*Technology*

# Development of High Performance Polyimides

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## Abstract

***We have developed various high-performance polyimides by incorporating functionalities such as transparency, heat dissipation, and stretchable polyimide into heat-resistant polyimide resin. Transparent polyimide is targeted for transparent displays and VR glasses, thermal conductive polyimide for small devices and automotive applications, and stretchable polyimide for stretchable applications.***


## 1. Introduction

### 1.1 About polyimides

As the structure of polyimides (PIs), polyamic acid is produced by the polymerization of acid dianhydride and diamine and then imide groups are formed through dewatering cyclization. As polyimides contain imide groups having high thermal cracking resistance and often have aromatic compound structure, their heat resistance is generally higher than that of other polymeric materials.

### 1.2 Background to the development of high performance polyimides

Polyimides are a polymeric material to which functionalities can easily be applied because various functional groups can be introduced into the principal and side chains of acid dianhydride and diamine, which are monomers to be used as raw materials. For that reason, polyimides are used in a wide range of applications.[1] This paper introduces new polyimide products developed by applying various functionalities, such as transparency, heat dissipation, and elasticity.

## 2. Transparent Polyimides and Transparent Polyimide Copper-clad Laminates

### 2.1 Background to the development

In recent years, there has been an increasing demand for transparent displays, etc. and thereby visibility is required. Among various materials, transparent, flexible, lightweight materials that do not break are gaining attention. **Table 1** lists the characteristics of various types of transparent materials.

Although glass has outstanding transparency, it is heavier than plastic polyimides and polyethylene terephthalate (PET) and it is difficult to manufacture glass as thin as several tens of $\mu$m. Meanwhile, although transparent PET is transparent and lightweight, it is difficult to use PET at high temperatures of 200°C or higher due to its heat resistance property. In addition, when it is repeatedly folded, crystal structures are formed and they make the folds cloudy which is disadvantageous.

With regard to general-purpose polyimides, charge transfer (CT) complexes formed in molecules and between molecules absorb visible light and thereby films are colored in yellow to brown. Accordingly, to suppress the formation of CT complexes so as to give rise to the transparency, flexible groups or alicyclic structure is introduced. Various companies are proposing such polyimides.[2] Polyimide films with a thickness of several $\mu$m can be manufactured with the casting film forming method and such films in some structures have high heat resistance with the thermal cracking temperature of 300°C or higher. In addition, because the primary and higher-order structures of polyimides are stable, they have an excellent property to resist repeated folding and thereby they have little discoloration. These characteristics bring an expectation that polyimides can be applied to transparent applications and various companies are researching and developing such materials.

### 2.2 Characteristics of the design of transparent PI-CCLs

Nippon Steel Chemical & Material Co., Ltd. developed transparent polyimide copper-clad laminates (transparent PI-CCLs) and they consist of lamination layers of polyimides and copper foils. Regarding our proprietarily designed polyimides, while the transparency was enhanced by introducing large functional groups into the side chains of polyimide molecular chains, to reduce the dimensional change rate, the thermal expansion coefficient was adjusted to the

**Table 1 Comparison of various transparent materials**

| | Transparency | Weight | Thinness | Flexibility | Heat resistance |
|---|---|---|---|---|---|
| PI | △～○ | ◎ | ◎ | ○ | ○ |
| PET | ○ | ◎ | △ | △ | × |
| Glass | ◎ | × | × | × | ◎ |

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same level as that of copper foils by introducing stiff molecules into the principal chains; it was controlled to be 25 ppm/K or smaller. In addition, while retaining the transparency, the thermal cracking temperature was controlled to be 450°C or higher by using totally aromatic ring structure for acid dianhydride and diamine, in place of the alicyclic or aliphatic series.[3)]

For transparent polyimide films, the surface conditions are very important. If there are projections and depressions on the surface, light scattering occurs and that makes the turbidity partly higher, which affects the visibility adversely. To prevent this, highly-smooth non-roughened copper foils are used for transparent PI-CCLs. Usually, the adhesion decreases in lamination with non-roughened copper foils. To enhance the adhesion, transparent polyimides are made of multiple layers, and flexible groups (e.g., ether groups) are introduced into the composition of polyimide layers that come into contact with copper foils.[4)]

The casting method is used to manufacture CCLs. Transparent polyimide precursor varnish is applied to copper foils and the solvent is removed through ustulation. Then the polyamic acid is hardened at high temperatures of 300°C or higher to obtain polyimides to form single-sided CCLs. In addition, a copper foil is laminated on a single-sided polyimide CCL to produce a double-sided CCL. **Figure 1** shows photographs of a transparent polyimide film and a conventional polyimide film (M series manufactured by Nippon Steel Chemical & Material). **Figure 2** shows the appearance of a transparent CCL roll and **Fig. 3** shows the composition of the transparent CCLs (single-sided and double-sided CCLs).

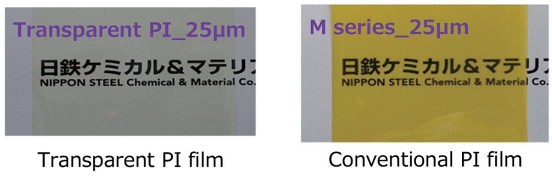



**Fig. 1 Photos of our PI film and conventional PI film**

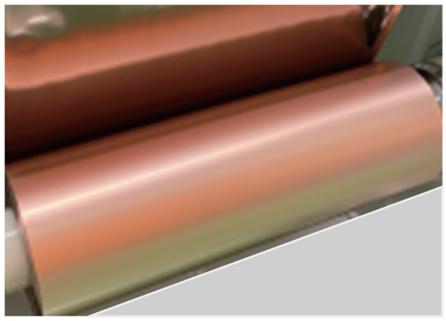
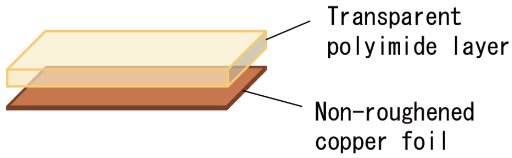
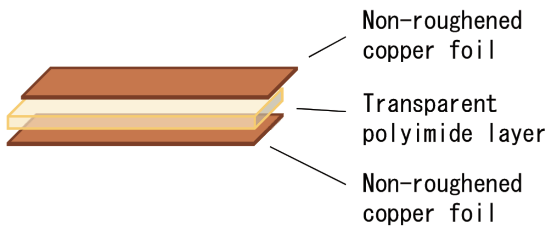


**Fig. 2 Appearance of transparent CCL roll (540 mm wide)**




**Single-sided CCL**




**Double-sided CCL**

**Fig. 3 Composition of Nippon Steel Chemical & Material transparent CCL**

### 2.3 Properties of transparent PI-CCLs

**Table 2** lists the properties of transparent PI-CCLs. The total transmittance, which is used as an indicator to show an optical property, is high and the yellow index and haze value (turbidity) are low. While the transparent PI-CCLs show transparency, their functionalities, such as thermal expansion coefficient, peel strength, and incombustibility, are at the same levels as those of the conventional M series.

**Table 3** compares our transparent PI-CCLs with similar materials manufactured by other companies. One company's material PI-A is transparent PI-CCLs manufactured from transparent polyimide films with the lamination method involving an adhesive. Because an adhesive is used, the haze value is relatively large.

Meanwhile, for another company's material PI-B, metal layers are formed on transparent polyimide films by sputtering so as to

**Table 2 Properties of transparent PI-CCL**

| | | Transparent PI-CCL | | Conventional |
|---|---|---|---|---|
| | | Single sided | Double sided | (M series) |
| Copper foil | Thickness (µm) | 18 | 18 | 18 |
| Polyimide | Thickness (µm) | 25 | 25 | 25 |
| | Total transmittance (%) | 86 | 86 | 68 |
| | Yellow index | 14 | 14 | >50 |
| | HAZE value (%) | 1.8 | 2.3 | 74 |
| | Coefficient of thermal expansion (ppm/K) | 24 | 21 | <25 |
| | Flammability (VTM-0) | ○ test in lab | ○ test in lab | ○ |
| 1 mm 180° PI/Cu peel strength (kN/m) | Cast side | 0.7 | 0.7 | >1.0 |
| | Laminate side | – | 1.4 | >1.0 |

**Table 3 Comparison of various transparent PI-CCL**

| | NSCM* | PI-A | PI-B |
|---|---|---|---|
| CCL formation method | Casting | Laminate | Spattering |
| HAZE value (%) | <2.5 | >7.0 | <2.5 |
| PI/Cu peel strength | ○ | △ | △ |

* Nippon Steel Chemical & Material

manufacture CCLs. In this method, the problem of controlling the adhesion between copper foils and polyimide films remains.

### 2.4 Proposal of applications of transparent PI-CCLs

**Figure 4** shows the transmittance of the transparent PI-CCLs developed by Nippon Steel Chemical & Material measured before and after heat resistance tests. The transparent PI-CCLs were heated at 250°C and 300°C for 30 minutes and the transmittance and color, etc., did not change before and after the heating. Our product is expected to be applied to high temperature processes as is the case with conventional flexible CCLs.

Circuits can be processed on transparent CCLs using copper foils and designated masks. **Figure 5** shows photographs of transparent CCL circuit products. Figure 5(a) shows a transparent circuit product with 1-mm lines. The letters on the white paper on the back are clearly seen through the film.

Meanwhile, to check the visibility of our transparent CCLs, imitation transparent displays were fabricated. Figure 5(b) shows the effects.

The numbers in Fig. 5(b) indicate the lines (wire width). Transparent circuit products were attached to PC screens and the wires with a width of 50 $\mu$m or smaller are barely visible from 1 m away. The 100-$\mu$m wires are also difficult to see from 3 to 5 m away. These results indicate that transparent circuit products may be applied to transparent displays as well as automobile fronts, antennas, and smart glass. We will develop the transparent polyimide and transparent PI-CCL market in line with the advancement of electronic device technologies in the future.

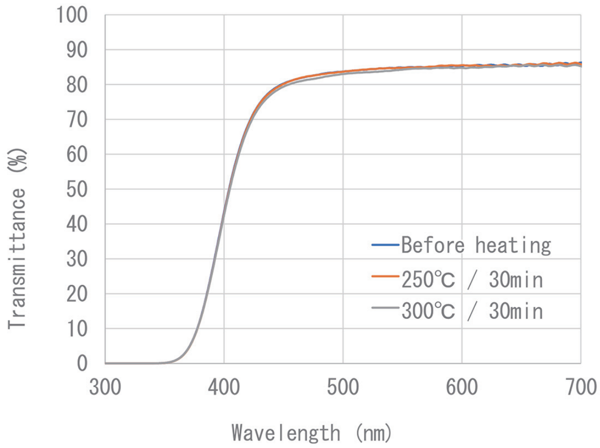
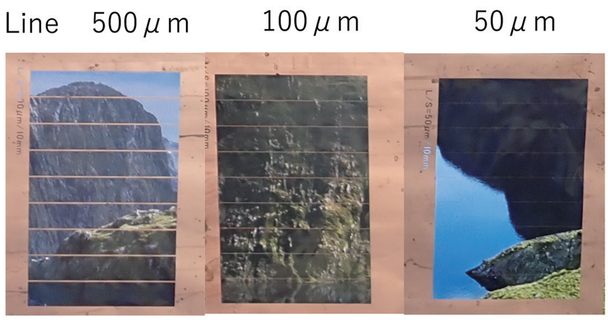



**Fig. 4 Wavelength dependence of transmittance**


**(a) The back is a white paper**




**(b) The back is a computer screen (The shooting distance: 1 meter)**

**Fig. 5 Transparent CCL circuit products**

## 3. Development of Thermal Conductive Polyimides

### 3.1 Background to the development

The demand for small electronic equipment, such as smartphones and PCs, and electronic devices (e.g., in-vehicle electronic parts) to be smaller and more highly integrated is increasing year by year. Quickly releasing the heat from heat sources (e.g., IC chips) and decreasing the temperature of heat-emitting parts are very important for both electronic equipment and users' safety. Polymeric materials are insulators in general and thereby their thermal conductivity is remarkably lower compared with metals.

Heat energy in matter is transmitted mainly by phonon propagation. To increase the phonon speed, we studied a technique to introduce stiff structure into the structure of polyimides and orient the molecular chains during film formation and thus we succeeded in improving the thermal conductivity of polyimides. In addition, the thermal conductivity of polyimides was further improved by charging fillers with high thermal conductivity. As described above, by combining the technology to improve the thermal conductivity of polyimides themselves with the technology to blend thermal conductive fillers, we have developed thermal conductive polyimides that exhibit adhesion at high temperatures and that have five times or more thermal conductivity than that of conventional PIs.

### 3.2 Thermal conductivity and heat resistance of polyimides

**Figure 6** shows the correlation between the glass transition temperature (Tg) of polyimides and the thermal conductivity in the perpendicular direction ($\lambda z$). The values of Tg, which is used as a heat resistance indicator, greatly vary according to the primary molecular structure of the polyimides. The polyimides produced from stiff acid anhydride (PMDA) (◇) have rather high Tg values. Meanwhile, the polyimides produced from flexible acid anhydride (BTDA) (△) and those produced from biphenyl acid anhydride (BPDA) (○) have low Tg except for some cases.

The values of the thermal conductivity in the perpendicular direction ($\lambda z$) also vary in the range from 0.10 to 0.30 W/mK according to the primary molecular structure of the polyimides. The structure having stiffness containing aromatic rings, which work to increase the phonon speed, as their principal chains, shows high Tg and high $\lambda z$.

Polyimides containing aromatic rings have in-plane orientation to orient aromatic rings in the planes and thereby their thermal conductivity also shows anisotropy. For the thermal conductive poly-

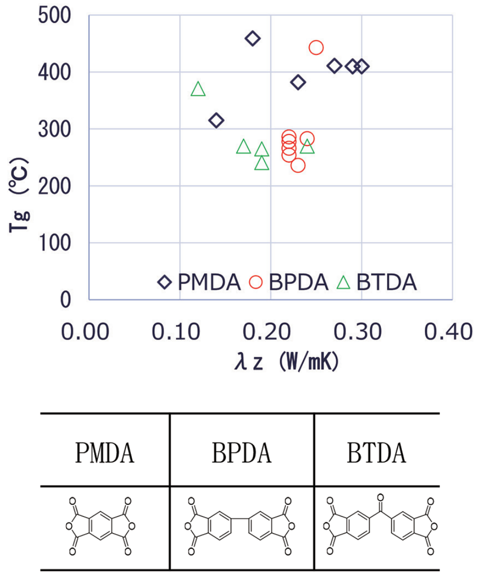



**Fig. 6 Correlation between the glass transition temperature and thermal conductivity of polyimide**

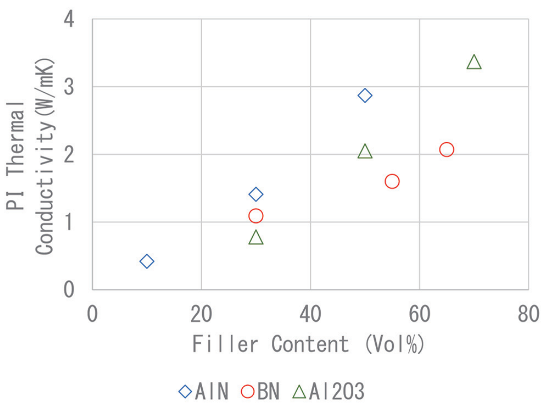



**Fig. 7 Correlation between filler content and the thermal conductivity of polyimide**

imides developed this time, the thermal conductivity in the plane direction is larger than that in the perpendicular direction. Currently, we are proposing thermal conductive polyimide resins according to applications.

### 3.3 Addition of fillers to polyimides

We have confirmed that adding thermal conductive fillers to polyimides improves their thermal conductivity. **Figure 7** shows the results when aluminum nitride (AlN), alumina ($Al_2O_3$), and boron nitride (BN) were added, along with the contents.

The thermal conductivity of fillers is higher in the order of aluminum nitride, boron nitride, and alumina in general. The thermal conductivity improvement effects of polyimides are affected by the content, size, and shape (e.g., spherical and scaly) of fillers and thereby designing based on the application and needs is important.[5)]

### 3.4 Properties of thermal conductive polyimides

**Table 4** lists the properties of our developed thermal conductive PI-CCLs. The table shows that the thermal conductive PI-CCLs

**Table 4 Properties of thermal conductive polyimide-CCL**

| Typical properties | | Thermal conductive PI-CCL | Conventional CCL (M series) |
|---|---|---|---|
| PI thickness ($\mu$m) | | 20 | 20 |
| Copper thickness ($\mu$m) | | 35 | 35 |
| PI thermal conductivity (W/mK) | Depth direction ($\lambda z$) | 1.1 | 0.2 |
| | Surface direction ($\lambda xy$) | 2.1 | 0.6 |
| 1 mm 180° peel strength (kN/m) | | 1.2 | >1.0 |
| Temperature of thermal decomposition at 5% weight loss (°C) | | >500 | >500 |

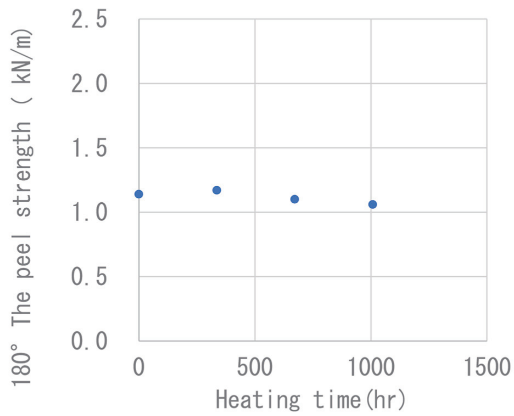



**Fig. 8 Heating test for the adhesion of thermal conductive polyimide-CCL (150°C)**

have adhesion with copper foils and retain their high heat resistance while their thermal conductivity is approximately five times higher than that of conventional polyimides.

**Figure 8** shows the results of heating tests of the adhesion of thermal conductive PI-CCLs. After the CCLs had been heated at 150°C for 1 000 hours, the 180° 1 mm peel strength was retained at 1.0 kN/m or higher and the adhesion did not decrease. These results show that the thermal conductive PI-CCLs retain the excellent heat resistance for an extended period of time.

From above, we expect the product can be applied in order to reuse waste heat from in-vehicle devices and plants and dissipate heat from smartphones, etc.

## 4. Stretchable Polyimide Films

As the flexible function of displays advances, displays are being handled in more various ways such as folded and rolled. In addition, materials for wearable devices that can follow human movement have increased in recent years. Under such circumstances, there are rapidly growing needs for stretchable, light, thin materials having high flexibility.

We introduced a soft rubber-like segment and an elastic region segment similar to conventional polyimides into the molecular structure of polyimides so as to develop high-elasticity polyimide films; the soft segment exerts high elongation and after a stretchable polyimide film has been extended, the elastic segment works to return to the original state. **Figure 9** shows the appearance before and after pulling a stretchable film. We assume stretchable films can be

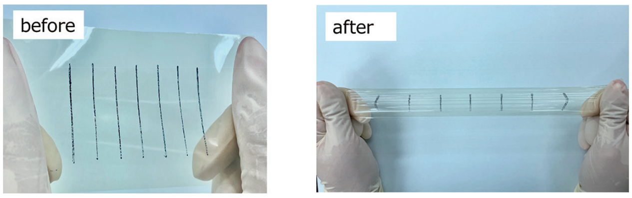



**Fig. 9 Appearance of stretchable PI film**

applied to stretchable applications.

**Table 5** lists the properties of the developed stretchable polyimide films. The elongation at break of general polyimide films is mostly 100% or smaller while that of the stretchable films developed this time exceeds 350%.

In addition, our stretchable films have tensile stress one tenth of that of the conventional product, showing softness close to rubber. The recovery rates after extension are currently 80 to 90% and we are working to improve the rate. Meanwhile, the thermal cracking temperature of the stretchable films is 400°C or higher as is the case with the conventional polyimide film. The stretchable films are expected to be applied, as a new material, to stretchable applications where heat resistance is required.

**Table 5 Properties of stretchable polyimide film**

| | Stretchable PI #1 | Stretchable PI #2 | Conventional PI-CCL (M series) |
|---|---|---|---|
| Thickness ($\mu$m) | 35 | 25 | 25 |
| Tensile strength (MPa) | 26 | 40 | 370 |
| Elongation (%) | 462 | 350 | 59 |
| Water absorption rate (wt%) | 0.1 | 0.1 | 1.1 |
| Temperature of thermal decomposition at 5% weight loss (°C) | 455 | 447 | >450°C |

## 5. Conclusion

The Integrated Research Laboratory of Nippon Steel Chemical & Material will develop new polyimides by utilizing our high-molecule design and synthesis technologies and applying high functionalities, such as transparency, heat dissipation, elasticity, and low dielectricity, to polyimides as well as develop new polyimide markets.

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