It was predicted that, with increase in the diameter of particles, transparency would decline sharply.

If, in a nanocomposite, nanoparticles with a diameter of 5 nm are positioned at the vertices of the hexagonal closest packed structure and dispersed homogeneously in resin at a concentration of 10 vol% and 20 vol%, the distance between particles is expected to be 4.7 nm and 2.7 nm, respectively (Fig. 3). Nanoparticles can easily aggregate because their specific surface area is particularly large compared with bulk materials. Therefore, it is very difficult to achieve homogeneous dispersion at a high concentration.

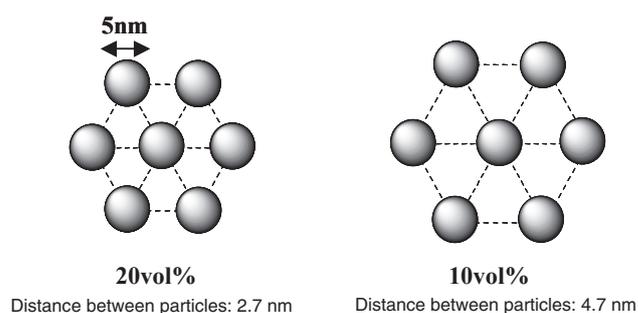


Fig. 3 Distance between particles expected in the nanocomposite : particle diameter, 5nm ; particle amount, 20vol% (left)/ 10vol% (right).

As a first step, aiming to develop a thermoplastic nanocomposite material in which zirconia nanoparticles of 5 nm in diameter are dispersed homogeneously at a concentration between 10 vol% and 20 vol%, we designed a nanoparticle dispersion resin.

2.2 Design of a nanoparticle dispersion resin

2.2.1 Nanoparticle dispersion into thermoplastic resin

We first considered a simple method of dispersing ZrO₂ nanoparticles throughout a thermoplastic resin such as PMMA or PS after modifying their surface with dispersants. However, with that method, homogeneous dispersion was difficult, and cloudiness by the aggregation of nanoparticles could not be prevented.

Fig. 4 shows the result of a trial for dispersion in which 10 vol% zirconia nanoparticles with a diameter of 5 nm were added to PMMA after their surface was treated with a phosphoric acid surface modifier. The composite became cloudy and the nanoparticles were found to have formed aggregates on the order of tens of micrometers. It is likely that insufficient interaction between the nanoparticles and resin has caused the aggregation of nanoparticles, their phase separation from the resin, and consequent cloudiness (Fig. 5).

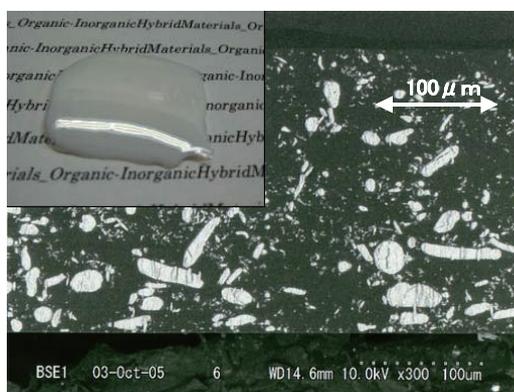


Fig. 4 TEM image (x300) of a cloudy nanocomposite section.

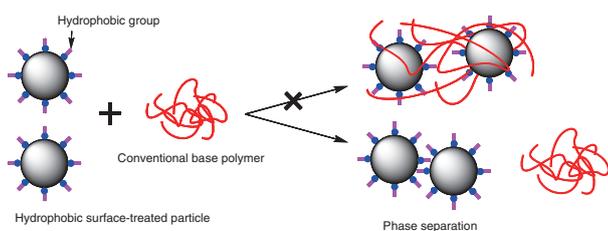


Fig. 5 Cohesion of particles in a cloudy nanocomposite.

To enable homogeneous dispersion, stronger interaction between matrix polymers and nanoparticles seems to be essential. However, it is easily predictable that random, multisite interaction between nanoparticles and resin may form physical gels that impair plasticity and fluidity.

2.2.2 Resin with single-ended anchoring groups

We believed the ideal system to be nanoparticle grafting with single-ended adsorptive resin as shown in Fig. 6. That is not a process of mixing nanoparticles and resin but of uniting them into one polymeric material. If this system is realized, the aggregation or phase separation of nanoparticles will be minimized because they are coated with resin. Also, the structure, having the anchoring group at only a single end, is expected to reduce the possibility of

gelation caused by resin bridging multiple particles.

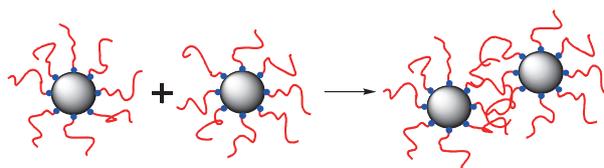


Fig. 6 Ideal thermoplastic nanocomposite.

According to this concept, we developed a dispersion resin with polystyrene (refractive index: 1.59) as its main backbone and explored the creation of a composite by using zirconia nanoparticles with a particle diameter of up to 5 nm.

For anchoring groups, we selected the phosphonic acid group and the carboxylic acid group that have strong interactions with metal oxides. By applying atom transfer radical polymerization (ATRP)^{7, 8}, we synthesized (A) a block copolymer that has more than one anchoring group at the single end and (B) a resin that has only one, strong anchoring group introduced to a single end (Fig. 7).

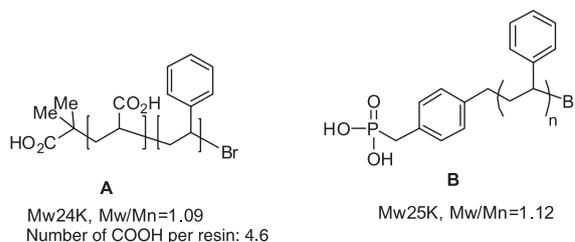


Fig. 7 Polymer design suitable for particle dispersion.

After adding an auxiliary dispersant, a plasticizer and the above described resins to the dimethylacetamide solution containing zirconia nanoparticles with a diameter of 5 nm and mixing them until they became homogeneous, we distilled the solvent and pressed the white composite powder thus gained (containing 41.7 wt% ZrO₂) at 180°C. As a result, we obtained transparent specimens with a thickness of about 1.5 mm. The observation of those specimens with a transmission electron microscope (TEM) revealed that both of them exhibited good nanoparticle dispersion. Fig. 8 shows the condition of a specimen created from Polymer A.

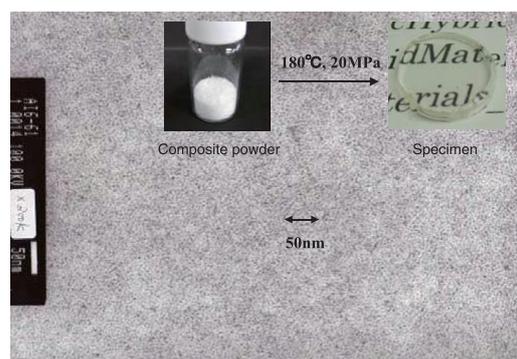


Fig. 8 TEM image (x300) of a section of the transparent nanocomposite using Polymer A.

2.2.3 Random copolymer

It became clear that gelation-free, homogeneously dispersed thermoplastic nanocomposite materials can be realized by introducing functional groups for adsorption to a single end of polymer using ATRP. However, in practice, it is more preferable to achieve it with less expensive random copolymers.

Therefore, we next investigated the detailed properties of random copolymers including the kinds of possible functional groups for adsorption, dosages, gelation behavior under multisite adsorption, nanoparticle dispersibility (transparency) and their relationships. As a result, it was confirmed that, by precise molecule design, random copolymers, too, can achieve homogeneous nanoparticle dispersion (high transparency) without causing gelation (insolubilization/infusibilization).

The optimal dosage of functional groups for adsorption depends on the strength of their adsorption power. Insufficient dosage causes the aggregation of nanoparticles, and excessive dosage leads to gelation. It is preferable and more usable if the functional groups have a wider range in the optimal number introduced per polymer. In the case of ZrO₂ nanoparticles, possible options are phosphoric acid (phosphonic acid), sulfonic acid and carboxylic acid in order of the strength of their adsorption power. A proper amount of each functional group can control transparency. However, the stronger the adsorption power, the more difficult control becomes because even a small dosage can cause gelation. The carboxylic acid has the widest range of dosages that can achieve homogeneous dispersion without causing gelation. In the dispersion of ZrO₂ nanoparticles with a diameter of 5 nm in styrene random copolymers, the best performance was achieved by keeping the number of carboxyl groups to between ten and fifteen per polymer.

2.2.4 Fluidity

In the above experiment conducted to confirm the principle, specimens were manufactured by pressing the powder with a thermal press machine. To create a more

practical molded material, melt-fluidity needed further improvement.

We therefore considered various aspects of controlling fluidity and transparency and discovered that it is extremely important to control the length of the side chains connecting the main chain to the functional groups, and the number of functional groups per polymer (Fig. 9). The fluidity of nanocomposites is poor when using a polymer whose adsorption sites have an acrylic acid structure in which carboxyl groups are directly connected to the main chain. To some extent, the longer the distance between the main chain and functional groups, the better the fluidity becomes and melt extrusion becomes possible with a lower pressure. However, too long a distance will degrade the stability of particle dispersion. It is essential to keep the distance to an optimal value.

Via the above optimization of material technology, we developed a thermoplastic nanocomposite material from ZrO₂ nanoparticles dispersed homogeneously in resin at a concentration of 12.5 vol% and succeeded in the creation of a 1.2-mm-thick, transparent molded body shaped as a convex and concave lens with a d-line transmittance of 92% (Fig. 10).

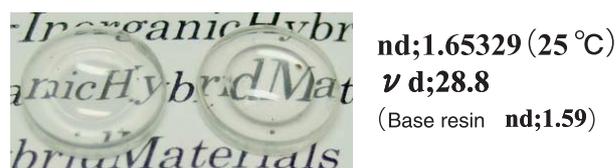


Fig. 10 Appearance of molded nanocomposite lenses.

3. Conclusion

It is no exaggeration to say that the expansion of the controllable refractive index range will always be one of the most challenging topics in the field of optical resin materials. Compared with inorganic materials, resin materials are lighter and excellent in moldability. On the other hand, their narrow range of controllable refractive indexes is a significant issue and effective organic-inorganic composite

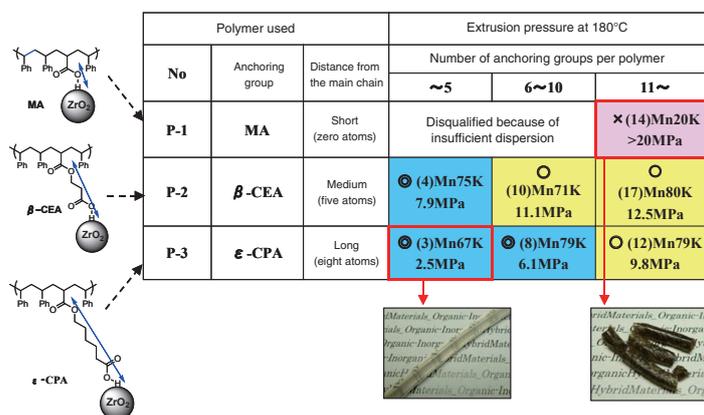


Fig. 9 Relation between the polymer design and melt-molding processability.

technology has been sought after. However, the application of such technology to thick optical components like lenses was still difficult not only in regard to transparency but also mass producibility. Under such circumstances, focusing on its improvement in mass producibility, we tackled the development of melt-moldable, thermoplastic nanocomposite materials and succeeded in the creation of a transparent molded body. Although there are still several outstanding issues for practical implementation, we hope for its further evolution in the future.

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