Development of Value Added Acrylic Film 'TECHNOLLOY®'

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Technolloy® is an acrylic resin (PMMA) film with extremely smooth, hard, and highly glossy surfaces.

Because of these characteristics, Technolloy® film is widely used for automobile interior and household electrical appliance parts, often as an alternative to organic solvent paints. In addition, this film is suitable for use as a substrate film for coating; its potential for use in optical film applications is extremely promising.

In this paper, we review some basic performance characteristics of our Technolloy® film, and provide some examples of its application.

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Introduction

1. Background Information

Technolloy® is the trade name for the acrylic resin (polymethyl methacrylate resin: PMMA) film created through Sumitomo Chemical Co., Ltd.'s research and development. Sumitomo Chemical takes care of every aspect of Technolloy®, from its manufacture in clean rooms through to its sale.

PMMA possesses special characteristics, such as optical clarity (high transparency), excellent durability (weather resistance) and a high level of surface hardness. Previously, it was most popularly utilized for aircraft windshields. In recent years, popular application areas of PMMA have shifted to tail light covers for automobiles, covers for lighting fixtures, signboard materials, displays, and large aquariums.

The most popular acrylic film on the market is a soft acrylic film (approximately 4B pencil hardness). This film is used primarily as a surface laminate material for polycarbonate (PC) boards, PVC wallpapers, and steel boards. Lamination systems have been devised for each application.[1)]

Acrylic film manufacturers include Mitsubishi Rayon Co., Ltd., Kaneka Corporation, and Sumitomo Chemical Co., Ltd. Total sales of acrylic film for the 2004 fiscal year are expected to reach approximately 2,300 tons.[2)]

Sumitomo Chemical's Technolloy® is an acrylic film made of a hard PMMA resin. Compared to conventional soft acrylic films, it is extremely hard (H pencil hardness).

Moreover, Technolloy® acrylic film gives a hi-gloss finish, features double-sided smoothness and has highly regular thickness. It makes the most of these special characteristics when used in surface design as a substitute for the metal plating and organic solvent coating of automobile parts, home appliances, and sanitary products.[3)] Furthermore, Technolloy® has already been adopted as a coating base material for scratch resistant films (hard coat) and low reflectivity performance. Thus, it is expected that Technolloy® will expand into optics related applications in the future.

In this paper we shall introduce the basic properties, special features, and applications for each grade of Technolloy®.

2. Film Processing Method

In general, there are two types of film molding methods for thermoplastic resins: the solvent casting method and the extrusion method. From cost and productivity points of view, the extrusion method is more often utilized.

Fig. 1 depicts the basic properties of film manufactured by general film molding methods.

The extrusion method can be roughly classified into two categories: a T-die extrusion method and a tubular film method. The T-die method involves a solidification process (whereby a film surface is changed from molten to solid state using a cooling roller), and is more popular for its superior surface smoothness and thickness controllability.

Companies such as Mitsubishi Heavy Industries Ltd., Hitachi Zosen Corporation, and Toshiba Machine Co., Ltd., have developed proprietary methods that produce unique product characteristics using the cooling method. They introduced film products manufactured through these new methods, for optical field applications, at the "International Plastic Fair 2005," held at Makuhari Messe in September 2005.

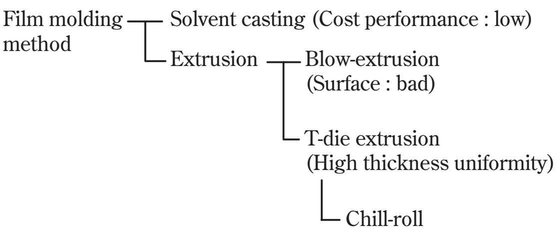


Fig. 1 Film molding method

Special Features and Application Examples of Technolloy® Grades

1. Basic Properties and Special Features of Technolloy® S001

The application of Technolloy® in cosmetic base materials for surface design is becoming more popular. Its special features include:

(1) Excellent weather resistance (PMMA has a long history in outdoor applications such as automobile tail lights and outdoor signboards.)

(2) Optical strain is not readily produced. (Produces minimal birefringence, as PMMA has a molecular structure that has a small anisotropy of polarizability.)

(3) Outstanding transparency (Total spectral transmittance) – more than 92% - considered to be the highest among all resins.

(4) High surface hardness (H – HB pencil hardness)

(5) Exceptional surface smoothness (Reduces incidences of "dot skip" flaws during photogravure printing process.)

PMMA has excellent weather resistance, gives a "deep and rich" visual impression, and creates minimal optical strain; these qualities make it suitable for use in display material components. It is also an excellent product choice for use as a base film in surface design applications.

Table 1 indicates the basic properties of S001, the standard grade of Technolloy®.

Table 1 Properties of S001 (125µm thickness)

		Method	Unit	S001
Optical	Total transmission	JIS K7105	%	> 92
	Haze	JIS K7105	%	< 1.0
	Yellowness index	–	–	< 0.5
Thermal	Tg	JIS K7121	°C	103
	Shrinkage	*	%	1.5 ± 1
Mechanical	Tensile strength	JIS K7113	MPa	> 60
	Tensile expansion	JIS K7113	%	> 25
Others	Pencil hardness	JIS K5400	–	H
	Density	JIS K7112	g/cm³	1.17

* Measured by our original method. Condition : 100°C × 10min. Direction : machine direction

Fig. 2 and **3** depict the results of an acceleration endurance test. (SWOM, 63°C) These results demonstrate that the optical properties of the film do not change under stress and the film is highly impervious (weather resistant).

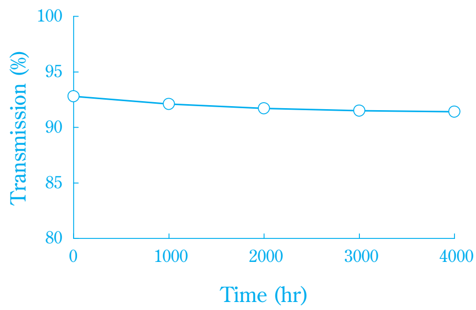


Fig. 2 Deterioration of Tt by SWOM

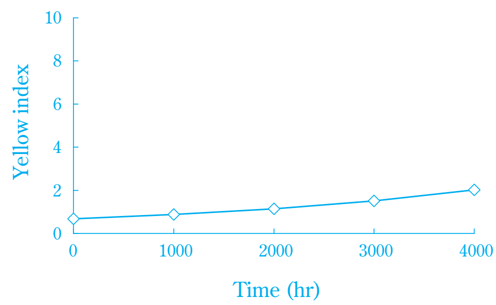


Fig. 3 Deterioration of Yellow Index (YI) by SWOM

Technolloy® S001 (125µm) is a typical grade choice for automobile interior component applications. **Fig. 4** depicts S001's optical spectrum in the ultraviolet ray – visible ray range. From this figure, it can be observed that the film maintains high transmittance in the visible ray area by screening many of the ultraviolet rays contained in sunlight. Ultraviolet rays can adversely affect various designed surfaces (for example, it can cause the deterioration of the reverse side of film onto which printed coating material has been applied).

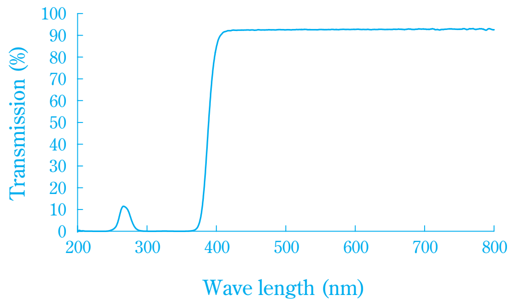


Fig. 4 Spectral transmittance

Fig. 5 depicts the result of a high temperature tension test conducted on Technolloy® S001. According to this result, if the film is processed at an appropriate temperature, it can be stretched without reaching its breaking point. Thus, it can be concluded that Technolloy® S001 possesses outstanding workability for various molding processes including thermoforming.

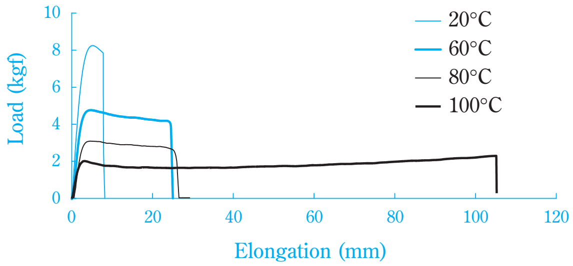


Fig. 5 Tensile characteristics of S001

Table 2 indicates the solvent resistance of Technolloy® S001. Although Technolloy®, like regular PMMA, is resistant to low concentration levels of alcohol, acid, and alkali, it is soluble in organic solvents such as aromatic hydrocarbons, ketones, and ethers. Therefore, when using PMMA as a base material, it is necessary to exercise caution when selecting a coating material containing an organic solvent.

Fig. 6 depicts the horizontal thickness distribution of Technolloy® S001 during extrusion molding. As seen in the figure, S001 thickness fluctuation is controlled within a 4% range for products having a width of up to 1,000mm.

Table 2 Chemical resistance of S001

Chemical	Condition	Resistance
10% ethanol	20°C, 24H	○
Petroleum benzine	20°C, 24H	○
Dioctyl phthalate	60°C, 168H	△
0.1N H_2SO_4	20°C, 24H	○
0.1N NaOH	20°C, 24H	○
Hair dye	60°C, 24H	△

○ ··· no change, △ ··· slight change

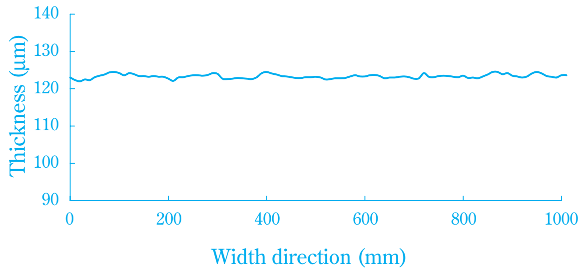
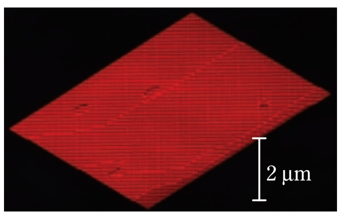


Fig. 6 Thickness fluctuation of S001

In acrylic films, granular objects called "fisheyes," between 20 – 30 microns in size, may be produced on the film surface. "Fisheyes" can cause surface unevenness during the printing or coating process, resulting in a poor appearance. This defect can be caused by rubber particles, aggregates, deteriorated resin ingredients, and environmentally foreign objects. Sumitomo Chemical has resolved these problems in Technolloy® by conducting stringent quality control to prevent foreign objects from mixing into the film during production, from the initial manufacture of the raw materials through to the final film molding process.

Fig. 7 depicts the surface roughness of the film. From the figure, it can be observed that the film sur-



Device : Contact type 3-D surface roughness measuring device
Results :
Ra : 0.022
Rz : 0.120
Rmax : 0.156 (μm)

Fig. 7 Surface roughness of S001

face is extremely even. Surface smoothness is similarly consistent on both sides of the film.

The effects of surface smoothness manifest most obviously when Technolloy® undergoes the printing process. As compared with conventional soft acrylic films, the chance of a printing defect called "dot skipping" occurring is significantly reduced. This makes our film preferable for clients.

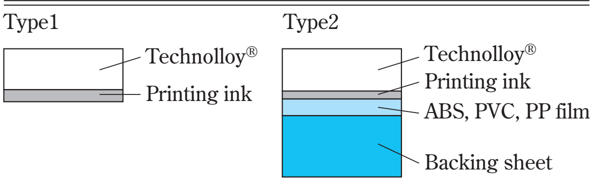
At the present time, Technolloy® can be made as thin as 75µm. We are proud to be the only company in the world that can currently provide hard acrylic film thinner than 125µm with such outstanding surface smoothness.

2. Applications of Technolloy®

(1) Application in Surface Designing

When using Technolloy® for the purpose of surface design for automobile interiors (by which acrylic film with simulated grain or metallic appearance prints are laminated onto component surfaces), the acrylic film can be incorporated in two ways, classifiable by molding method. **Table 3** depicts cross sections of the structure of these two alternative surface design molding methods.

Table 3 Laminated structure with use application



(i) Technolloy® Auto Interior Design Application – Type 1

Type 1 is a single layer transparent acrylic film on which simulated grain and metallic finishes have been directly printed. Generally, it requires special equipment (such as molds and a film supply system) to perform vacuum/injection molding within a single mold.

To ensure creation of a "deep and rich" impression, the most commonly used film thickness is 125µm.

(ii) Technolloy® Auto Interior Design Application – Type 2

A second application of Technolloy® for auto interior design involves the lamination of a transparent Technolloy® film onto a base formed of other resins (ABS, PP and PVC). Incorporating advance thermoforming into this production process allows for the use of existing injection molding machines.

The most popular thickness used for the surface layer film for this type of application is 125µm as in the Type 1 application. However, the total thickness of the sheet after lamination onto the base sheet must be approximately 500µm to maintain the shape of the product molded by thermoforming.

(2) Comparisons of Surface Designing Methods

Manufacturing methods of grain patterned automobile interior components include:

- Hydraulic Pressure Transfer Method: In this method, a water-soluble pattern printed on transfer paper is transferred onto a base material using hydraulic pressure. Although this method is advantageous in that it allows for a high degree of freedom in the shape of the surface to be transferred onto, it requires a finish coat to be applied over the transfer.
- Insert Method: In this method, a previously thermoformed surface film is inserted into a mold; injection molding is used to apply grain patterned film onto the thermoformed base. Although this method allows for the use of general molding equipment, it breaks the production process into two distinct processes.
- In-Molding Method: In this method, separate vacuum and injection moldings are performed simultaneously within a single mold. This method has an advantage in that the final product can be obtained through a single process, thus reducing steps in production and eliminating the coating process. **Fig. 8** depicts the In-Molding Method.

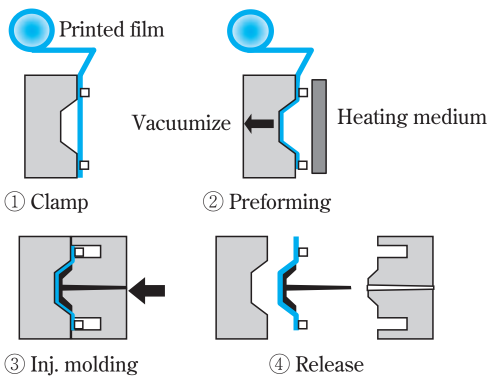


Fig. 8 Flow sheet of in-molding process

3. Development of Films that are Resistant Against Heat Whitening

(1) Heat Whitening Defect

Research has been conducted to improve Technolloy®'s impact resistance while at the same time retaining the excellent surface hardness unique to acrylic resins. More specifically, Technolloy® possesses a structure in which rubbery elastic particles are distributed to function as "island ingredients" within an "ocean" of acrylic resin. These rubbery particles allow increased resistance to the discoloration commonly associated with heating and bending.

However, if the temperature increases beyond the point at which the film becomes soft during the thermoforming process described above, rubbery particles in the vicinity of the film surface escape from the stress of the solidification status that has occurred during the molding process. This causes irregularities on the film surface, and allows the rubbery particles to reflect exterior light irregularly. As a result, the film surface may appear slightly whitish. **Fig. 9** depicts the mechanism of this phenomenon.

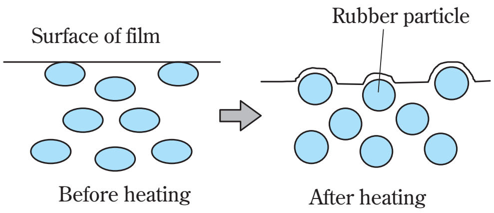


Fig. 9 Mechanism of surface irregularities under heating

(2) Optimization of Resin Materials

Fig. 10 and **11** illustrate the resistances to heat whitening and impact associated with various rubbery particle sizes commonly used in acrylic resins. Although it is necessary to reduce the particle size in order to reduce whitening caused by heat, it is obvious from these figures that an adequate particle size is required to obtain the necessary impact resistance. In addition, although increasing the number of rubber particles in the film improves impact resistance, it also increases the potential for discoloration during heating. Thus, it is extremely difficult to reduce whitening level while at the same time increasing impact resistance using conventional rubbery particles.

We have overcome these apparently conflicted qualities by adding the appropriate number of rubbery particles within a specific structure. We have recently developed and launched Technolloy® S013, a grade of film that maximizes impact resistance, yet minimizes the level of whitening caused by heat.

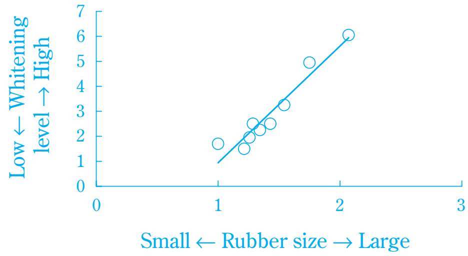


Fig. 10 Whitening level after heating vs. rubber size

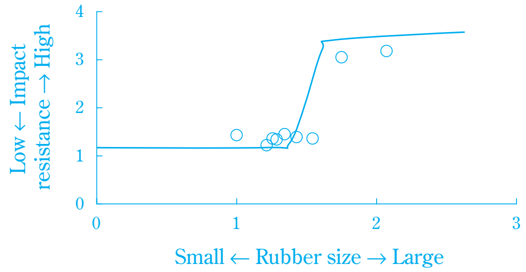


Fig. 11 Impact resistance vs. rubber size

4. Development of Stress Whitening Resistant Films

Bending or stretching of films during the course of various manufacturing processes may cause whitening in acrylic resins. This phenomenon is generally referred to as stress whitening. Technolloy® compensates for this tendency through the use of a structure in which rubber particles are distributed to become "island ingredients" within an "ocean" of acrylic resin. This structure improves the impact resistance of the film material.

The manifestation mechanism of impact resistant properties in film material has been explained in several documents.[4), 5)] These documents explain the manifestation mechanism as follows: when film material receives external force such as bending and stretching, stress concentration occurs in the contained rubber particles, which have low modulus elasticity in the equatorial direction; the stress thus causes polymer molecule flux, and provides impact resistance. Whitening is caused by micro voids in the surface of the film.

Fig. 12 depicts a scanning electron microscope photo of a cross section of the whitened area when the Technolloy® S001 film is bent to 90°. Minute cracks (crazes) are produced between rubber particles. Craze related whitening can be reduced by: (i) Decreasing the craze size by reducing the pressure level at the stress center; and (ii) Increasing resistance to crazing at the stress center. Method (i) is accomplished by increasing the number of rubber particles added and reducing particle size. For method (ii), it is crucial to carefully design rubber particle interface materials.

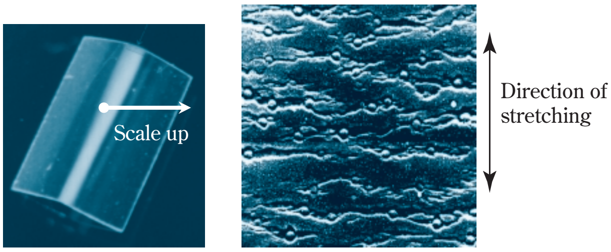


Fig. 12 Observation of whitening part by SEM

Based on these perspectives, we have developed a new grade of stress whitening resistant film, Technolloy® S014. In Technolloy® S014 we have optimized material design, while at the same time maintaining balance between surface hardness and strength of the film.

No stress whitening is observable in Technolloy® S014, even when the film is bent to 90° at ambient atmospheric temperature.

Table 4 indicates general properties of S013 (heat whitening resistant grade) and S014 (stress whitening resistant grade).

Table 4 Properties of S013, S014 (125µm thickness)

		Method	Unit	S013	S014
Optical	Total transmission	JIS K7105	%	> 92	> 92
	Haze	JIS K7105	%	< 1.0	< 1.0
	Yellowness index	–	–	< 0.5	< 0.5
Thermal	Tg	JIS K7121	°C	100	96
	Shrinkage	*	%	1.5 ± 1	2.5 ± 1
Mechanical	Tensile strength	JIS K7113	MPa	> 55	> 40
	Tensile expansion	JIS K7113	%	> 40	> 30
Others	Pencil hardness	JIS K5400	–	F	HB
	Density	JIS K7112	g/cm^3	1.17	1.17

* Measured by our original method. Condition : 100°C × 10min.
Direction : machine direction

5. Development of Matt Grades

In addition to the previously described high-gloss films, matt finish films are also popular for surface design. Matt films are most widely used for metallic looking parts and components. Key market-derived requirements for matt films include:

(i) Using a resin that contains a diffusing agent
(ii) Performing irregular transfer onto the film surface using a roll that has an irregular surface
(iii) Applying matting agent onto the film surface

When using matt films for the purpose of surface design, the following requirements must be achieved: the degree of matting required by the user must be easily obtained; once a certain degree of matting has been determined, it must remain stable even after going through several thermal histories. To meet these requirements, Sumitomo Chemical has carefully examined the available processes, and selected the best coating method for manufacturing matt films.

Technolloy® is often utilized in areas that require a molding process such as automobile interior components, as described above. It is thus necessary that the film possesses thermoforming properties, as it may have to go through thermoforming or insert molding processes. Although in general, coating film must be flexible for thermoforming, flexible films tend to have poor scratch resistance and chemical resistance. Alternatively, if the film has been hardened, there is a concern that the surface may become crazed during the thermoforming process.

To solve these problems, we selected a coating material characterized by both flexibility and skin hardness when developing Technolloy® matt grades. We also added an appropriate matting agent to the material. We have successfully developed matt grades that possess excellent appearance and moldability by making the most of the surface smoothness of the Technolloy® base material, as well as by using a precise coating process that does not allow any surface defect (i.e., change in degree of matting after the coating process) to occur.

There are three standard Technolloy® matt grades: S001 M20 and S001 M30, based on S001, and S014 M20, based on S014. Depending upon customer's needs, films having levels 10–50 at 60° gloss are available.

Table 5 indicates general properties of Technolloy® matt grades.

Technolloy® matt grades are suitable for applications in decorative films that demonstrate unique characteristics unobtainable on glossy films. For example, a unique design can be achieved by printing on the opposite side of the matt surface.

Table 5 Properties of Matt grades (125μm thickness)

		Method	Unit	S001M20	S001M30	S014M20
Optical	Total transmission	JIS K7105	%	> 85	> 85	> 85
	Haze	JIS K7105	%	68 ± 5	55 ± 5	68 ± 5
	gloss (60°C)	JIS K7105	–	20 ± 4	30 ± 5	20 ± 4
Thermal	Tg	JIS K7121	°C	103	100	96
	Shrinkage	*	%	1.5 ± 1	1.5 ± 1	2.5 ± 1
Mechanical	Tensile strength	JIS K7113	MPa	> 60	> 60	> 60
	Tensile expansion	JIS K7113	%	> 25	> 25	> 30
Others	Pencil hardness	JIS K5400	–	2H	2H	2H
	Density	JIS K7112	g/cm³	1.17	1.17	1.17

* Measured by our original method. Condition : 100°C × 10min.
Direction : machine direction

6. Technolloy® as Coating Base Material for Cellular Phone Windows

Because of its outstanding surface smoothness, Technolloy® matt is most suitable for application as a general coating base material.

Conventionally, cellular phone windows have been made up of a 1–2mm acrylic resin base with a hard film coating applied to their surfaces. Recently, demand has increased for thinner materials to help improve the appearance and compactability of cellular phones. With conventional acrylic resin base materials, however, thinner material results in lowered impact resistance. This is exacerbated by the fact that, in a falling ball impact test, an acrylic substrate — onto the surface of which a hard coat film has been laminated — demonstrates a significantly lower impact resistance than does the original substrate with no coating film.

On the contrary, if Technolloy® S001 (thickness of 0.65mm) is used as a base material, a high level of impact resistance can be maintained in a falling ball impact test, despite the application of a scratch resistant hard coating.

Fig. 13 compares the 50% breaking height of standard acrylic films (between 0.8mm – 1.5mm thick) and Technolloy® S001 (0.65mm thick). A 5μm scratch resistant film layer (UV-hardened polyfunctional acrylate film) was laminated onto each of these bases. Each impact resistant film was then placed on a cradle (simulation of a cellular phone window) with a 42×32mm opening area. An iron ball weighing 5.46g was dropped on the film from increasing heights to obtain the 50% breaking height of the film.

As the test results clearly indicates, the scratch resistant film laminated to 0.65mm thickness Technolloy® S001 possesses similar impact resistance to that of the scratch resistant film laminated to a 1.5mm thick standard acrylic film. This suggests that using Technolloy® S001 as a base material allows a reduction in thickness without the loss of the practical strength required for cellular phone windows.

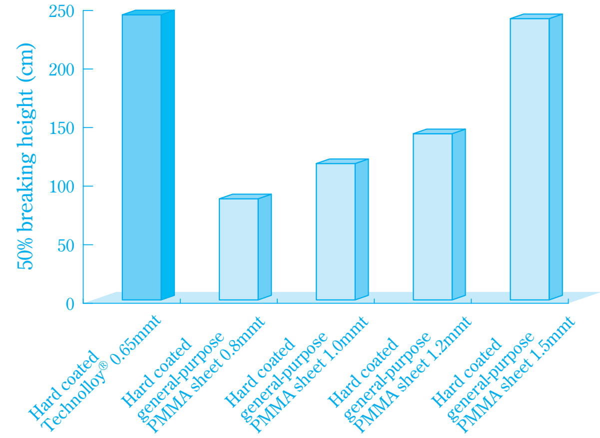


Fig. 13 Falling ball impact test

7. Specifications of Technolloy®

As Technolloy® products are manufactured in a clean room, the optical strain level is low and the number of foreign objects (for example, fish eyes) in our products is minimal.

Fig. 14 depicts Technolloy® immediately after manufacture. **Table 6** provides specifications for the standard grades of Technolloy®.

The available thickness range of Technolloy® is quite broad: 75–800μm. Films within this range can be provided in the form of a roll. Furthermore, products over 500μm thick can be provided in the form of leaf-cut sheets. Thus, we have established a system that accommodates a variety of market needs.

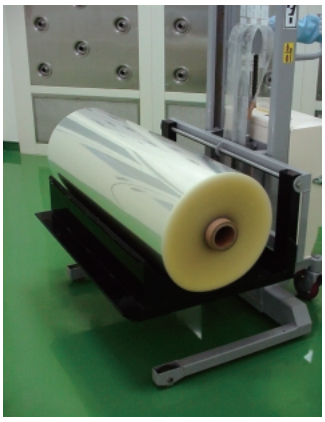


Fig. 14 Technolloy® film roll

Table 6 Thickness, width and length of Technolloy® products

Grade	Thickness (µm)	Width and length (mm)
S001	75, 125	1050 × 1000
		1115 × 1000
	250	1115 × 500
	650, 800	1200 × 250
		(Possible in sheet form)
S013, S014	125	1050 × 1000
		1115 × 1000
S001M	75,125	1115 × 1000

8. Advantages of Surface Design Technology Using Technolloy®

PMMA is an environmentally friendly resin (composed only of carbon, oxygen and hydrogen).

PMMA provides pollution control alternatives, by preventing the dispersion of organic solvents, and as a substitute for metal plating. Another advantage of PMMA is that it can be recycled effectively, and can be reused through its addition into resins for injection molding. In this sense, we believe that Technolloy® can contribute to the increasing recyclability of home electrical appliances and automobiles.

Conclusion

Our company continues to expand and develop the available range of applications for Technolloy®, particularly in the area of surface design film materials that can replace traditional coating materials such as paint for grain patterned automobile interior components and on home electrical appliance surfaces. In addition, it can be expected that the range of applications will soon expand to include its use as a highly functional coating base material, as in the cellular phone window example discussed above.

In order to improve Technolloy®'s market share in the area of value added products, and to fulfill more diverse and advanced market needs, we shall continue to develop products that demonstrate increasing and improving performance.

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