● Expanding Applications of UFO Polymers

UFO Development Laboratory
Tsugio Kimura, Hiroshi Inukai, Satoshi Kayamori, and Michihiro Kawai

1. Introduction

The term UFO is the acronym for Uniform Functional Oligomer, the name of the group promoting this project. The idea is to provide polymers with low molecular weights and high functionality (narrow molecular weight distribution and copolymerization composition distribution, and few impurities that adversely affect performance) that are useful for solving resource and environmental problems at the lowest possible cost through a highly efficient and environmentally friendly process using high-temperature bulk continuous polymerization based on radical polymerization.

When the commercial plant was completed in our Nagoya Plant in 2001, we began full-scale production and development activities under the name "ARUFON." We find our target customers not only in Japan, but also in South Korea, Taiwan, and Southeast Asian countries.

This technology and products derived from it have already been reported in the Toagosei Annual Research Report (TREND)[1)-5)], this issue, and at academic conferences, etc. This article introduces a wide range of applications of UFO polymers, including recent development topics, with a focus on examples that have received high praise from customers and have led to their adoption.

2. UFO technology

2.1 SGO technology

UFO technology is based on Solid Grade Oligomer (SGO) technology, which was successfully industrialized for the first time in the world by JohnPolymer (JP, Wisconsin, USA). It was originally inspired by the research on Thermal and Chemical-Initiated Co-polymerization of St/AA at High Temperatures and Conversions in a Continuous Stirred Tank Reactor by Dr. Hamielec (McMaster Univ., Canada). JP industrialized it and has provided products to the global market as dispersants for the St/AA systems, additives for various graphic arts, and resins for styrene/acrylic high-solid and powder paints.

2.2 From SGO to UFO technology and products

SGO was originally characterized by its ability to produce low molecular weight polymers at high efficiency without the use of large amounts of initiators or chain transfer agents thanks to its high temperature reaction field and continuous operation. As soon as we introduced the technology from JP and received the full disclosure of the details, we realized that this technology had the potential to be developed into a new product group, application fields, or even a more innovative technology.

UFO = SGO + LGO + α + β

LGO: Liquid oligomer
α: Technologies and products to be developed as an extension of SGO technology
β: Next-generation technologies and products that revolutionize SGO technology

With the above as our basic development concept, we have worked on technology and product development. Of the technologies and products we developed, we will introduce those that have reached the stage where their value can be tested in the form of concrete products in the world.

In addition, related departments within our company have been actively promoting these applications: in the construction materials field, LGO and its derivatives are used primarily in the solvent-free products "Acrye"[5)] and "Though Quick," while emulsion-related groups are strongly promoting the use of macromonomers obtained directly from the UFO process as reactive polymer surfactants.

3. Sealants

Sealants for buildings are elastic polymers used to fill gaps between sizing materials and metal curtain walls, providing watertight and airtight sealing while maintaining aesthetic appeal. In association with the spread of high-rise buildings and prefabricated construction, a wide variety of sealants have been developed and selected for appropriate applications.

In recent years, there has been a need to improve the durability from the viewpoints of resource and energy conservation, as well as environmental considerations. In the building industry, efforts are being made to improve housing quality and performance through revisions to the Building Standards Act, the Act on the Promotion of Housing Quality Assurance, and the Construction Material Recycling Act.

We have also been researching polymers for sealants with good weather resistance, and developed grades that are suitable for sealants. All are liquid polymers with low glass-transition temperatures. UH-2000 and UH-2130 that contain hydroxyl groups are suitable as the base polymer for sealants, and UP-1000 and UP-1110, which are low-viscosity non-functional acrylic polymers, are suitable as plasticizers.

In the following sections, we will explain the grades for each application.

3.1 Base polymer

Sealants using "UH Series" as the base polymer are two-component sealants, and their most significant feature is the outstanding weather resistance compared to other existing sealants. **Figs. 3-1** and **3-2** show the results of accelerated weathering tests. This is due to the fact that UFO polymers are pure polymers without the use of chain transfer agents or polymerization initiators that adversely affect weather resistance.

Of the UH Series, UH-2130 contains cyclohexyl groups as a component of highly weather-resistant paints, and exhibits even higher weather resistance.

The second characteristic is the low odor. We believe this is due to the fact that UFO polymers do not contain mercaptan-based polymerization chain transfer agents, residual polymerization catalysts, or volatile organic solvents.

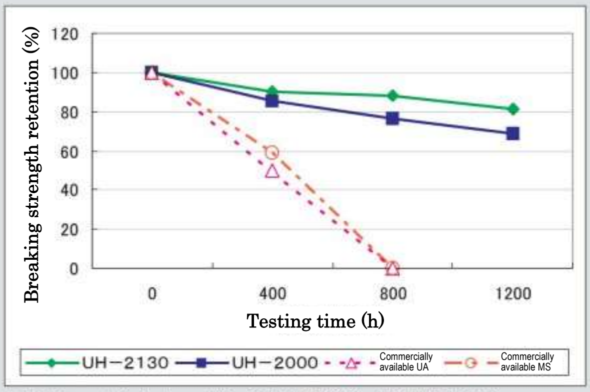


Figure 3-1: Weather resistance test (strength retention) using Metal Weather
(In the figure, UA indicates acrylic urethane and MS modified silicone)

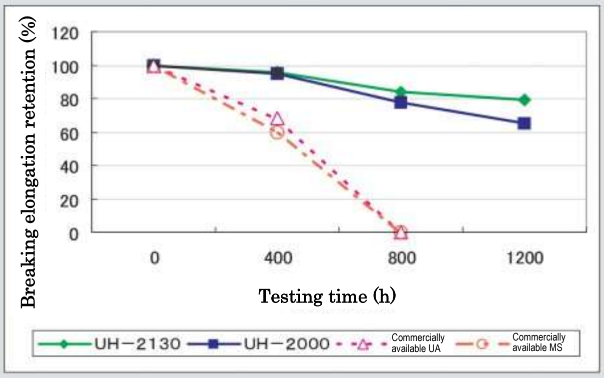


Figure 3-2: Weather resistance test (elongation retention) using Metal Weather

3.2 Plasticizer

In general, plasticizers are used for sealants to reduce viscosity and improve workability.

"UP Series" is a group of polymers with molecular weights and viscosity suitable for plasticizers, and they are resistant to bleeding and can enhance the weather resistance and contamination resistance of sealants.

In addition, UFO polymers can be considered environmentally friendly materials because they do not use substances that are suspected of having endocrine disrupting effects (so-called endocrine disruptors).

In particular, when UP-1000 is used in modified silicone sealants, which are in increasing demand as building sealants, unprecedented high weather resistance can be exhibited.

Table 3-1 shows the results of tensile properties and fluorescent ultraviolet (QUV) accelerated weathering tests conducted by our company.

Compared to dioctyl phthalate (DOP), which is conventionally used as a plasticizer, the compatibility with modified silicone and physical properties are at a comparable level, while high weather resistance that is not possible with DOP is exhibited.

UP-1000 can also be used as a plasticizer for polyurethane- and acrylic urethane-based sealants.

However, when UP-1000 is used in a one-component modified silicone sealant together with a primary amino silane as an adhesion promoter, delayed curing may occur. UP-1110 was developed to address this issue, and is suitable as a plasticizer for one-component modified silicones.

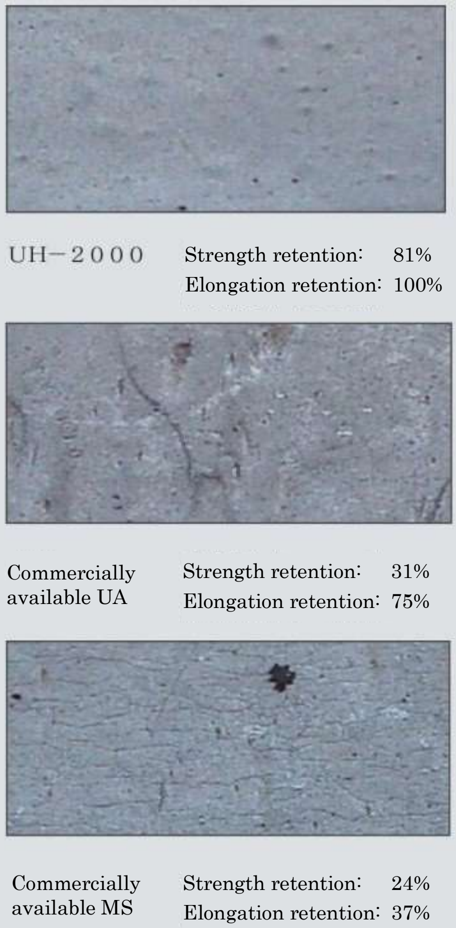


Photo 3-1: Results of 2-year exposure in Okinawa

Table 3-1: Tensile properties and accelerated weathering of modified silicone sealants

Base polymer	Plasticizer	Initial value			After 2,000 hours of QUV	
		50% modulus (MPa)	Breaking strength (MPa)	Elongation at break (%)	Retention (%) Breaking strength	Retention (%) Elongation at break
Modified silicone	UP-1000	0.2	0.9	420	92	98
	UP-1110	0.2	1.0	400	95	96
	DOP	0.2	1.1	440	0	0

Photo 3-1 shows the results of outdoor exposure testing of the sealants in Okinawa. The high weather resistance of UFO polymers is clearly shown.

For reference, **Photo 3-2** shows a photograph of a sealant using a UFO polymer.

Photo 3-2: Sealant with UFO

4. Paint substrate

We developed a weakly solvent-soluble UFO polymer for use as a topcoat for anticorrosion paints and building paints.

White paints of these polymers can be adjusted with normal formulations, and curing agents can also be weakly solvent-soluble isocyanates. **Fig. 4-1** shows the relationship between solid content in paint and Iwata cup seconds when thinner (LAWS) was added to white paint. This UFO polymer can be used to increase the solid content to a higher level than commercial low solids paints or strong-solvent type high solids paints (using xylene as the thinner), making it suitable as a high solids paint[6].

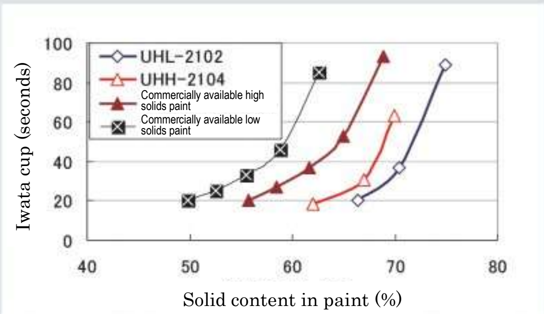
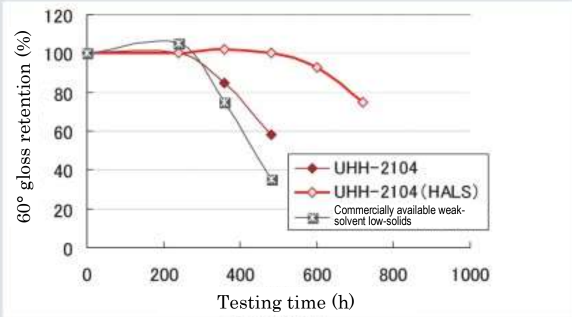


Figure 4-1: Solid content and viscosity of white paints

Fig. 4-2 shows the results of accelerated weathering test using a SUV weather meter. This UFO polymer is characterized by its high weather resistance, which is equivalent to that of low solids (high molecular weight) paints or better. This is due to the fact that UFO technology does not use secondary materials and uses monomers that provide high weather resistance. Further weather resistance improvement can be achieved by adding light stabilizers (HALS).



HALS: Tinuvin292 (Ciba Specialty Chemicals)

Figure 4-2: SUV accelerated weathering test results

For reference, **Photo 4-1** shows a photograph of a paint and coating film using UFO polymer.

Photo 4-1: Weak solvent paints and coatings using UFO

5. Plastic additive

Plastic additives include a wide variety of additives such as moldability modifiers, stabilizers, plasticizers, and compatibilizers. With the recent emphasis on environmental issues such as dehalogenation, endocrine disruptors, and recycling, the plastics industry has been actively considering alternative materials, new additives and formulations.

Because UFO polymers deliver excellent weather resistance, chemical resistance, and safety at low cost, and because compatibility, Tg, functional groups, refractive index, etc. can be easily controlled by selecting the copolymerization monomers, they have the characteristic of allowing various designs as plastic additives. We are currently developing acrylic-based polymer additives for the plastics market. This article introduces the latest developments, focusing on fluidity-improving agents and reactive modifiers.

5.1 Fluidity-improving agent

In association with the growing need for thinner walls and larger sizes in plastic molding, there is a demand for fluidity-improving agents that improve only fluidity while maintaining the original physical properties.

The market for transparent ABS grew rapidly during the trend toward transparent consumer designs and has continued to grow steadily year by year. Applications are diverse, including home appliances, office equipment, pachinko machine parts, and miscellaneous goods, and it is used in various places not only in transparent applications but also to enhance design. The transparency of transparent ABS is achieved by increasing the MMA ratio of the continuous phase and matching its refractive index to that of the rubber phase. Therefore, conventional fluidity improvers such as mineral oils and lubricants used in standard St-based resins exhibit poor compatibility with transparent ABS, and increasing the amount added causes haze (cloudiness). There is thus a need for fluidity improvers that maintain transparency without reducing impact resistance or Heat Deformation Temperature (HDT).

We recommend UFO polymers of the three grades shown in **Table 5-1**. Below are evaluation results using ethylene bis-stearamide (EBSA) for comparison.

Table 5-1: Fluidity-improving agent for transparent ABS/HIPS

Grade	Composition	Type	Results with addition of 5 parts			
			Trans-parency	Fluidity	HDT	Impact resistance
UP-1021	Acrylic	Liquid	○	100% up	-10°C	20% Down
XFM-121	Acrylic	Liquid	○	100% up	-7°C	10% Down
XFM-920	Styrene/acrylic	Solid	○	50% up	-2°C	30% Down
EBSA	Ethylene bis-stearamide	Solid	×	100% up	-7°C	0% Down

Fig. 5-1 shows the number of parts added and the Melt Flow Rate (MFR) increase rate. Each liquid grade of UP-1021 and XFM-121 showed a 100% increase in MFR with the addition of 5 parts, which was a result comparable to EBSA used for comparison. XFM-920 shows a 100% increase in MFR with the addition of 7 parts.

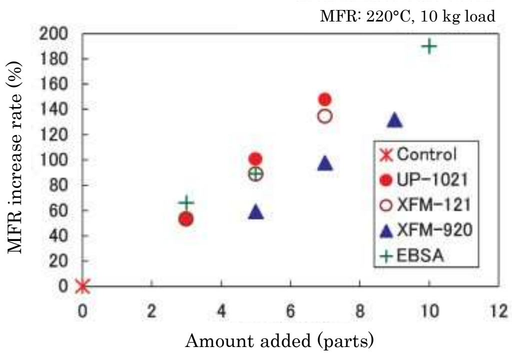


Figure 5-1: Relationship between the number of parts added and the MFR increase rate

Fig. 5-2 shows the HAZE with addition of each additive. EBSA already begins to develop haze at a 50% MFR increase and cannot be used for high-flow applications. On the other hand, no increase in HAZE is observed with UFO polymers until a 100% increase in MFR.

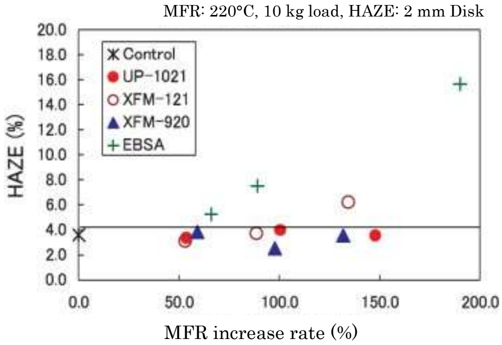


Figure 5-2: Relationship between MFR increase rate and HAZE

Fig. 5-3 shows the effect on impact strength. UP-1021 and XFM-920 slightly deteriorate impact strength. On the other hand, XFM-121, which is an improved grade focusing on impact strength, improves fluidity with almost no reduction in impact strength.

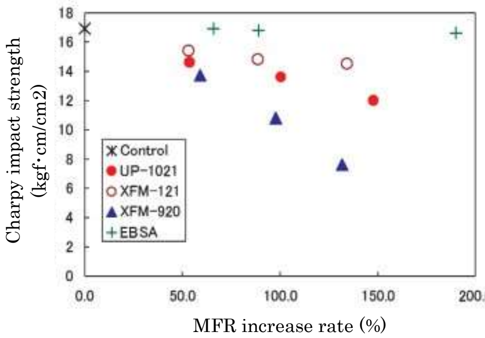


Figure 5-3: Relationship between MFR increase rate and impact strength

Fig. 5-4 shows the effect on HDT. While liquid grades of UP-1021 and XFM-121 cause a 7 to 10°C decrease in HDT for a 100% MFR increase in a similar fashion to EBSA, a characteristic of XFM-920 is that it causes only a 3°C decrease in HDT. XFM-920 is recommended when fluidity improvement is desired without lowering HDT.

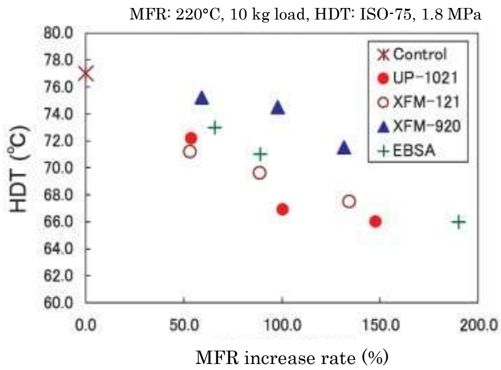


Figure 5-4: Relationship between MFR increase rate and HDT

5.2 Reactive modifier

XG/UG Series are grades that contain epoxy groups. XG-4000 and 4010 are liquid grades that are useful as reactive plasticizers to provide flexibility to thermosetting resins, polyesters and polyamides. UG-4030 to UG-4100 are solid grades that can react with polyester, polyamide, and polycarbonate terminals and modify the resins[7].

Table 5-3: ARUFON reactive modifier

Grade	Molecular weight Mw	Epoxy value (mmol/g)	Tg (°C)
XG-4000	3,100	0,7	-61
XG-4010	2,900	1.4	-57
UG-4030	11,000	1.8	52
XG-4040	9,200	2.1	63
XG-4050	9,000	0,7	70
UG-4070	9,700	1.4	58
UG-4100	8,600	1.1	52

Fig. 5-5 shows the rate of increase in torque when XG-4020, 4030, and 4040 were added to PET to be mixed and kneaded in a Plastomill at 270°C, respectively. With a mixing and kneading time of approximately 2 minutes, it exhibited 3 to 6 times the torque compared to PET with no additives. It is assumed that the epoxy group reacted with the PET terminal and elongated the chains, which increased the melt viscosity. While polyester has the disadvantage of low melt tension and difficulty in extrusion molding, its extrudability can be greatly improved by adding UG and adjusting melt tension. **Fig. 5-6** shows the state of the strand delivered from a twin-screw extruder.

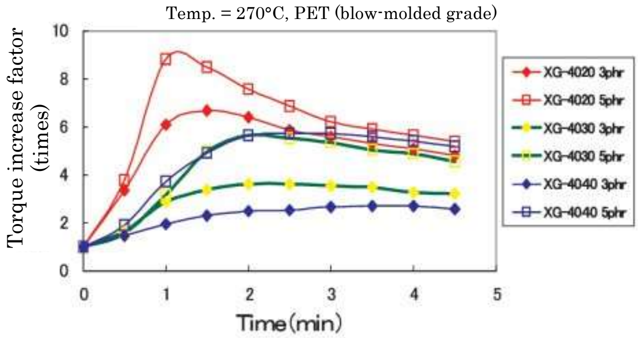


Figure 5-5: Modification of PET melt viscosity

No addition UG-4030 3 parts

Figure 5-6: Modification of PET melt tension (270°C)

Without additives, the crystalline polymer PET has low viscosity and low melt tension at 270°C, making it unable to maintain its strand shape. However, adding three parts of UG-4030 produces thick, firm strands that can be drawn properly, as shown in the photo.

As shown above, the epoxy groups of the XG/UG Grade, which are highly reactive, can react with base resin terminals and modify them in a short time. The following modification effects, including improved extrudability, have also been observed, and we are carrying out development of their applications.

[1] Improvement in extrudability

[2] Strength enhancement by chain elongation (recycled PET, etc.)

[3] Function as a compatibilizer (dispersion of rubber, wax, etc.)

[4] Prevention of whitening upon folding in sheets and films

[5] PET and PBT crystallization speed improvement

5.3 Others

In the development of UFO polymers into plastic additives, we have developed plasticizers and dispersants in addition to the fluidity-improving agents and reactive modifiers described in this article. They have already been introduced in the Toagosei Annual Research Report TREND No. 5[4]. Please refer to that issue.

6. Aqueous chemicals

6.1 Resins containing long-chain ester groups

With UFO technology, in which radical polymerization is carried out at high temperatures, various alcohols can be efficiently introduced as esters at the same time as polymerization. In particular, polymers containing carboxyl groups and long-chain ester groups can be synthesized in a single step by using relatively inexpensive long-chain alcohols that also serve as a polymerization solvent[8], although these groups are usually introduced by copolymerizing commercially available and expensive long-chain (meth)acrylates with other monomers simultaneously.

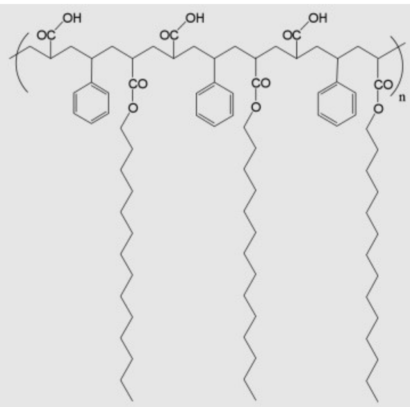


Figure 6-1: Structure of the UFX-5000 Series

We named the resins we synthesized by this method the UFX-5000 Series, and began approaching the market with polymers containing long-chain ester groups that use styrene-acrylic-based resins, which we have sold in the past, as the basic backbone (**Table 6-1**).

Table 6-1: Physical properties of the UFX-5000 Series

Brand name	Molecular weight Mw	AV (mg-KOH/ g-resin)	Tg-DSC (°C)	Softening point (°C)	Long-chain type
UFX-5000	4,500	215	65	125	C14
UFX-5010	15,000	170	70	130	C14
UFX-5022	14,000	235	75	135	C20

Alkaline aqueous solutions of these resins have extremely low aqueous solution viscosity compared to similar styrene-acrylic-based resins, as shown in **Fig. 6-2**, due to the presence of long-chain ester groups.

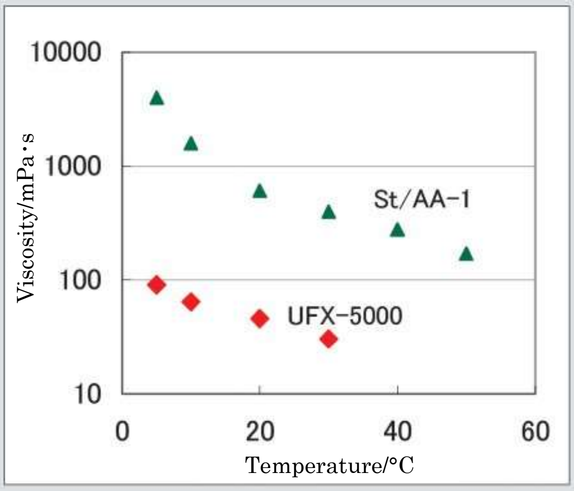


Figure 6-2: Temperature and viscosity of aqueous ammonia solution (NV = 30%) (St/AA-1; Mw=4900, AV=215)

Furthermore, as shown in **Table 6-2**, it has excellent dispersibility of organic pigments such as carbon and low dispersion viscosity. This is assumed to be due to the adsorption of hydrophobic long-chain alkyl side chains to carbon and the distribution and stabilization of hydrophilic carboxyl groups into the aqueous phase.

Table 6-2: Carbon pigment dispersibility

Evaluation item	UFX-5000	St/AA-1
Dispersion viscosity (mPa·s)	8.0	Poor dispersion (high viscosity)
Dispersion pH	8.3	
Dispersed particle diameter (nm)	127	
60° gloss (glossy film)	81.1	—

Carbon: FW18 manufactured by Degussa (particle size: 15 nm)
Pigment concentration: 12.5%, 5% dispersant added.

In addition, coating films formed by coating the ammonia solution of UFX-5000 Series showed higher water resistance than those of commercial styrene-acrylic-based resins (**Table 6-3**).

Table 6-3: Water resistance of coating film

Brand name	Drying temperature				Water contact angle 30 s → 90 s
	60°C	80°C	100°C	120°C	
UFX-5000	Dissolved	△	○	○	82 → 80 (difference 2)
UFX-5010	Whitening	○	○	○	85 → 83 (difference 2)
UFX-5022	Dissolved	△	○△	○	80 → 78 (difference 2)
St/AA-2	Poor film formation	Poor film formation	Peeling in 30 minutes	Whitening in 6 h	75 → 68 (difference 7)

St/AA-2: Resin with Mw = 12,500, AV = 213, Tg (DSC) = 73°C
An aluminum plate is coated with aqueous ammonia solution. Drying for 10 minutes, film thickness 10 μm. Water resistance spot test was judged at room temperature × 24 hrs. Water contact angle was measured on a film dried at 100°C × 10 minutes.

One reason for this may be that, as shown in **Photos 6-1** and **6-2**, coating with ammonia solution of UFX-5000 Series results in excellent film-forming properties despite being a high Tg resin, and good film-forming conditions can be obtained at room temperature. Since this tendency increases and the inflection point during DSC measurement becomes less clear as the amount of long-chain ester groups increases, it is assumed to be ascribed to the interaction between the long-chain ester groups. However, it is still a low molecular weight resin, and caution is required since films formed with the resin alone are brittle. We also examined the crystallinity of the coating film by powder X-ray diffraction (XRD) analysis, but observed no significant crystallinity.

Photo 6-1: Coating film of UFX-5010

Photo 6-2: Coating film of St/AA-2

We expect that these long-chain ester group-containing resins will be useful as dispersants for carbon and waxes, alkali soluble resins with good film forming properties, surface sizing agents to add water resistance to paper, paint additives, etc.

6.2 Aqueous plasticizer

Zero-VOC has recently come to be demanded in the fields of emulsion-type paints and adhesives. Plasticizers, including mainly phthalate esters represented by dibutyl phthalate (DBP), which have been widely used in these fields, have become designated substances under the VOC regulations and are also considered problematic as endocrine disruptors.

Of the products using UFO technology, which can synthesize polymers of very low molecular weights easily, we began approaching the market with UCX-3510, a low molecular weight liquid polymer which contains carboxyl groups and has a low Tg, as a safe and environmentally friendly alternative to DBP and other plasticizers (**Table 6-4**).

Table 6-4: Physical properties of aqueous plasticizer

Brand name	Molecular weight (Mw)	AV (mgKOH/g)	Viscosity mPa·s/25°C
UCX-3510	2,000	63	5,000

This resin is readily dispersed in water using alkali such as aqueous ammonia. When added to anionic emulsions such as vinyl acetate or acrylic emulsions, it functions as a film-forming aid and then plasticizes the resin after film formation. Because it has a higher molecular weight than DBP and is acrylic-based, it does not evaporate over long periods, undergoes minimal decomposition under light, and maintains the plasticity of the coating film.

Fig. 6-3 shows the results of weighing the amount of plasticizer remaining after heating the plasticizer for 120 minutes. Although the normal operating environment is expected to be much cooler, UCX-3510 is clearly far less volatile.

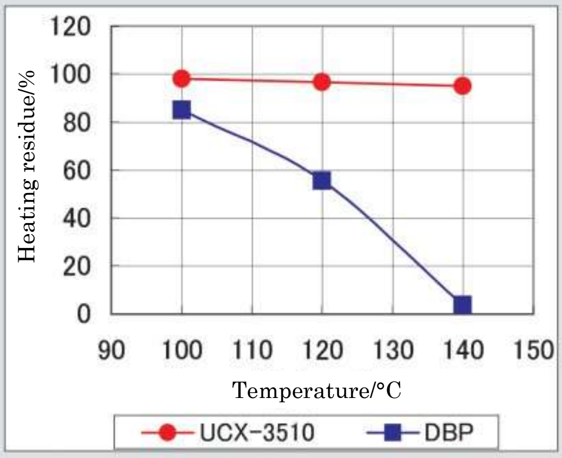


Figure 6-3: Difference in heating residue between UCX-3510 and DBP (120 min)

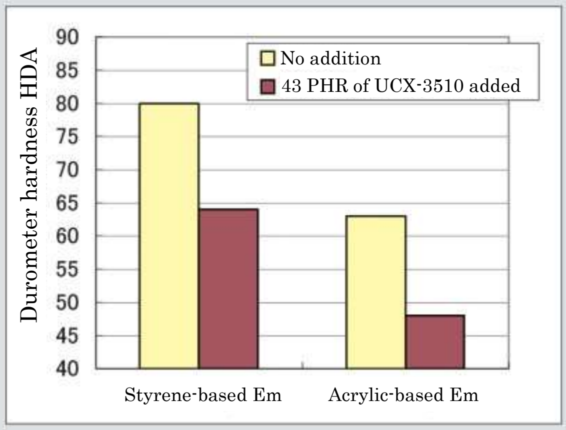
Table 6-5 shows the results of pencil hardness and water resistance spot test when the amount of UCX-3510 addition to acrylic emulsion (Em) was increased. While the hardness decreased as the amount added increased, a certain amount resulted in an optimum value for water resistance. This is assumed to be due to the improved film formation conditions caused by good compatibility.

Table 6-5: Hardness and water resistance with addition of UCX-3510

PHR for amount of UCX-3510 added	Pencil hardness	Water resistance spot 2hr
0	2H	○
5	2H	○
10	2H	◎
20	H	◎
30	H	◎
50	HB	○'
75	3B	○'

Em: Non-styrene acrylic Em, Tg (calculated) = 53°C
Coating: Approx. 10 µm, glass plate, predrying + 100°C for 1 min.

In addition, evaluation of plasticity by durometer hardness showed that it yielded a film that was quite soft with little surface tackiness (**Fig. 6-4**).



Measurement: Retention 10 s/23°C, JIS K 7215

Figure 6-4: Plasticity of emulsion (Em) (durometer hardness)

Fig. 6-5 shows data on the effect of UCX-3510 on lowering the film-formation temperature. Although it may be necessary to use slightly more than Texanol, a well-known film-forming aid, it is clear that it has a film-forming aid-like function.

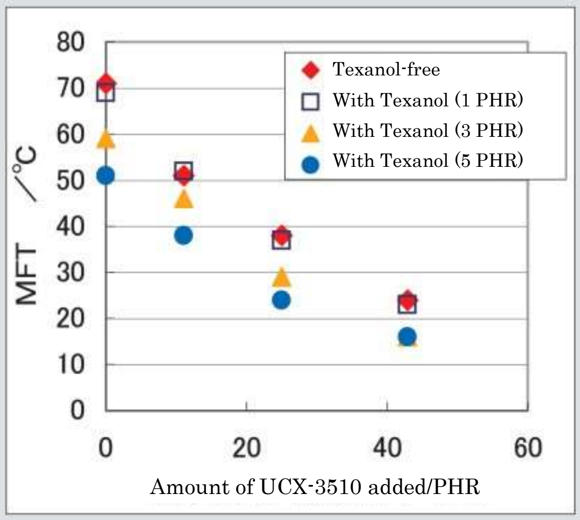


Figure 6-5: Amount of plasticizer addition and decrease in film formation temperature (MFT)

We expect that these aqueous plasticizers will be useful as materials that allow easy hardness/softness adjustment of emulsion-type products through simple addition while maintaining plasticizing performance over long periods.

7. Resins with special structures

7.1 Macromonomer

Using the unique polymerization conditions of the UFO process, macromonomers with terminal double bonds can be produced at extremely low cost. Their characteristics include a much lower cost compared to conventional macromonomers, and the ability to freely introduce functional groups. **Table 7-1** shows our typical grades.

Table 7-1: ARUFON macromonomers

Grade	Functional group	Molecular weight Mw	f *1	Acid value (meq)	Tg (°C)	Polarity	Type
UM-9001	-COOH	2600	0.96	2.4	-28	Low	Liquid
UM-9030	-COOH	3700	0.94	3.3	56	High	Solid
UM-9040	-COOH	5900	0.99	4.6	75	High	Solid
XM-9060	non	3500	0.94	-	-60	Low	Liquid
XM-9070	non	2900	1.00	-	-35	Medium	Liquid
XM-9080	Epoxy	2800	0.8	0.07 (Epoxy)	-50	Low	Liquid

*1: Number of terminal double bonds per polymer chain

Examples of applications of these macromonomers are emulsions using UM-9030 and UM-9040 with carboxylic acids as reactive emulsifiers. Macromonomers can graft onto the surface of emulsion particles to improve emulsion stability, etc.

7.2 Hybrid resin

Using the high temperature conditions of the UFO process, hybrid graft polymers of acrylics and other types of high-molecular weight polymers can be synthesized at low cost. It is currently under development. The following hybrid resins are examples that have already been produced at the laboratory level.

[1] PP-acrylic resin
[2] PE-acrylic resin
[3] PBd-acrylic resin

Other combinations with various resins are also possible, and these hybrid resins are expected to develop into next-generation UFO polymers.

8. Conclusion

"ARUFON," a family of UFO polymers, has earned high praise from users for its excellent cost-performance and amid growing societal concern about resources and the environment.

In addition to the applications described in this article, tackifiers produced by this technology have been confirmed to provide an excellent balance of adhesive strength and holding power in the fields of adhesives, including pressure-sensitive adhesives. As mentioned earlier, polymer emulsions obtained by using UFO macromonomers as Reactive Polymer Surfactant (RPS) can produce stable fine particles of several tens nm in size. It has also been found that crosslinked films using COOH bonded to particles via macromonomers exhibit characteristic film properties. By using UFO macromonomers as raw materials for graft polymers, it will be possible to commercialize applications that have been functionally satisfactory but had significant price barriers.

As you can see, the plasticity and performance of UFO polymers are high, and we will continue to develop polymers that will be useful to the users under the slogan of "delivering high performance polymers from simple processes at low cost."

Reference

1) S. Kayamori, Toagosei Annual Research Report, **3**, 42 (2000).
2) H. Inukai, Toagosei Annual Research Report, **4**, 29 (2001).
3) M. Kawai, Toagosei Annual Research Report, **5**, 2 (2002).
4) M. Furuta, Toagosei Annual Research Report, **5**, 34 (2002).
5) H. Yamamori, Toagosei Annual Research Report, **5**, 43 (2002).
6) H. Inukai, The Industrial coating, **172**, 42 (2001).
7) R. Ichiki, Y. Furuta and M. Kawai, Proceedings of the 11th Polymer Materials Forum, 53 (2002).
8) USP6, 355, 727