ABS Resin “TOYOLAC”

Technical Guide

Toray Plastics (Malaysia) Sdn. Bnd.

Contents

1. Secondary Properties and Features

Temperature Dependence of Mechanical Property

On the basis of its characteristic hardness and rigidity, “TOYOLAC”General Purpose grades (GP) can be regarded as hard, rigid and tough engineering materials. The relationships between Izod Impact strength, Flexural Modulus and several temperatures are shown in Fig. 1-1 & 1-2 respectively.

Fig 1-1 Temperature dependence of Izod Impact Strength of “TOYOLAC” GP Grades

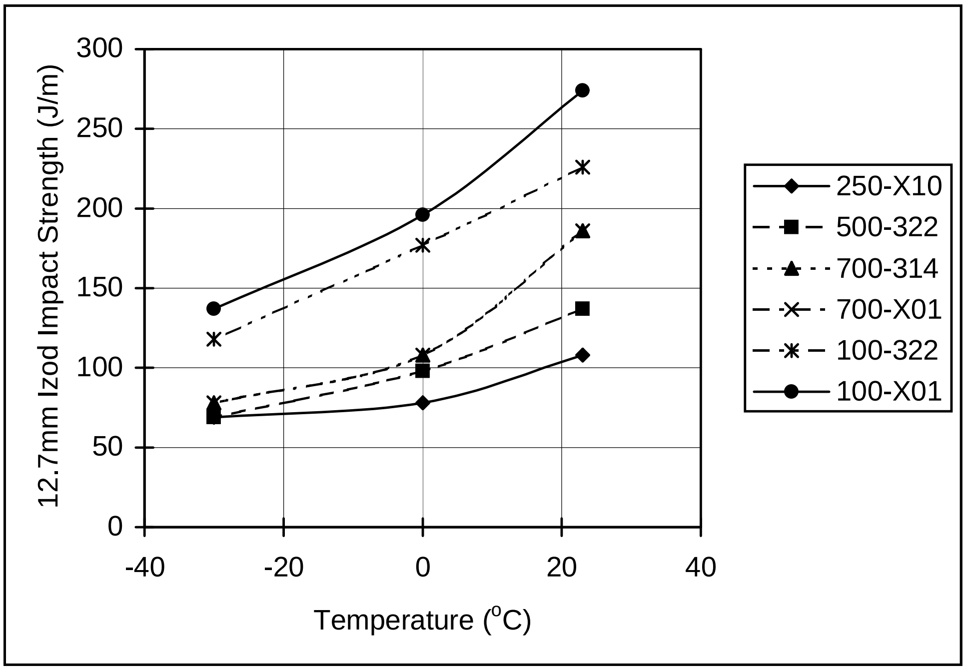
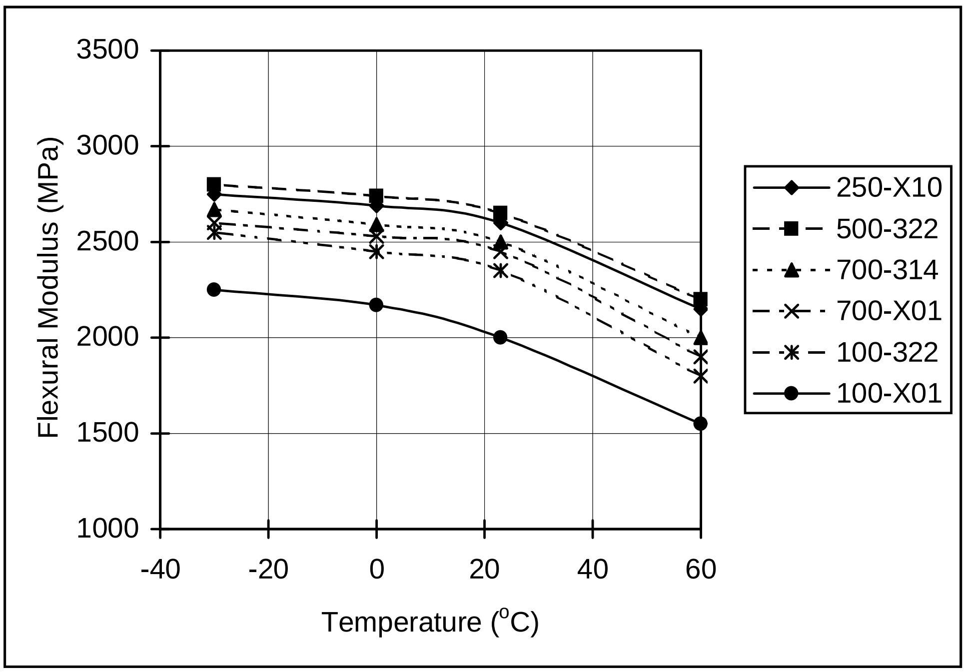


Fig. 1-2 Temperature dependence of Flexural Modulus of “TOYOLAC” GP Grades



Creep Property

Products subjected to a given load develop a corresponding predictable effect. If it continues to increase without any increase in load or stress, the material is said to be experiencing creep or cold flow. Creep is defined as increasing strain over time in the presence of a constant stress. The rate of creep for any given plastic material depends on the basic applied stress, time and temperature. Therefore, it should need to be considered this property beforehand.
Creep properties of "TOYOLAC" 100 and 500 are shown as below. "TOYOLAC" 500 is having most excellent creep property among "TOYOLAC" general purpose (GP) grades.

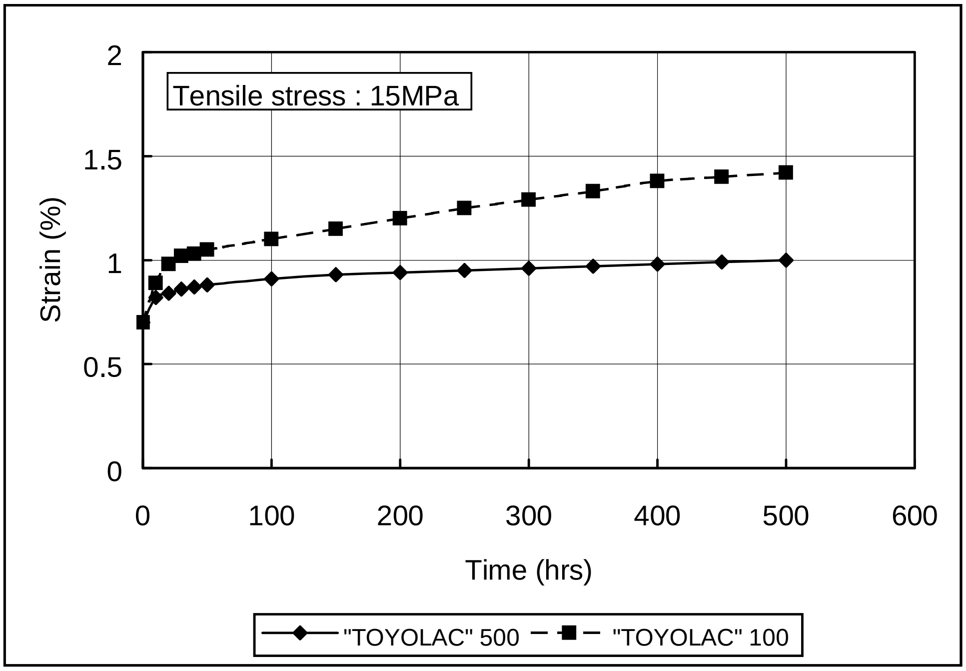


Fig 1-3 Creep Property of "TOYOLAC" 100 & 500

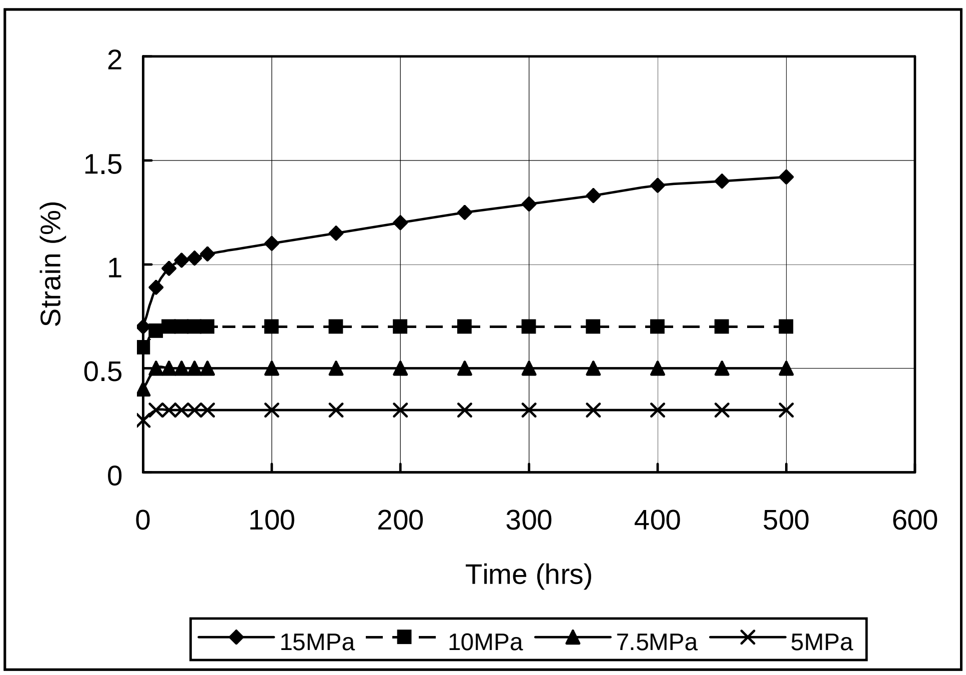


Fig 1-4 Creep Property of "TOYOLAC" 100

Electrical Property

Electrical properties of “TOYOLAC” general purpose grades are shown below table. Temperature, humidity and frequency do not have a damaging effect on “TOYOLAC” general purpose grades. Therefore, “TOYOLAC” is suitable for parts of electric equipments. Moreover, “TOYOLAC” can be used as insulator materials because it has high volume resistibility, high dielectric strength, low dielectric constant and power factor due to included styrene. However, this excellent electrical property may cause electrostatically charged problem. Consequently, it should be needed anti-static treatment depending on applications.

Table 1: Electrical Properties of “TOYOLAC” GP Grades

Properties	Units	Cond.	“TOYOLAC”		
			250, 500	700	100
Dielectric Strength (ASTM D149)	KVmm	Short Time	22~23	22~23	23~26
Specific Volume Resistibility (ASTM D257)	Ω cm	23 °C	$>10^{16}$	$>10^{16}$	$>10^{16}$
Specific Surface Resistibility (ASTM D257)	Ω	23 °C	$>10^{16}$	$>10^{16}$	$>10^{16}$
Dielectric Constant (ASTM D150)		60 Hz 10^3Hz 10^6Hz	3.13~3.19 3.09~3.15 3.02~3.08	3.08~3.13 3.03~3.09 2.95~3.02	3.02~3.08 2.99~3.03 2.89~2.95
Power Factor (ASTM D150)		60 Hz 10^3Hz 10^6Hz	4.2E-3~4.7E-3 5.6E-3~6.6E-3 6.2E-3~6.7E-3	4.2E-3~4.3E-3 5.6E-3~6.6E-3 6.2E-3~6.7E-3	4.2E-3~4.7E-3 5.6E-3~6.6E-3 6.2E-3~6.7E-3
Hot Wire Ignition (UL746A)	PLC	1.5mm	250 : 4 500 : 4	4	4
High-Voltage Arc Resistance to Ignition(UL746A)	PLC	1.5mm	250 : - 500 : 0	0	0
Comparative Tracking Index (UL746A)	PLC	3.0mm	250 : - 500 : 1	0	1

Chemical Resistibility

1. Introduction

The resistance of ABS resin to chemical environment has been measured in several methods. One is to immerse the sample in the environment for varying periods of time and determine the per cent change in weight. A second method is to immerse tensile specimens in the chemical environment and periodically check in tensile properties. Change in weight and retention per cent of tensile strength of ABS resin immersed several chemicals are shown as attached paper (Appendix-1). It has been found that ABS resin when completely immersed in water, machine oil, diluted acid and diluted alkali for extended periods of time up to 7 days suffer no weight gain and no loss in tensile strength. And it forms cloudy solutions in ketones, aldehydes, esters and some chlorinated hydrocarbons, that means it could dissolve in those chemicals. It is unaffected by most diluted alcohols, however some hydrocarbon solvents will cause softening and swelling on prolonged contact.

2. Environmental Stress Cracking and Crazing

ABS, like most polymers will undergo stress cracking and crazing while subjected to exposure to certain chemical environments under high stress for given periods of time. This cracking and crazing will occur even though some chemicals will have no effect on unstressed (relaxed) parts, and therefore simple immersion of test pieces in an inadequate measure of chemical resistance of the polymer. There are two cases of stress generation, one is to be generated by external force (external stress), another is to be remained in molding parts (residual stress). Residual stress in molding parts is generated by uneven cooling speed and fluctuation of melting flow on molding. Residual stress is relaxed in gradually with time. However, having contact with a chemical agent accelerates degradation. It may cause cracking and crazing trouble. These phenomena are so called "Environmental Stress Cracking and Crazing (ESC)".

Cracking phenomenon is observed on molding surface when it is soaked into a chemical agent under applied stress. Nevertheless, cracking and crazing may not occur lower than certain stress or strain. Those stress and strain are so called "Critical Stress" and "Critical Strain" under contacted with certain chemical agent.

However, occurrence mechanism is complicated and not clarified yet. General mechanism is shown as follows;

Main Occurrence Mechanism

A. First Stage : Penetration of environmental material is happened by expansion stress (tensile stress)

B. Second Stage : Expansion pressure is occurred by penetration of environmental material. Moreover, penetration of environmental material is accelerated. And transformation of polymer chain is accelerated, cracking and crazing cause.

Related Phenomena and Parameter

A. In case of Compression Stress, environmental stress cracking and crazing never happen.

B. Critical Strain is proportional to Mole Volume.

$$\varepsilon_c \propto V_s(\delta_p - \delta_s)$$

ε_c : Critical Strain
V_s : Mole Volume
δ_p : Solubility Parameter of polymer
δ_s : Solubility Parameter of environmental material

C. Expansion stress is occurred by difference of concentration between swelling region and non-swelling region

D. Critical Strain;

$$\varepsilon_c \propto \sqrt{(r / EL)}$$

r : Surface tension of interparticle of agglomerated polymer
E : Modulus
L : Distance of particle-particle boundaries
(proportional to particle diameter)

When stress is applied to molding parts of ABS resin, strain may occur, and crazing may occur in matrix phase (glassy polymer ; AS phase). Crazing is stretched in a highly orientated or slipped polymer chain. Density in this crazing area is 50~60% of normal area. So it consists of orientated polymer including microscale void.

Cracking may be caused by exposure a chemical agent while the part is under stress. This phenomenon is related to interaction between a chemical agent and polymer surface. Namely, it is affected by wetting property (contact angle θ) of a chemical agent. And also this interaction is related to mole volume of a chemical agent.

There is a liner relationship between "Critical Strain ε_c and $V^{1/3}/\cos\theta$ as shown below figure. Stress cracking is accelerated by higher mole volume of chemicals.

3. The Critical Strain Values for ABS resin

The critical strain values for ABS in various chemicals are shown as below table. This test method is also shown as below. This test method is sophisticated laboratory method which should give the plastics engineer a better opportunity to select the proper ABS resin for specific end user. In turn, this should allow for better prediction of performance based on high correlation between laboratory and actual field results.

Table-2 Chemical Resistibility of “TOYOLAC” GP Grade

Chemicals	Critical Strain
Distilled Water	○
10% Hydrochloric acid	○
10% Sulfuric acid	○
10% Acetic acid	○
90% Acetic acid	×
10% Sodium hydroxide	○
98% Methyl alcohol	×
98% Ethyl alcohol	×
98% Isopropyl alcohol	×
n-Hexane	○
Ethylene glycol	○
Machine oil	○
Silicon oil	○
Silicon grease	○
Gasoline	×
Diesel oil	*

○ : >1.0%
* : 0.5~1.0%
× : <0.5%

Test Method of ESC in Toray

(1) ESC evaluation method for volatilized chemical agent

A. A chemical agent which is easy to volatilize is charged into the bottom of desiccator, and UL test piece (127 × 12.7 × 1.5mmt) is set on the 1/4 ellipse-jig (refer to below Figure). This jig is kept for 1 week under 23^{o}C. After 1 week, measures the length of crack position(X) and calculate the critical-strain by using following formula.

B. Next step, dismantle the test piece from jig, bends this test piece along 30 ϕ pillar, and measures the length of crack position(X) and calculates the critical-strain same as above mention. (This testing is so called Pillar Bending Test). Then, bends this test piece forcibly, and observes on the surfaces of this test piece (This testing is so called Enforcement Bending Test).

$$\varepsilon = \frac{b.t}{2a^2} \left\{1 - \frac{X^2 (a^2-b^2)}{a^4}\right\}^{-3/2} \times 100\ (\%)$$

ε	: Critical strain (%)
a	: Major axis of jig (mm) [127mm]
b	: Minor axis of jig (mm) [38mm]
t	: Thickness of test piece (mm) [1.5mm]
X	: Length of crack position (mm)

(2) ESC evaluation method for non-volatilized chemical agent

A. A chemical agent which is not easy to volatilize is applied onto surface of test piece which is set on the 1/4 ellipse-jig. The other testing step is same as above method.

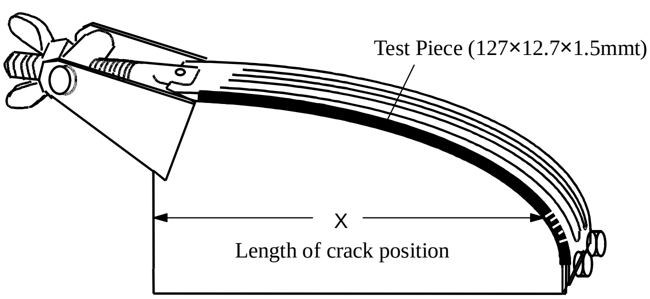


Figure of 1/4 Ellipse-Jig

(3) Test Condition

A. Treatment time : 1 week (basically)
B. Treatment temperature & humidity : 23 ^{o}C / 50%RH
C. Calculation formula of critical strain

Light Resistibility

1. Introduction[1)]

Polybutadiene based polyblends such as Acrylonitrile-Butadiene-Styrene (ABS) are known to be very sensitive to photo-degradation when exposed in conditions of natural weathering. The polybutadiene component has been shown to be the prime reason for the fast degradation of ABS. Photo-Oxidation of ABS has been suggested to lead to a crosslinking of rubber component and then in turn to destroy the elastomeric properties of the rubber phase. This crosslinking has been postulated to result from reactions of alkoxy radicals with polybutadiene units. More recently a mechanism accounting for the photo-oxidation of ABS has been discussed on the basis of experimental results obtained in conditions of short wavelength irradiation. And also, evolution of photo-chemical degradation of ABS has been studied in conditions of long wavelength irradiation.

2. Mechanism of degradation[1)2)3)]

(1) Polybutadiene

It is based on the oxidation of carbon atoms in α-position to the double bonds (Polybutadiene), which leads to the formation of primary hydroperoxides. By photochemical (or thermal) homolysis of hydroperoxides several oxidation photoproducts can be obtained (saturated ketones, carboxylic acid and ester). The photo-discoloration of ABS appears to be an important factor that may control the stoichimetories of the photo-oxidation of the polybutadiene nodules. The nature of the chromophores responsible for this discoloration, also important from a practical point view, as those products lead to yellowing of ABS irradiation, has been described in some scientific papers.

(2) Poly(styrene-co-acrylonitrile)

Irradiation of SAN at short or long wavelengths leads to the formation of a polystyryl radical. If this radical is formed in a succession of styrene units it follows the oxidation scheme unit liked to an acrylonitrile unit, one may envisage three ways of evolution of the macroalkoxy radical further by oxidation of polystyryl radical. Finally, the tertiary radical is oxidized following a classical oxidation mechanism and leads to hydroperoxides, alkoxy radicals, ketones and acids.

3. Antioxidation of ABS (light resistibility)

Hindered Amine Light Stabilizer (HALS) is one of a radical trapping agent, it is using as light stabilizer for ABS and PS. The stabilized mechanism of HALS is to prevent decomposition of hydroperoxides, and also nitroxy radical (>NO·) traps alkoxy radicals. Then nitroxy radical is effectively recycled in this stabilized cycle.

<Reference>

1. X. Jouan, J. L. Gardette, Polym. Deg. Stab., 36, 91(1992)
2. X. Jouan, J. L. Gardette, J. Polym. Sci., 29, 685(1991)
3. B. Maihot, J. L. Gardette, Polym. Deg. Stab., 44, 237(1994)

4. Light resistance performance of “TOYOLAC” ABS resin

The graphs below are plotted color difference (ΔE*) of "TOYOLAC" 700 & 100 against irradiation time of Xenon-weatherometer. The graphs show the almost linear increase in ΔE* against irradiation time. Light resistance grade is much better in light resistance ability than standard grade. Discoloration is depending on color shade and pigment content. Therefore, these data are typical value of our "TOYOLAC" (White & Gray colors), not guarantee that the same results, as those described will be obtained.

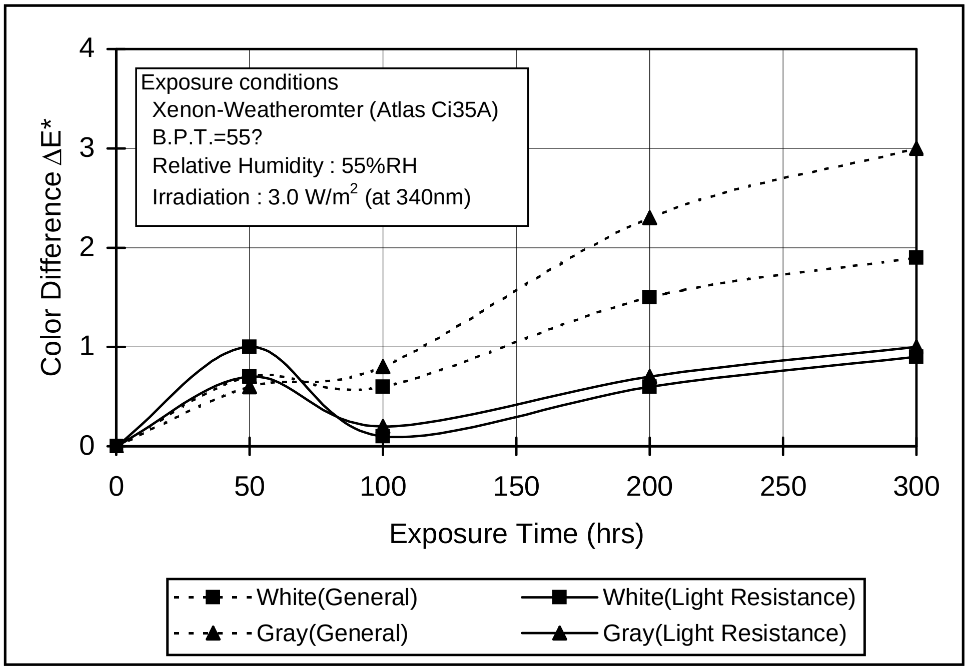


Fig 1-5 Light resistance performance of “TOYOLAC” 700 -314

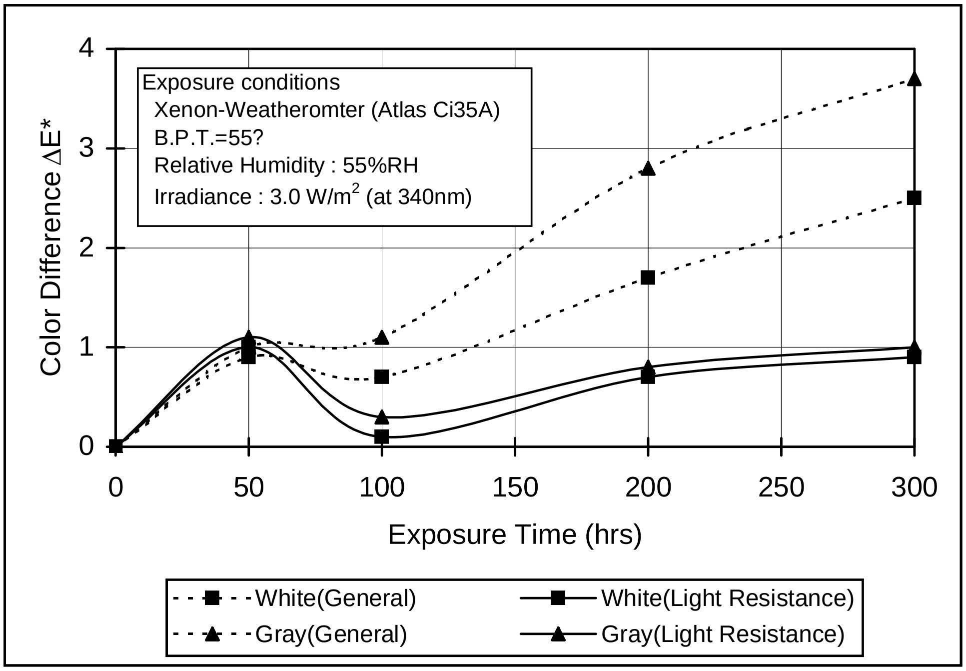


Fig 1-6 Light resistance performance of “TOYOLAC” 100 -322

5. Light resistance test in our laboratory

Many kinds of weathering machines are assorted in Japanese and our laboratories, Xenon and Sunshine-weatherometer, UV carbon arc fadeometer, and HPUV method. And those machines can be followed ASTM and JIS standards exactly. We can carry out several light resistance tests that are required by customers at any time. As above mentions, discoloration is depending on color shade and pigment content. Therefore, we suggest that the light resistance test is necessary to be carried out in advance. And also we can propose the light resistance grades that meet to the customers' requirements.

Recycle Property

Regrind material such as runners, sprues and short-shots of "TOYOLAC" ABS resin can be used for recycle materials. Recycle property of "TOYOLAC" 700 -314 is shown as below table 1-3. Those data show that there is no significant deterioration in mechanical properties of recycled materials. However, please refer to further information that is mentioned Regrind below.

Table 3 . Recycle properties of "TOYOLAC" 700 -314

	Units	"TOYOLAC" 700 -314				Test Method
Blend ratio of recycle material		**0%**	**10%**	**30%**	**50%**	
Tensile Strength at Yield	MPa Kg/cm^2	50 510	50 510	50 510	51 520	ASTM D 638
Tensile Elongation at Break	%	35	33	32	28	
Flexural Strength	MPa Kg/cm^2	76 770	76 770	76 770	77 780	ASTM D 790
Flexural Modulus	MPa Kg/cm^2	2,450 25,000	2,450 25,000	2,480 25,300	2,520 25,800	
Izod Impact Strength 12.7mmt, V-notched, 23^{o}C	J/m Kgcm/cm	186 19	186 19	186 19	176 18	ASTM D 256
3.2mmt, V-notched, 23^{o}C	J/m Kgcm/cm	196 20	196 20	196 20	186 19	
Distortion Temp. under Load 6.4mmt, 1.82MPa Loading	^{o}C	87	87	87	86	ASTM D 648
Melt Flow Rate 220^{o}C , 98N	g/10m.	23	23	24	24	ISO 1133
Specific Gravity	-	1.05	1.05	1.05	1.05	ASTM D 792

The values shown on the above table are typical values that has been obtained using test pieces molded from typical lots and not intended for specification purpose

2. Processing

Drying

Commonly, ABS resin is absorbent (hygroscopic) and absorbs moisture in proportion to environmental humidity. The absorbing process of moisture is reversible process. Therefore, wetted pellets can be removed moisture to environmental air with lower humidity. Dried pellets should absorb moisture until the amount touches equilibrium amount with the moisture in the air. The absorbing moisture content depends on the relative humidity in the air, how long the resin was exposed.

While "TOYOLAC" ABS resin is exposed to humidity, the moisture is absorbed onto surface and into inside of the pellets itself, recycled materials and molded parts. Typical equilibrium moisture of "TOYOLAC" general-purpose grade is around 0.2~0.3% at 23 ^{o}C , 50%RH, and 0.5~0.6% at 40 ^{o}C, 95%RH. The rate of absorbed moisture is depending on pellet size, shape and environmental temperature.

Non-dried ABS resin can cause silver streaking problem on molded parts. The recommendable moisture content for "TOYOLAC" general-purpose grades is less than 0.1%, more desirable is 0.05%. Generally, below drying conditions are recommended.

Drying Temperature	:	80 ~ 90 ^{o}C
Drying Time	:	3 ~ 5 hours

Typical drying variables by using oven with internal air circulation are shown Figure 2-1. It shows that higher moisture content in initial will be required longer drying time.

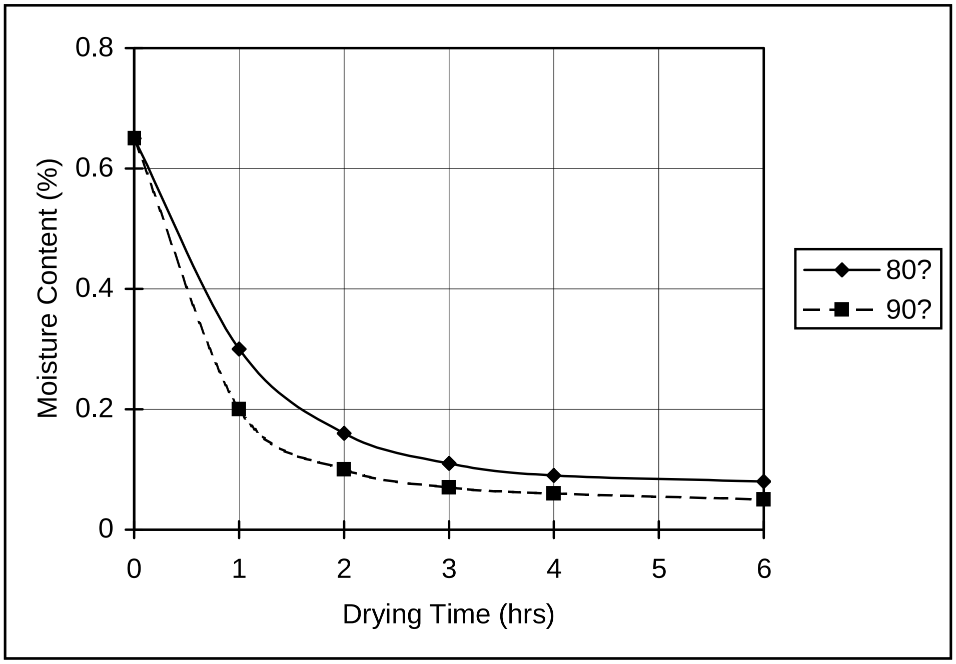


Fig 2-1 Drying Variables of "TOYOLAC" General Purpose Grade.

Mold Shrinkage

Generally, mold shrinkage is depending on actual molding conditions and dimension of molded parts. The mold shrinkage rate of “TOYOLAC” is shown as below table 1-4.

Table 1-4 Mold Shrinkage Rate of “TOYOLAC” GP Grades

Molding Temp.	Grades Measuring Point		“TOYOLAC”					
			250 -X10	500 -322	700 -314	700 -X01	100 -322	100 -X01
230°C	T.D.	A	0.44%	0.44%	0.46%	0.47%	0.47%	0.50%
		B	0.50%	0.49%	0.52%	0.53%	0.53%	0.53%
	M.D.	C	0.47%	0.47%	0.49%	0.50%	0.50%	0.54%
250 °C	T.D.	A	0.50%	0.47%	0.49%	0.51%	0.50%	0.54%
		B	0.54%	0.53%	0.55%	0.57%	0.57%	0.58%
	M.D.	C	0.50%	0.50%	0.52%	0.53%	0.54%	0.59%

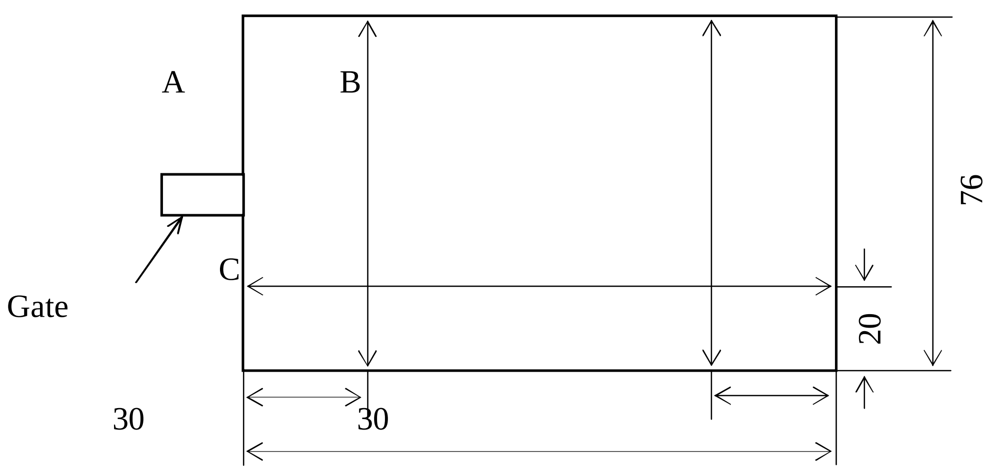
Those data are typical values that have been obtained using test pieces shown below figure. Therefore, it should be made own tests to determine the suitability of the mold shrinkage rate for the design.

<Molding Conditions>

Molding Machine : Toshiba Machinery, IS50A
Molding Temperature : 230, 250 °C
Mold Temperature : 60 °C
Injection Speed : Medium (FCV B-0 : fill-in time 2 sec.)
Injection Pressure : Min. injection pressure + 0.98MPa
Holding Time : 13 sec.
Cooling Time : 30 sec.
Mold Dimension : Refer to below figure

<Measurement method of test piece dimension>

Measure test piece dimension after 24 hours remaining under 23 °C , 50%RH



Thickness : 3.0mm

Spiral Flow Length

"TOYOLAC" ABS resin has excellent flow ability. The flow ability of "TOYOLAC" general purpose grades that are evaluated as the Spiral Flow Length, is shown as below figure for a function of the injection temperature with injection pressure as parameter. It is useful for comparing the flow ability of products under the same conditions even if this test has not been standardized.

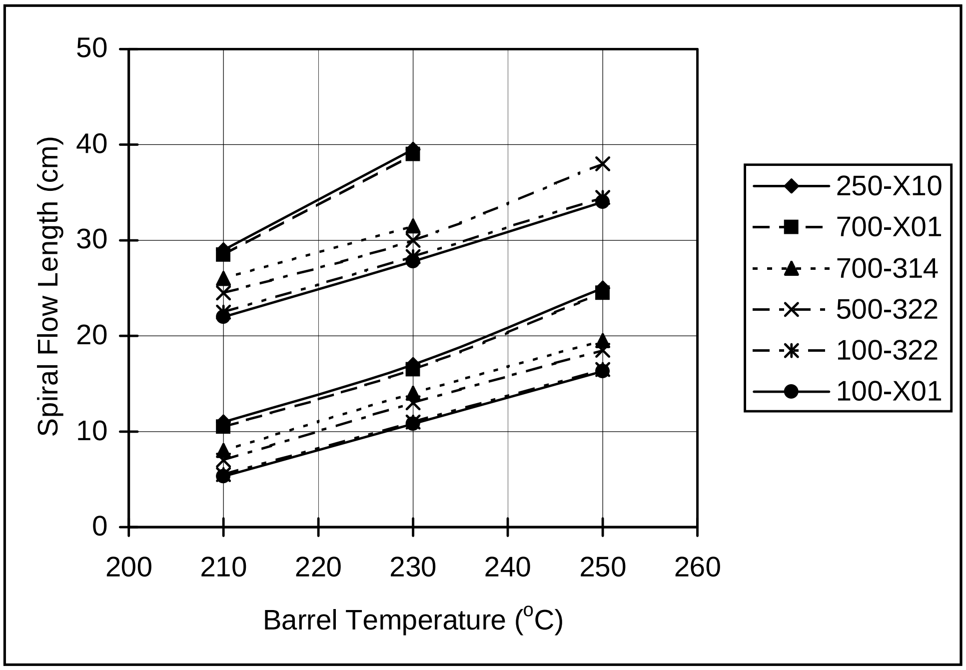


Fig 8. Spiral Flow Length of "TOYOLAC" GP Grades.

<Molding Conditions>

Molding Machine	:	Toshiba Machinery, IS50A
Molding Temperature	:	210, 230, 250°C
Mold Temperature	:	60 °C
Injection Speed	:	Medium (FCV B-0 : fill-in time 2 sec.)
Holding Time	:	13 sec.
Cooling Time	:	20 sec.
Mold Dimension	:	10W × 2mmt (Spiral Flow)

3. Molding (Injection)

Injection Temperature

Generally, the barrel temperature of injection molding machine should increase from the hopper to the nozzle gradually. “TOYOLAC” General Purpose Grades start softening around 90 ~ 110°C although it is depending on grades. Typical barrel setting temperature is shown as below.

Table 3-1 Typical Barrel Setting Temp. of “TOYOLAC” General Purpose Grades, and Flame Retardant Toyolac 844V-X05, 824V-X01, 834V-X01, NH82

Nozzle	Zone-4	Zone-3	Zone-2	Zone-1	Hopper
230 ~240 °C	230 ~240 °C	230 ~240 °C	220 ~230 °C	220 ~230 °C	210 ~220 °C

Table 3-2 Typical Barrel Setting Temp. of “TOYOLAC” Flame Retardant Toyolac 884-X01, 828-X01

Nozzle	Zone-4	Zone-3	Zone-2	Zone-1	Hopper
200 ~210 °C	200 ~210 °C	200 ~210 °C	190 ~200 °C	190 ~200 °C	180 ~190 °C

Table 3-3 Typical Barrel Setting Temp. of “TOYOLAC” High Heat Grades

Nozzle	Zone-4	Zone-3	Zone-2	Zone-1	Hopper
250 ~260 °C	250 ~260 °C	250 ~260 °C	240 ~250 °C	240 ~250 °C	240 ~250 °C

Table 3-4 Typical Barrel Setting Temp. of “TOYOLAC” Glass Fibre Grades

Nozzle	Zone-4	Zone-3	Zone-2	Zone-1	Hopper
240 ~250 °C	240 ~250 °C	240 ~250 °C	240 ~250 °C	230 ~240 °C	230 ~240 °C

It should be properly controlled according to the injection molding machines, the shapes and size of the products, and the mold structure. Temperature in excess of above recommended could result of discoloration or burn marks troubles. Those troubles are a sign of damage to the material. Melt temperature of resin should be between 230°C and 250°C. It should be checked frequently and maintained within above recommended range to prevent defect of appearance and mechanical properties.

If shutdown is required, remove the material from the machine and purge out completely to avoid burning trouble.

Injection Speed & Pressure

Injection speeds will be depending on products shape, gate structure and runner dimensions. Basically moderate injection speed is preferable in order to prevent orientation of rubber particles due to excessive sheer.

Injection pressure should be controlled to mold full parts consistently with acceptable appearance. Many parameters affects injection pressure, such as injection temperature, products shape, nozzle and gate size, runner dimensions and mold temperature. Typical injection pressure range is 70~140MPa for “TOYOLAC” General Purpose Grades. It is important that injection pressure should drop off to holding pressure after fill-up immediately.

Mold Temperature

The mold temperature affects the surface quality and the level of residual stress in the molded products. To provide a molded product having excellent surface finish and less residual stress, the mold temperature should be controlled as high as possible, ranging between 40^{o}C ~ 80^{o}C. However, higher mold temperature may cause longer cycle time and warpage problem. It should be taken attention excessive mold temperature.

Purging

General maintenance and equipment cleaning should include frequent purging with natural color ABS resin or AS resin. If prolonged shut-down is required, reduce barrel temperature less than 150^{o}C, remove the material from the injection machine and purge with natural ABS resin or AS resin. Continue this operation until hopper is empty throughout and confirm barrel temperature has been dropped less than 150^{o}C.

Regrind

Runners, sprues and shot-shots of “TOYOLAC” ABS resin molded under proper molding conditions can be used for recycle materials. Those non-degraded regrind up to a 20% can be reprocessed with fresh pellets of the same grade. Please do not mix it up with other grades of “TOYOLAC” ABS resin or other plastics. And dry it up before reprocessing.

4. Troubleshooting

Typical molding problems and problem solutions are shown as following table. Most cause of molding troubles is the tangle of any kind of factors such as improper molding conditions, imperfect design of mold and moldings. Any one of the suggested remedies may solve a particular problem. However some problems may require a combination of suggested remedies.

Table Of Checklist of Troubleshooting of "TOYOLAC" GP Grades

Problems / Problem Solution Checklist	Short Shots	Flash	Sink Marks	Burn Marks	Poor Weld Line	Low Gloss	Jetting	Excessive Warpage	Scratches	Air Marks	Silver Streaking	Crack, Whitening
Increase Injection Speed	●		●		●	●		●				●
Decrease Injection Speed				●			●			●	●	
Increase Injection Pressure	●		●		●				●			
Decrease Injection Pressure		●		●				●			●	●
Increase Mold Temperature	●				●	●	●				●	●
Decrease Mold Temperature			●					●	●			
Increase Barrel Temperature	●				●	●	●	●				●
Decrease Barrel Temperature		●	●	●					●		●	
Decrease Nozzle Temperature				●								
Increase Nozzle Temperature					●	●						
Check Nozzle, Sprue, Runner & Gate size	●		●	●			●		●		●	●
Check Gate Position & Number	●				●		●		●		●	
Improve Venting	●			●	●	●				●	●	
Increase Filling Qty	●		●						●			
Decrease Filling Qty		●										
Check Clamping Force		●										
Increase Holding Pressure						●						
Decrease Holding Pressure		●						●				●
Increase Holding Pressure Time			●			●						
Decrease Holding Pressure Time		●						●				●
Increase Cooling Time			●						●			
Decrease Screw r.p.m.											●	
Check Pellet Drying											●	