Background and Near Future of Development of Colorless Transparent Polyimides

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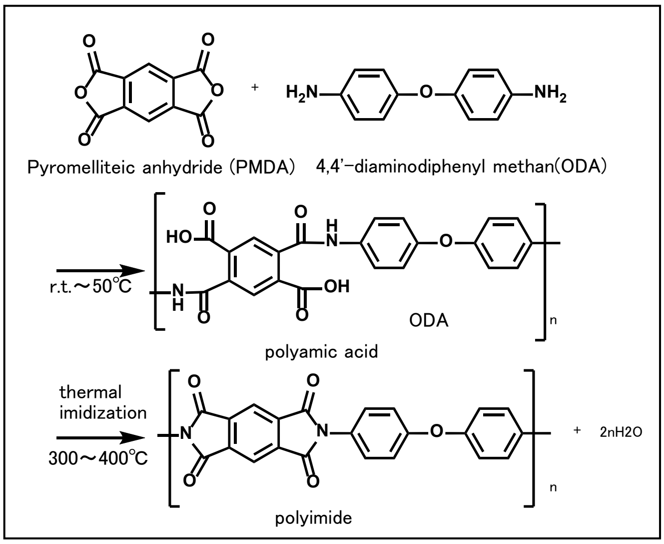
Abstract

Two types of PFAS free polyimide are introduced. Those are a transparent polyimide which has both high heat resistance and high transparency and thermoplastic polyimide which has excellent electrical properties that can be used under high frequency conditions.

Introduction

The history of polyimides has begun in early 1960's when Du Pont released a polyimide film made of pyromellitic dianhydride (PMDA) and 4,4'-diaminodephenyl ether (ODA). We MGC established a joint venture company to manufacture and sell PMDA and supplied PMDA for many years. As shown in the reaction formula, the polyimide film is produced by a two-step condensation reaction from PMDA and ODA via the intermediate polyamic acid. Polyimide film began to be manufactured mainly in USA and Japan, and in recent years, it has been increasingly manufactured in Asian countries such as South Korea, Taiwan and China.



Market trend of polyimides

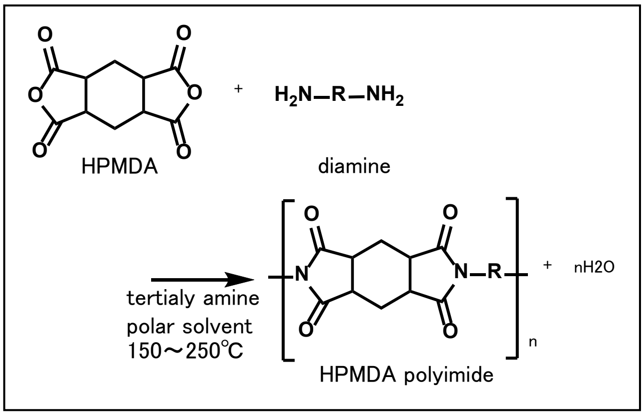
Although the global market size for polyimide has been growing year by year, it decreased slightly to 7,100 tons in 2019, 7,000 tons in 2019, and 6,600 tons in 2020, and has remained flat since then. Similarly, the Japanese domestic market decreased slightly to 930 tons in 2018 and 850 tons in 2019 and has remained flat since then. It has been mainly used as an insulating material in copper-clad laminates in the electric field, and in recent years it has been improved to have low dielectric properties. The sales amount is approximately 470 million to 540 million US dollars in the global market, and around 70 million US dollars in Japan. Among them, the Chinese market is the largest.

Transparent polyimide films are now being used as base materials for cover window of foldable displays, transparent conductive films, etc. Other uses include transparent insulating layers for copper-clad laminates, optical filters, and optical sensor substrates. Sales amount is approximately

9 million US dollars in 2020, 13 million US dollars in 2021 and forecasted to be 35 million US dollars in 2025, indicating a large growth rate.

Background of development of colorless transparent polyimides

We MGC manufactured and sold PMDA, a raw material for polyimide, for many years. Although MGC is currently withdrawing from the PMDA market, MGC has successfully mass-produced 1,2,4,5-cyclohexantetracarboxylic dianhydride (HPMDA), which is obtained by hydrogenating the benzene ring of PMDA.



Conventionally produced polyimides have aromatic rings in a conjugated structure, forming charge transfer complexes inter- and intra-molecules. For this reason, conventional polyimide films are colored from yellow to reddish brown, making it unsuitable for application where visible light enters and exits. Therefore, MGC started exploratory experiments using HPMDA to develop transparent polyimide that could be used like glass substrates in the latter of 2002. Fluorine-containing polyimides[1] and alicyclic polyimides [2] have already been reported as transparent polyimides. By introducing a fluorine substituent or incorporating an alicyclic structure, the resulting polyimides becomes transparent because it becomes difficult to form a conjugated structure. HPMDA polyimide is expected to have high solubility in solvents, but HPMDA has lower reactivity than PMDA and is difficult to polymerize polyimide. MGC has succeeded industrial one-pot synthesis in which a tertiary amine is used as a catalyst and polymerized by heating at 150 to 250℃ in a polar solvent with removing water produced by imidization reaction[3]. By introducing the alicyclic structure, the absorption edge shifted to shorter wavelengths as expected, and visible light region shows a transmittance around 90% (Fig. 1). Table 1 shows properties of S100 and S200. Since the refractive index is around 1.6, approximately 10% is lost due to reflection, but transmittance can be increased by providing an antireflection layer.

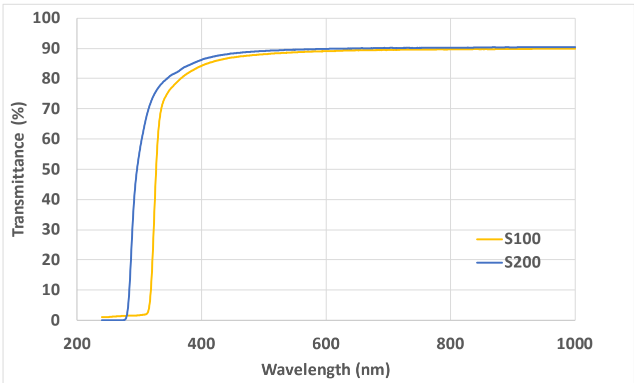


Fig 1 Transmittance curve of S100 and S200

Near future of development of colorless transparent polyimides

The European Chemicals Agency (ECHA) has proposed a plan to regulate PFOA (perfluorooctanoic acid) in 2017 and C9-C14 PFCA (perfluoro carboxylic acid) and PFAS (perfluoro alkyl substances) in 2021, and some have already been implemented.

Most transparent polyimides use fluorinated diamines and fluorinated acid dianhydrides, ant although regulations have not yet been finalized, there are concerns that their use may be restricted. As already mentioned, many of our polyimides use HPMDA to achieve transparency, and we are receiving an increasing number of requests for PFAS-free polyimide. We already proposed S100 and S200 to some customers, we will continue to develop PFAS free polyimide according to the requests of each customer. For example, we are developing a substrate for cover window of foldable displays that requires a large elastic modulus. S100 has a small elastic modulus, so it lacks physical properties as a base material for the cover window, but it is transparent, has high heat resistance, and has the property of not leaving any bending marks when bent over a long period of time (Fig 2 and 3), so we continue to propose parts that require bending resistance.

The static bending test method is explained in Fig 4. A test piece with width of 1cm and a length of 5cm is placed against metal plate and fixed with a clip, left to stand for a specified time in an

Table 1 Properties of S100 and S200

item	unit	S100	S200	method
thickness	μm	50	50	
Transmittance	%	88.7	89.7	JIS K 7136
YI	–	2.1	1.5	JIS K 7136
L	–	94.1	94.6	JIS K 7136
a/b	–	0.0 / 1.1	0.0/0.8	JIS K 7136
HAZE	–	0.2	0.3	JIS K 7136
Reflactive index		1.61	1.59	@594nm
Glass (Tg)	°C	308	327	TMA
Td1%	°C	485	483	TGA
CTE (100-200°C)	ppm/K	73	61	TMA
Tensile modulus	GPa	2.4	2.4	JIS K 7127
Tensile strength	MPa	98	98	JIS K 7127
Elongation	%	10	7	JIS K 7127
Dielectric (1MHz)	–	3.7	3.8	capacitance
Dissipation (1MHz)	–	0.019	0.014	capacitance

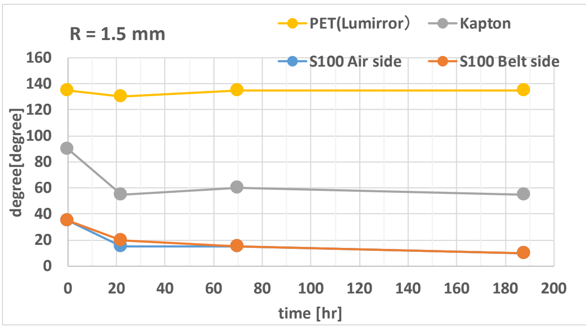


Fig 2 Result of static bending testR1.5mm, 70°C/dry

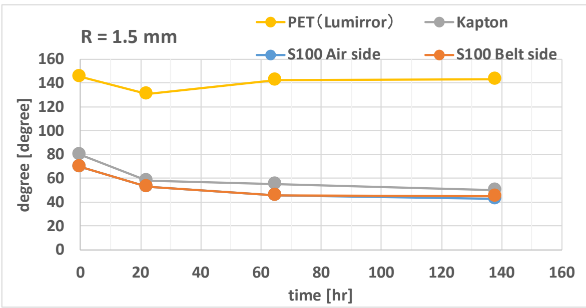


Fig 3 Result of static bending test（R1.5mm, 65°C/90%RH 24hr）

atmosphere under the specified test conditions, and the test piece is transferred to a constant temperature and humidity (23°C, 50%RH). The angle formed by the test piece is measured at each elapsed time (Fig 4).

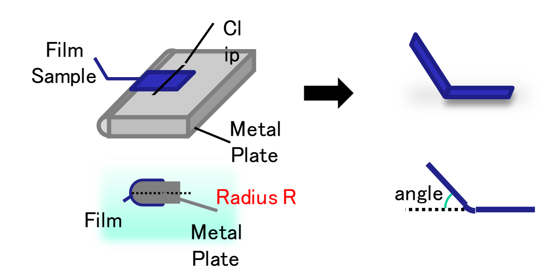


Fig 4 Static bending test method

Development of thermoplastic polyimide

We have developed a new thermoplastic polyimide "Therplim" (MGC-TPI) to take a new approach by leveraging our extensive knowledge of polyimide monomers such as PMDA and the knowledge gained from developing transparent polyimide.

In the thermoplastic resin market, global demand for polyetheretherketon (PEEK) has rapidly increased by two or three times over the past decade years, and high growth is expected to continue in the future[4]. Although PEEK exhibits excellent physical properties, its glass transition temperature (Tg) is relatively low at 143°C, which limits its use at high temperature even in high-end applications. In response, several companies are developing thermoplastic polyimides (TPI). Fully aromatic thermoplastic polyimide resins and thermoplastic polyetherimide resins that are already commercially available have high Tg of well over 200°C, and have long been highly rated for high heat-resistant applications[5]. However, these thermoplastic polyimide materials have some room for improvement, such as difficulty in processing due to their high Tg, slow crystallization rate, and dielectric properties. Generally known methods for imparting thermoplasticity to polyimide resin include (1) incorporating flexible bonding groups int the main polymer chain structure, (2) breaking the linearity of the main polymer chain, and (3) incorporating an aliphatic structure[5]. In developing MGC-TPI, we adjusted the structural balance of these structure based on various studies. As a

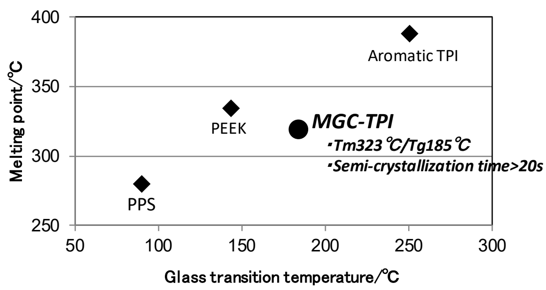


Fig 5 Thermal properties of MGC-TPI and super engineering plastics

Table 2 Mechanical properties of MGC-TPI

	Method	Unit	MGC-TPI
Bending strength	JIS K7171	*MPa*	120
Bending modulus		*GPa*	2.6
Tensile strength	JIS K7161	*MPa*	80
Tensile modulus		*GPa*	2.5
Tensile fracture strain		*%*	21
Oxygen index	JIS K7201	–	25.5
Water absorption (23℃,dip/24h)	JIS K7209	*%*	0.1

result, we succeeded in achieving both high crystallinity (fast crystallization rate) and easy formability (low Tm/high Tg, good flowability), and also achieved unique physical properties such as low dielectric properties in a PFAS free structure. However, in MGC-TPI, we have selected a structural design that increases the proportion of aliphatic structure in order to dominantly express high crystallinity and electrical properties that existing materials do not have, and this results in a lower heat resistance (heat aging resistance, flame retardancy) are inevitably reduced. The various properties are explained in Fig.5 and Table 2.

Table 3 Electrical properties of MGC-TPI

	condition	Method	Unit	TPI
Dielectric constant	1GHz	IEC62810	–	2.8
	10GHz		–	2.7
Dissipation tangent	1GHz		–	0.004
	10GHz		–	0.004
Breakdown voltage	–	ASTM D149	kV	45.5
Tracking resistance	–	JIS C 2134	V	600
Volume resitivity	–	IEC60093	Ω・m	5.3×10^{15}
Surface resistivity	–		Ω	1.6×10^{16}

MGC-TPI has unique thermophysical properties. Crystallinity is imparted by optimizing the aliphatic structure and its proportion in the main polymer chain, and the crystallization speed is extremely fast, so it can be used under general injection molding conditions or film extrusion molding conditions that involve rapid cooling. Even in this case, it is possible to complete most of the crystallization. Its melting point is 323°C, which is lower than PEEK, making it easier to mold. Although the Tg is 185°C, which is lower than commercially available TPI (less than 200°C), it has the advantage of being able to be molded even if the mold temperature for injection molding and the roll temperature for film extrusion are set to relatively low temperature. As shown in Table 2, the introduction of an aliphatic structure has the disadvantage of lowering the oxygen index and other flame-retardant indicators. On the other hand, by imparting crystallinity, water absorption is low at 0.1% in water for 24 hours, and 0.7 to 0.8wt% even when saturated, indicating low water absorption for a polyimide (Fig 6).

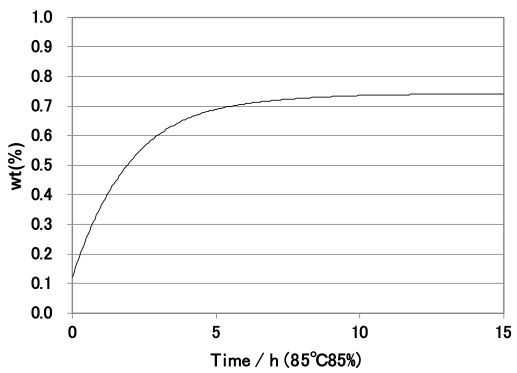


Fig 6 water absorption rate of MGC-TP

MGC-TPI for 5G related applications

Table 3 shows the electrical properties of MGC-TPI. Dielectric properties are measured in the high frequency band, which are important in 5G-related application, and both the dielectric constant and the dissipation tangent show low values. And the tracking resistance and breakdown voltage are better than those of fully aromatic super engineering plastics. These properties are

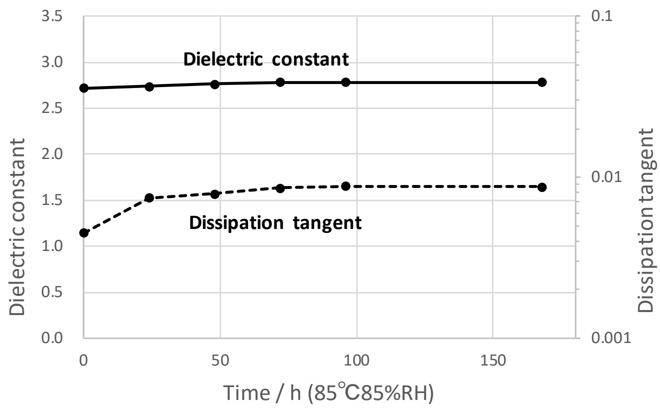


Fig 7 Dielectric properties under water absorption

because of imparting aliphatic structure into MGC-TPI. Since MGC-TPI is a crystalline polymer, it does not easily absorb water and its water absorption exhibits the lowest value among polyimide materials. Fig 6 shows the water absorption rate of the thin sample measured over time under 85℃/85%RH conditions. Although a certain amount of water absorption occurs, the saturated value is at 0.7 to 0.8wt%. Regarding low dielectric materials, the dielectric properties of any material generally deteriorate in proportion to the amount of water absorption[6]. Therefore, low water absorption is an important factor for low dielectric materials. Although the dielectric properties of MGC-TPI also deteriorate with water absorption, the degree of deterioration is limited because the water absorption is low as mentioned above (Fig 7) and the dissipation tangent maintains a low value.

As mentioned above, MGC-TPI has various properties that conventional polymer materials do not have and has excellent easy moldability. Therefore, it is possible to develop new applications by applying it to various shapes and various composite materials. It is now possible to form 12.5μm thickness film, and we expect new developments that take advantage of low dielectric properties.

Conclusion

Two unique polyimides developed by MGC were described. They are expected as PFAS free polyimide, to be used in high frequency conditions requiring low dielectric properties and as film both with high heat resistance and high transparency.

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