ABS Resin Additive for the Improvement of its Chemical Resistance

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Reduction of greenhouse gas emissions is now an urgent issue. For automobiles that have high emissions, measures are being taken to replace metallic components with plastic alternatives for the purpose of reducing CO_2 emissions through a reduction in weight and fuel consumption. ABS resin in particular is popular for interior and exterior components of automobiles because of its optimal balance of mechanical strength and low weight. However, ABS resin has a disadvantage of having a low chemical resistance, and its improvement in this aspect is therefore required. This article introduces 'FUNCTIVE,' a resin additive that Sanyo Chemical has developed to improve the chemical resistance of ABS resins.

ABS resins

An ABS resin is a thermoplastic resin consisting of three components: acrylonitrile, butadiene, and styrene. More specifically, ABS resin is a mixture of acrylonitrile/styrene copolymer (AS resin) and polybutadiene (polymer alloy). Since ABS resins have all the features that are derived from its components, namely heat resistance and mechanical strength of acrylonitrile; impact resistance of butadiene; and glossiness, machinability, and stability of styrene, it also offers an excellent balance between stiffness (rigidity) and impact resistance, which are generally said to be in a trade-off relationship.

Furthermore, it is easy to conduct post-processing such as printing, coating, and adhesion, as well as high-function developments including flame retardancy addition, fiber reinforcement, and alloy development with other resins[1]. It is also widely distributed[3] owing to its relatively low costs[2]. Because of these features, it is used in a wide range of applications, including household appliances, automotive components, housing equipment materials, and OA products[1].

However, ABS resin is an amorphous resin, which is the root cause of its relatively low chemical resistance compared to crystalline resins such as polyolefin. In particular, contact with chemicals such as organic solvents in paints and adhesives; edible oils; clothing detergents; sunscreens; and cosmetics, can cause issues such as [1] softening, embrittlement, dissolution, and the associated appearance defects; and [2] generation of microcracks and visible cracks[1]. In particular, [2] is also called solvent crack, chemical crack, stress crack, environmental stress crack, etc., and is the most typical cause of defect occurrence in ABS resins. Conventional measures aimed at resolving these issues included secondary processing such as surface treatment and replacement with other resins that were higher in chemical resistance, which resulted in restrictions in product designs such as increased costs. Therefore, there were strong demands for the improvement of chemical resistance in ABS resins.

'FUNCTIVE': An ABS resin additive for the improvement of the resin's chemical resistance

Using our interface control and polymer design technologies, Sanyo Chemical has developed, manufactured, and marketed a wide variety of resin excipients. We developed 'FUNCTIVE,' a resin additive to improve the chemical resistance of ABS resins through the utilization of knowledge that we accumulated over many years of work on similar products **(Table 1)**.

FUNCTIVE's mechanism of action

ABS resin is composed of polybutadiene dispersed inside the AS resin. This is shown in the electron microscopy image in **Fig. 1**, where the white parts correspond to the AS resin, and the black parts to polybutadiene. It is assumed that [1] the damaging chemical permeates into the AS resin and makes the resin swell; [2] it then reaches the AS resin/polybutadiene

Table 1 Lineup of 'FUNCTIVE' products

	FUNCTIVE Y-200	FUNCTIVE P-600
Appearance	Yellow granule	Yellow
Melting point (°C)	135	203
Molecular weight (Mw)	Approx. 30,000	Approx. 30,000

<Test conditions> Melting point: DSC method, molecular weight: High temperature GPC method

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interface; and [3] it reduces the adhesion force at the AS resin/polybutadiene interface and forms the starting points for the subsequent cracks[4] when a chemical comes in contact with a molded product (**Fig. 2**). For injection molded products in particular, the molding stress (residual stress) remains in the molded product, and the microcracks described above may grow into cracks of visible sizes, which can ultimately cause the molded products to break.
'FUNCTIVE' by Sanyo Chemical was developed to efficiently inhibit the permeation of chemicals with a small addition in order to improve the chemical resistance of ABS resins. We achieved this by designing the molecular structure so that 'FUNCTIVE' itself features a high chemical resistance, and that it disperses through the ABS resin in striation by controlling its own compatibility with the ABS resins. When 'FUNCTIVE' is added, it is dispersed in striation within the AS resin and partially covers polybutadiene, as shown in **Fig. 3**. Based on this, it can be deduced that 'FUNCTIVE' inhibits the spread of chemical permeation into the AS resin and prevents the chemicals from reaching the AS resin/polybutadiene interface, thereby preventing the formation of cracks (**Fig. 4**).

Effectiveness of 'FUNCTIVE' and examples of application

[Effectiveness of 'FUNCTIVE']
(1) Test piece preparation method
Test pieces for evaluation were prepared in accordance with the following procedure. An ABS resin and 'FUNCTIVE' were dry blended and then melted and kneaded using a twin screw extruder (KZW15TW-45MG manufactured by TECHNOVEL CORPORATION) (barrel temperature: 250°C), which was followed by injection molding (with FNX80III manufactured by NISSEI PLASTIC INDUSTRIAL CO., LTD.) (nozzle temperature: 250°C, die temperature: 50°C). ABS resin and 'FUNCTIVE' were then preliminarily dried with a hot air dryer before use (80°C, 3h).
(2) Chemical resistance test
Chemical resistance was evaluated by the Bergen quarter-elliptical test method[5] (**Table 2**). In this test, a higher critical strain value indicates a greater chemical resistance, and while the actual strain value depends on the intended application and requirements, a material is generally considered as chemically resistant when its critical strain value is 0.7 or higher[6].
Table 2 shows the results of chemical resistance tests (critical strain values) against various chemicals. Clearly, the addition of 'FUNCTIVE' improves the critical strain value and achieves the necessary chemical resistance level (i.e., critical strain values of $\varepsilon \geq 0.7$). Similar results were obtained with polycarbonate/ABS alloy (PC/ABS), although the description is omitted in this article. The appropriate 'FUNCTIVE' grade differs depending on the type of chemical, and 'FUNCTIVE Y-200' for the hydrophobic chemicals (gasoline, hydrocarbons, etc.), and 'FUNCTIVE P-600' for hydrophilic chemicals (ethanol, detergents),

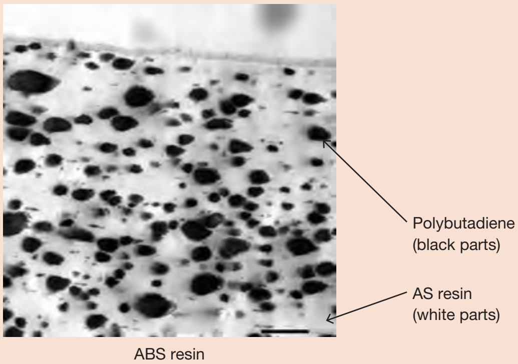
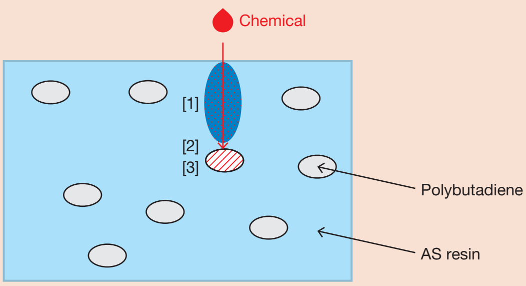
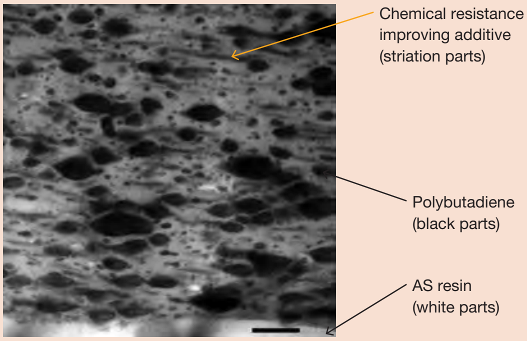


Fig. 1 Electron microscope image
(stained with ruthenium tetroxide and osmium tetroxide)



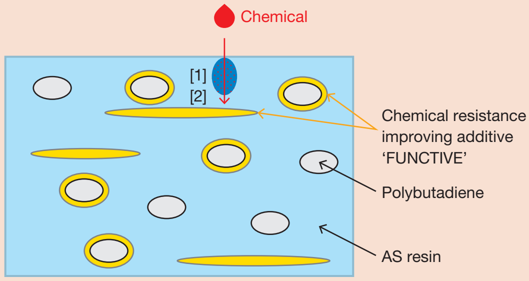
[1] Chemical permeates into AS resin and makes it swell
[2] Chemical reaches polybutadiene
[3] AS resin/polybutadiene adhesion force decreases and becomes the starting point of a crack

Fig. 2 Conceptual drawing of chemical degradation of ABS resin



ABS resin/‘FUNCTIVE’ (5 wt%)

Fig. 3 Electron microscope image
(stained with ruthenium tetroxide and osmium tetroxide)



[1] Chemical permeates into AS resin
[2] It is blocked by the chemical resistance improving additive and prevented from further permeating into AS resin and reaching the AS resin/polybutadiene interface.

ABS resin/‘FUNCTIVE’

Fig. 4 Conceptual drawing of the action by the chemical resistance improving additive

drug products (sunscreen), etc.

(3) Mechanical properties

The mechanical properties of ABS resin after the addition of ‘FUNCTIVE’ are presented in **Table 3**. Evidently, ‘FUNCTIVE’ did not alter the mechanical properties of the resin by much. The amount of change in MFR is small, and the impact on formability is also small.

Although ABS resins are generally opaque, there are also transparent grades (transparent grade ABS resins). In the past, the transparency could be compromised if one tried to add chemical resistance to the transparent grade ABS resins. ‘FUNCTIVE P-600’ was designed to improve the chemical resistance while maintaining the transparency of the transparent grade ABS resins. **Fig. 5** shows the appearance of the molded products before and after the chemical resistance test. Notably, the appearance of the molded transparent grade ABS resins containing ‘FUNCTIVE P-600’ does not deteriorate after the test, while the appearance does deteriorate in the resin without ‘FUNCTIVE’. **Table 4** shows the results of the chemical resistance evaluation, which

Table 2 Evaluation results

Test chemical	Critical strain value (ε)*1				
	ABS only	ABS/FUNCTIVE Y-200 (5%)	ABS/FUNCTIVE P-600 (5%)	ABS/FUNCTIVE Y-200 (2.5%) P-600 (2.5%)	ABS/FUNCTIVE Y-200 (5%) P-600 (5%)
Gasoline	0.6	>1.0	0.7	0.8	>1.0
Ethanol for disinfection*2	0.8	0.8	>1.0	0.9	>1.0
Clothing detergent (weakly acidic)*3	0.5	0.8	>1.0	>1.0	>1.0
Bathroom detergent (neutral)*4	0.6	0.8	>1.0	>1.0	>1.0
Sunscreen*5	0.9	0.9	>1.0	>1.0	>1.0

*1: The test piece of size 126 mm × 12 mm × 3 mm was fixed on the test tool for Bergen quarter-elliptical test method, the test chemical was applied, and it was allowed to stand at 23°C and 50 RH% for 20 h to calculate the critical strain value ε based on the crack occurrence position.
*2: 70% aqueous solution, *3: “Attack NEO Antibacterial EX W-Power” manufactured by Kao Corporation,*4: “Bath Magiclean” manufactured by Kao Corporation
*5: “Neutrogena Ultra Sheer Dry-Touch Sunscreen (SPF55)” manufactured by Johnson & Johnson K.K.

Table 3 Mechanical properties

Test item	ABS only	ABS/FUNCTIVE Y-200 (5%)	ABS/FUNCTIVE P-600 (5%)	ABS/FUNCTIVE Y-200 (2.5%) P-600 (2.5%)	ABS/FUNCTIVE Y-200 (5%) P-600 (5%)
Bending strength*1 (MPa)	76	72	73	74	68
Bending modulus*1 (GPa)	2.4	2.4	2.4	2.3	2.2
Tensile strength*2 (MPa)	51	44	49	48	45
Izod impact strength*3 (kJ/m^2)	28	9	17	9	8
MFR*4 (g/10 min)	20	20	33	22	27

*1: JIS K7171, test speed 10 mm/min, *2: JIS K7161, test speed 50 mm/min, *3: JIS K7110, notched, *4: JIS K7210, measurement temperature 220°C, load 10 kgf

Before chemical resistance test		After chemical resistance test[*1]	
Transparent ABS only	Transparent ABS/FUNCTIVE P-600 (5%)	Transparent ABS only	Transparent ABS/FUNCTIVE P-600 (5%)

*1: Test chemical: "Attack NEO Antibacterial EX W-Power" manufactured by Kao Corporation

Fig. 5 Appearance of molded products (transparent grade ABS resin)

Table 4 Evaluation results (transparent grade ABS resin)

Test chemical	Critical strain value	
	Transparent ABS only	Transparent ABS/FUNCTIVE P-600 (5%)
Ethanol for disinfection[*1]	0.3	>1.0
Clothing detergent (weakly acidic)[*2]	0.4	0.7
Bathroom detergent (neutral)[*3]	0.4	>1.0
Sunscreen[*4]	0.4	0.6

*1 70% aqueous solution
*2 "Attack NEO Antibacterial EX W-Power" manufactured by Kao Corporation
*3 "Bath Magiclean" manufactured by Kao Corporation
*4 "Neutrogena Ultra Sheer Dry-Touch Sunscreen (SPF55)" manufactured by Johnson & Johnson K.K.

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indicate that the protective effect is particularly high against ethanol for disinfection.

[Examples of application]

It is assumed that application in the following purposes will be possible by improving the chemical resistance of ABS resins:

[1] Automobile exterior components

Door handles, side mirror housing, spoilers, radiator grills, etc. By preventing cracks caused by solvents in paints, 'FUNCTIVE' will lead to improved selection freedom for paints and productivity.

[2] Automotive interior components

Console box, door trim, instrument panel, etc. 'FUNCTIVE' can prevent cracks in ABS resins and surface deterioration that can be caused by contact with chemicals such as sunscreen or alcohol.

[3] Household appliances

Display frames of washing machines, refrigerators, TVs, PCs, gaming consoles, etc. 'FUNCTIVE' can prevent cracks caused by contact with chemicals such as detergents or alcohols.

[4] Housing equipment

Bathroom, washstand, and kitchen, etc. 'FUNCTIVE' can prevent cracks caused by contact with detergents, etc.

Future developments

With the spread of the novel coronavirus disease (COVID-19), disinfection with alcohol has become a routine measure to prevent the spread of infection, which has led to the exposure of many other plastic products to alcohol. Therefore, it will be necessary to further improve the alcohol resistance of ABS resins in the near future. We showed that 'FUNCTIVE' can significantly improve the chemical resistance of ABS resins and ABS-based polymer alloys, and therefore contribute to the expansion of applied components and applications. In the future, we plan to respond to the diversifying needs of resin quality improvement and will develop new grades of additives with even greater chemical resistance improvements and even lower additive concentration requirements.

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