

# ● Plastic Additive ARUFON

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We tried applying the liquid low molecular weight acrylate polymer ARUFON “UP Series,” which is produced by the Uniform Functional Oligomer (UFO) process, to the field of plastic additives (plasticizer, processing aid, and dispersant for inorganic fillers). ARUFON was compatible with various thermoplastic resins and exhibited a plasticizing effect. In particular, it excels in plasticizing PVC, ABS, PMMA resins, etc. It can also be used as a processing aid for transparent polystyrene-based resins (transparent ABS, transparent HIPS) and resin for PMMA to improve moldability without loss of transparency. Furthermore, it became clear that ARUFON could improve the dispersion of inorganic fillers in polyolefin-based resins and impart specific characteristics.

## 1. Introduction

Plastic materials are widely used in familiar fields such as automobiles, construction materials, home appliances, and packaging. As is well known, demands for consideration of the environmental impact have grown stronger even for plastic materials and auxiliary materials, and new plastic materials and plastic compounds are being designed with halogen-free and endocrine-disruptor-free properties. For example, there have been developments of halogen-free (eco-friendly) materials as substitutes for PVC, and endocrine-disruptor-free materials as substitutes for DOP. What has proven to be difficult among these issues is the development of soft PVC substitute materials, and many researchers are examining soft materials using polyolefin resins<sup>1,2)</sup>, PET resins, ABS resins, and PMMA resins. Although flexible materials can be designed by adding rubber or elastomer components, the fields of use are limited due to the cost and moldability. In addition, plasticizers are required to control moldability or flexibility, but conventional plasticizers have insufficient compatibility.

Our ARUFON is an acrylic polymer obtained by the Uniform Functional Oligomer (UFO) technology<sup>3)</sup>. The acrylic polymers obtained by the UFO process, which are characterized by bulk, continuous, thermally initiated polymerization, have low molecular weights. Since a wide range of polar polymers can be obtained by selecting monomers, ARUFON is expected to be compatible with a variety of resins. We therefore tried applying it as a plastic additive. In this article, we will show the excellent compatibility of ARUFON and its plastic modification effects as a plasticizer, processing aid, and dispersing agent for inorganic materials (fillers).

## 2. Compatibility of ARUFON with thermoplastic resins

### 2.1 ARUFON grades

ARUFON is available in three main grades. The grades include the non-functionalized “UP Series,” the hydroxyl group-containing “UH Series,” and the carboxylic acid-containing “UC Series,” and they are used as plastic additives, paints for plastics, paints for building materials, sealants, etc. Among these, the “UP Series” shown in **Table 1** is a liquid acrylic polymer that has been developed for application as a plasticizer.

**Table 1: General physical properties of ARUFON “UP Series”**

Grade name	Molecular weight <sup>1)</sup> (Mw)	Nonvolatile content <sup>2)</sup> (%)	Viscosity <sup>3)</sup> (mPa·s)	SP value <sup>4)</sup>
UP-1000	3,000	≥98	1,000	11.7
UP-1010	1,700	≥98	4,500	15.1
UP-1020	2,000	≥98	500	12.7
UP-1021	1,500	≥98	400	13.6
UP-1060	2,200	≥98	900	14.0
UP-1061	1,500	≥98	600	14.3
UP-1070	2,000	≥98	3,800	14.1
UP-1080	6,000	≥98	5,000	11.3

1) GPC, PSt conversion.

2) Value obtained by quantifying and subtracting the low boiling point content by GC

3) Measured at 25°C, Type E, 4) In-house evaluation results. (Reference value DOP 13.8)

The values are measured values, not standard values.

### 2.2 Compatibility of ARUFON “UP Series”

The prerequisite for functioning as a plasticizer is good compatibility with the target resin. We tested the compatibility of ARUFON “UP Series” with typical thermoplastic resins such as PVC, PMMA, and ABS. As shown in **Table 2**, “UP Series” exhibited favorable compatibility with a wide variety of thermoplastic resins. In addition, we found that there were more types of compatible resins for UP-1020, which has a lower molecular weight, even though UP-1000 and UP-1020 have the same monomer composition. Another finding is that UP-1010 is more compatible with various resins due to its high polarity and low molecular weight.

**Table 2: Compatibility with various thermoplastic resins**

Thermoplastic resin	Content	ARUFON		
		UP-1000	UP-1020 UP-1021	UP-1010
PVC	10%	○	○	○
	25%	○	○	○
PMMA	5%	○	○	○
	10%	○	○	○
ABS	5%	×	○	○
	10%	×	○	○
PS	5%	○	○	○
	10%	×	○	○
PC	5%	○	○	○
	10%	○	○	○
PET	5%	○	○	○
	10%	○	○	○
EVA	5%	○	○	○
	10%	×	×	×
Acrylic sol PMMA	50%	×	—	○

### 3. Plasticizer

#### 3.1 Application to PVC

As a result of evaluating the plasticization performance of ARUFON “UP Series” with PVC, the resin that uses the most plasticizer, we found that UP-1021 had the best plasticization efficiency among ARUFON grades, as shown in Fig. 1. Compared to DOP, a common plasticizer, the plasticization efficiency had a high value of 1.1 to 1.2. Comparing among members of “UP Series,” the plasticization efficiency depended on the viscosity of the plasticizer, and the resulting PVC was softer in the order of UP-1021, UP-1000, and UP-1010.

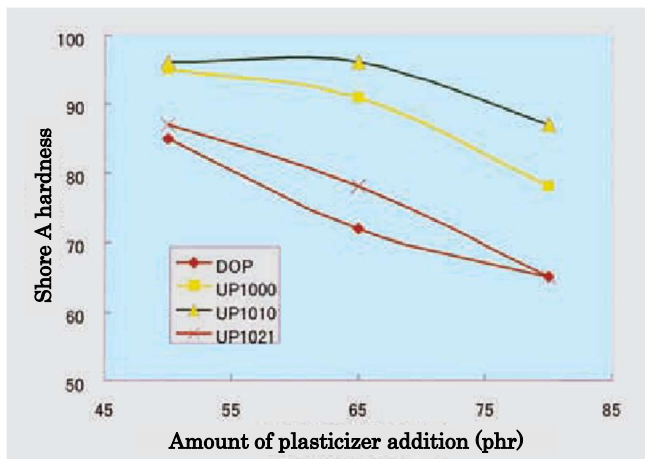


Figure 1: PVC plasticization test results

Other physical properties of ARUFON include excellent resistance to bleeding, heat-induced weight loss, weathering, and migration. Overall, ARUFON has a balance of physical properties comparable to polyester-based plasticizers, but its most distinctive feature is its volume resistivity, which is one order of magnitude higher (Fig. 2). Although the mechanism of this phenomenon is unknown, if the electrical insulation of PVC sheets depends on the migration of chloride ions derived from PVC, then the ARUFON “UP Series” (such as UP-1010) is presumed to have a function of trapping chloride ions. Because of this high volume resistivity, we expect that it can be applied to wires and insulating materials as the scope of application in the PVC field.

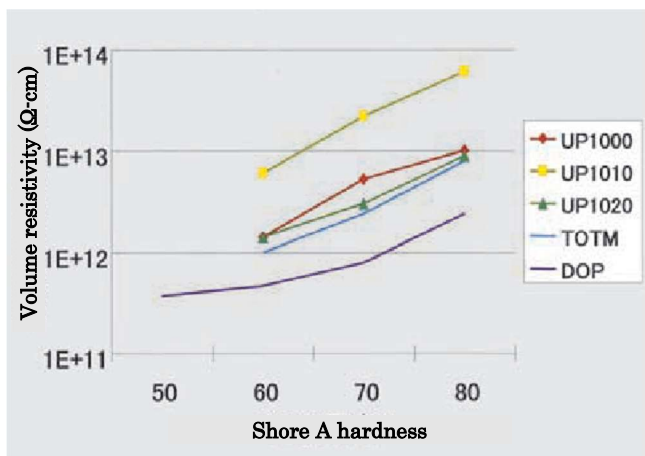


Figure 2: Volume resistivity of plasticized PVC sheets

#### 3.2 Application to ABS

The grades that exhibited compatibility and plasticization performance with ABS at large amounts of addition were UP-1010, UP-1061, and UP-1070. Fig. 3 shows a comparison of these plasticizing effects, with UP-1061 being the best. In a similar fashion to PVC, plasticizers with lower viscosity showed higher plasticization efficiency in ABS. While an example using DOP, a typical plasticizer, is also shown, the compatibility is insufficient and plasticization was not achieved. More interestingly, we found that the transparency of ABS improved as more “UP Series” was added to ABS. ABS has a sea-island structure of AS resin and butadiene rubber.

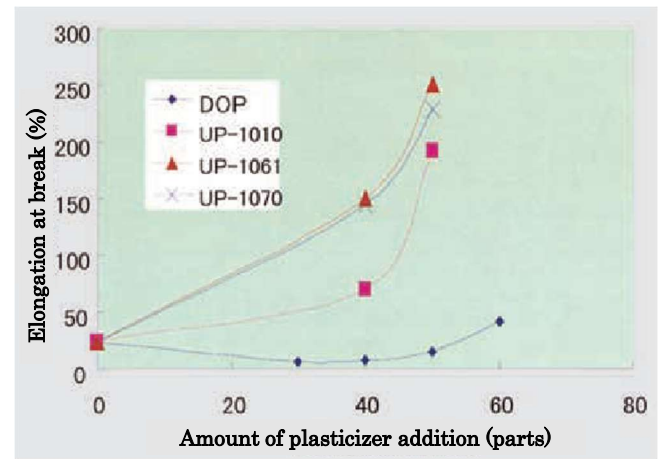


Figure 3: ABS plasticization test results

The refractive indices<sup>5)</sup> of AS resin and butadiene rubber are 1.57 and 1.52, respectively, and general ABS resins are opaque due to these differences in refractive index. However, when “UP Series” (refractive index = 1.45 to 1.47) becomes compatible with the AS resin, the refractive index of the AS resin matrix (the sea phase) decreases, which is presumed to improve transparency. The DMS results also show that comparing the Tg changes of butadiene rubber and AS resin in plasticized ABS, the Tg of AS resin clearly decreased (Table 3). Thus, ARUFON “UP Series” exhibited good compatibility with the AS resin phase of ABS, achieving the plasticization of ABS that had been impossible with conventional plasticizers.

Table 3: DMS measurement results of plasticized ABS

Sample name	Tg of AS phase	Tg of BR phase
ABS	116°C	-76°C
ABS/UP-1010=100/50	56°C	-71°C

We were able to confirm that blending UP-1021 with UP-1061, which had the best plasticizing effect on ABS, further improved the plasticization performance (Fig. 4). While the Shore A hardness was 90 or more when 50 parts of UP-1061 was added to ABS resin, blending with UP-1021 (blending ratio UP-1061/UP-1021 = 70/30) at the same 50-parts addition reduced the Shore A hardness to approximately 80, an improvement in flexibility of more than 10 points.

## 4. Processing aid

As mentioned earlier, ARUFON has favorable compatibility with many thermoplastic resins. Since it is a low molecular weight polymer, we expected that the addition of a small amount would be effective in reducing the melt viscosity of each resin. The results are presented below.

### 4.1 Application to transparent polystyrene-based resins

Transparent polystyrene-based resins include transparent high-impact polystyrene resin and transparent ABS resin, which have become widely used in consumer products such as home appliances during the recent trend toward transparent designs. These transparent polystyrene-based resins have the disadvantage of being prone to discoloration during injection molding, which compromises the appearance of the molded product. In the past, process oils and similar materials were used as processing aids to reduce melt viscosity during injection molding, allowing molding at lower temperatures. However, due to insufficient compatibility with the resin, problems such as deteriorated transparency and bleeding occurred.

We evaluated the performance after adding ARUFON to transparent polystyrene-based resins in small amounts. **Table 5** shows the results. UP-1021, which was also introduced for plasticizer applications, is liquid and has low viscosity, and it was most effective in reducing melt viscosity. It also did not compromise the transparency. However, the thermal deformation temperature tended to decrease due to the low T<sub>g</sub>. On the other hand, UH-2160 also suppressed the decrease in thermal deformation temperature of the compound, as it has a T<sub>g</sub> of 75°C or higher. In addition, these ARUFON polymers did not reduce impact resistance.

**Table 5: Processability improvement effect on transparent PS resins**

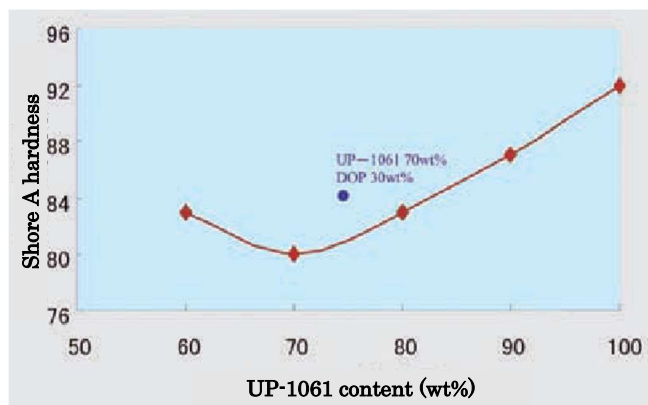
Physical properties of transparent ABS/ARUFON compound					
Resin/plasticizer	Plasticizer added (parts)	Izod impact strength (kgf/cm)	MFR (g/10min)	Vicat softening point (°C)	Transparency
JSR55/	0	25	10	101	Favorable
JSR55/UP-1201	3	25	15	95	Favorable
TOYOLAC 900/	0	24	5	95	Favorable
TOYOLAC 900/UP-1021	3	24	8	90	Favorable
TOYOLAC 900/UH-2160	3	26	7	95	Favorable

Physical properties of transparent HIPS/ARUFON compound					
Resin/plasticizer	Plasticizer added (parts)	Izod impact strength (kgf/cm)	MFR (g/10min)	Vicat softening point (°C)	Transparency
SX100/	0	18	8	91	Favorable
SX100/UP-1021	3	18	13	86	Favorable
SX100/UH-2160	3	18	10	91	Favorable

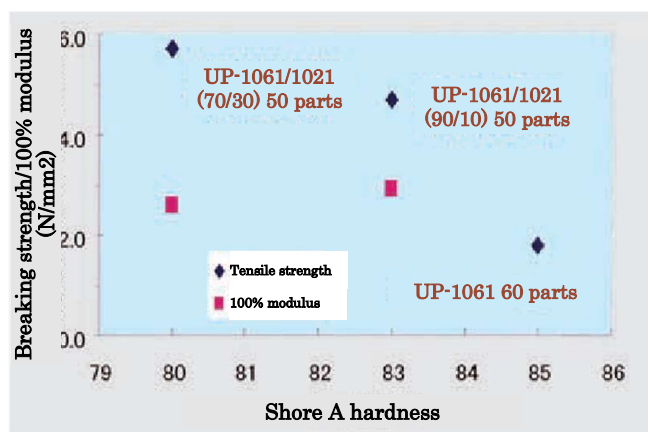
### 4.2 Application to PMMA

PMMA resins containing rubber components are used in sheet and film applications because they have higher toughness than ordinary PMMA resins<sup>7)</sup>. However, the rubber component also increases melt viscosity, making it difficult to produce ultra-thin films by extrusion molding. When we evaluated the fluidity in the melted state by adding UP-1021 to rubber-containing PMMA resin, we found that the melt viscosity could be improved dramatically while maintaining transparency (**Table 6**).



**Figure 4: Plasticizing effect of UP-1061/UP-1021 blended plasticizer**

The advantage of plasticizer blends is that the desired flexibility can be obtained with less amount of addition thanks to the plasticization efficiency improvement effect, and the strength of the plasticized ABS compound can be increased (**Fig. 5**).



**Figure 5: Plasticizing effect of blended plasticizer and mechanical strength**

We propose the following plasticization mechanism for the blended plasticizer. Because of the low polarity of UP-1021, its compatibility limit with ABS is about 30 parts by itself, and its compatibility is basically poor. However, when a small amount is added, it is dispersed in ABS resin at the micro level or smaller. This dispersed state consequently reduces the cohesive force of the AS polymer chains in the ABS resin, which aids plasticization.<sup>5)</sup>

### 3.3 Application to PMMA

When 80 parts of ARUFON UP-1010 were added to PMMA resin, a soft PMMA compound was obtained. It did not compromise the transparency characteristic of PMMA resin (**Table 4**).

**Table 4: Results of PMMA resin plasticization**

Sample name	Tensile strength (N/mm <sup>2</sup> )	Elongation (%)	100% modulus (N/mm <sup>2</sup> )
PMMA	18.8	23	-
UP-1010 80 parts	4.6	236	2.3
Research prototype 80 parts	7.2	236	3.8

PMMA: ACRYPET IR H70

**Table 6: Melt viscosity modification of PMMA resins by the UP Series**

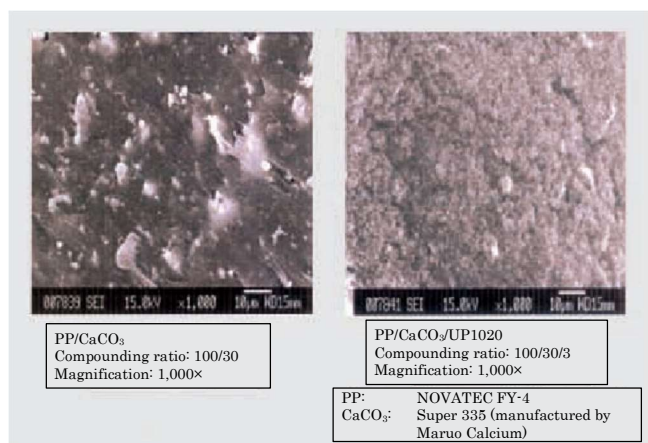
Sample name	Shore D hardness	MFR (g/10min)	HAZE		
			H	T	D
PMMA	86	0.56	4	91	4
PMMA + UP-1020 20 parts	79	0.97	15	86	13
PMMA + UP-1021 20 parts	76	2.88	5	89	4

**5. Dispersion of inorganic materials (fillers)**

Finally, we will describe the dispersion effect of inorganic fillers in olefin-based resins. In general, acrylic polymers have few applications as resin modifiers because of their poor compatibility with olefin-based resins. However, we found that adding the “Up Series” to olefin resin/filler systems not only improved the dispersibility of the filler but also modified the physical properties.

**5.1 Application to PP/filler systems**

10 to 30 parts of talc or calcium carbonate are added to PP to improve rigidity and impact resistance. The problem in this process is the dispersibility of the filler. For example, insufficient dispersion of calcium carbonate results in low impact resistance. Therefore, maleic acid-modified PP, stearic acid, etc.8) are usually used, but this leads to problems such as high price and blooming. As shown in Fig. 6, the agglomerates of calcium carbonate are eliminated and the calcium carbonate is dispersed at the primary particle level when ARUFON UP-1020 is added to the PP/calcium carbonate system. We have also confirmed that the addition of UP-1020 improved the elongation at break (Table 7), and was able to show that “UP Series” has the performance of a filler dispersing agent in polyolefin resin.



**Figure 6: SEM photograph of PP/CaCO3 fracture surface**

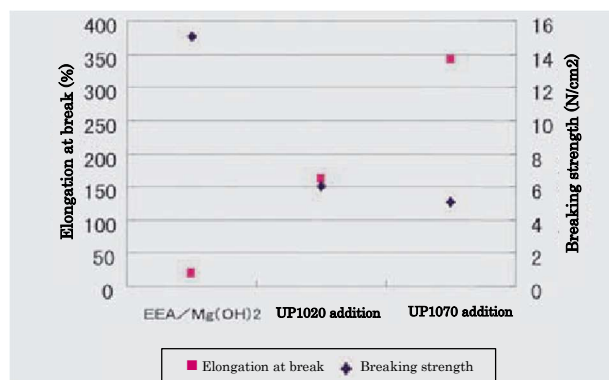
**Table 7: Mechanical characteristics of PP/CaCO3**

Sample name	Tensile strength (N/mm <sup>2</sup> )	Elongation (%)	Aging test (80°C, 3 day)
PP	35	665	Occurrence of warping
PP/CaCO3=100/30	27	46	Occurrence of warping
PP/CaCO3/Stearic acid=100/30/3	24	224	Occurrence of warping and bleeding
PP/CaCO3/UP1020=100/30/1	26	230	No warping or bleeding
PP/CaCO3/UP1020=100/30/3	25	279	No warping or bleeding

**5.2 Application to eco-friendly electric wires**

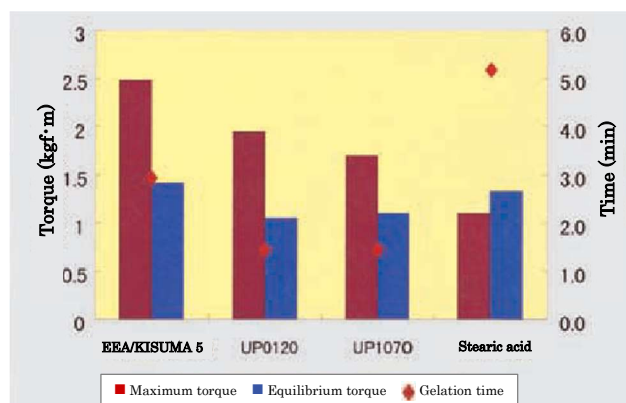
Although olefin-based electric wires are used as a substitute for PVC electric wires, brominated and phosphorous compounds are used as flame retardants because olefin-based resins are inherently less flame-resistant. However, in the event of an actual fire, gases of brominated and phosphorus compounds are generated, which affect human health and the environment. Therefore, flame-retardant olefin-based resin compounds that do not use these compounds are being developed. These are called eco-friendly materials, and electric wires made from these materials are called eco-friendly electric wires. An issue with eco-friendly electric wires is that they have poor flexibility due to the addition of about 100 to 250 parts of magnesium hydroxide per 100 parts of resin as a flame retardant. Therefore, we tried applying ARUFON to eco-friendly electric wires, since we found it to be effective in modifying olefin-based resin/filler systems as described above.

Since EEA resin has higher polarity and better flexibility than other olefin-based resins, it is suitable for eco-friendly electric wire materials. However, the elongation and flexibility decrease when magnesium hydroxide is added in large amounts such as 200 parts. However, we found that the elongation and flexibility of eco-friendly electric wire compounds could be improved by adding about 10 parts of ARUFON UP-1020 and UP-1070 per 100 parts of magnesium hydroxide (Fig. 7).



**Figure 7: Mechanical characteristics of EEA/Mg(OH)2/ARUFON**

In addition, although high filling with magnesium hydroxide increases melt viscosity during molding (Fig. 8), torque measurements with Plastomill confirmed that the melt viscosity was reduced to two-thirds, indicating improved productivity during extrusion molding.



**Figure 8: Moldability of EEA/Mg(OH)2/ARUFON**

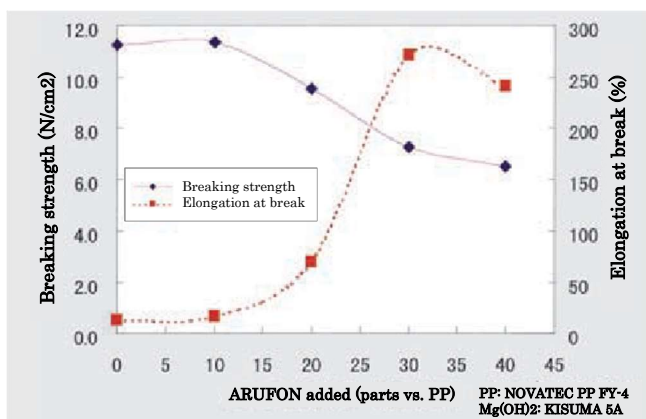


Figure 9: Mechanical characteristics of PP/Mg(OH)<sub>2</sub>/ARUFON

Examination of eco-friendly electric wires is not limited to EEA resin and includes cases using PP resin. We similarly confirmed the elongation modification effect of ARUFON addition: in a PP/magnesium hydroxide (= 100/200) system, adding 20 parts of ARUFON (research prototype) per 100 parts of PP, which corresponds to 10 parts or more per 100 parts of magnesium hydroxide, resulted in a dramatic improvement in elongation (Fig. 9).

## 6. Conclusion

The low molecular weight acrylic polymers obtained by the UFO technology were compatible with a variety of thermoplastic resins and exhibited unique characteristics. ARUFON grades include reactive polymers, which were not introduced in this article, and they have high potential for applications other than plastic additives. We will continue further development to discover ARUFON's unique characteristics and bring to market functional polymers that will be more useful to the world.

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