● Monofunctional Oxetane with Excellent Toughness "OXT-211 (POX) & OXT-213 (CHOX)"

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1. Introduction

"ARON OXETANE" is a compound that has an oxetane ring, a four-membered cyclic ether, as the cation-curable functional group.

Polymerization of cation-curable materials is initiated by photo-latent or thermally latent initiators. Compared to radical curing materials currently used as UV curing resins, cation-curable materials have the following characteristics.

- Thin-film curing is possible even in air because there is no polymerization inhibition by oxygen.
- Curing by dark reaction (post-polymerization) proceeds even after light irradiation is completed.
- The use of ring-opening polymerization monomers can reduce curing shrinkage.
- Many oxetane compounds are safe materials even at low molecular weights and can be used to reduce the viscosity in composition systems.

We have already launched four types of "ARON OXETANE" products, and are carrying out market development for them domestically and overseas (**Fig. 1**).

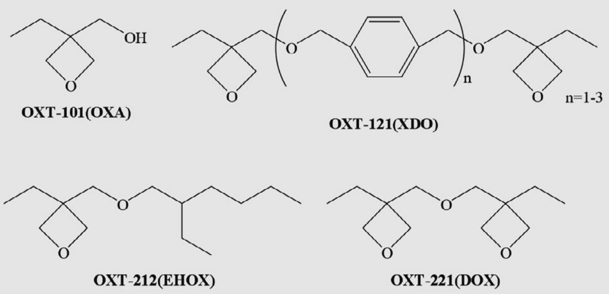

Figure 1: Currently marketed ARON OXETANE

However, there are not sufficient choices of cation-curable materials on the market. We have been developing distinctive monofunctional monomers to meet the market's demand for new materials (Fig. 2). In the process, we discovered that cured products of "OXT-211 (POX)" and "OXT-213 (CHOX)" have excellent toughness, and we brought them to market after establishing manufacturing capabilities and securing compliance with the Act on the Regulation of Manufacture and Evaluation of Chemical Substances (low production volume). This article introduces the monofunctional oxetanes with excellent toughness ("OXT-211 (POX)" and "OXT-213 (CHOX)").

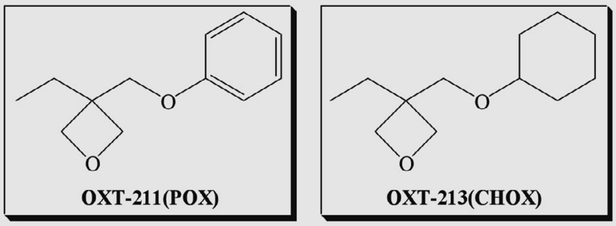

Figure 2: ARON OXETANE under development

2. Physical properties as liquids

OXT-211 (POX) and OXT-213 (CHOX), both introduced in this article, are sold as colorless, transparent liquids purified by distillation. Their basic physical properties as liquids are shown below (**Table 1**). These monomers have low viscosity and are compatible with general-purpose organic solvents such as acetone, isopropanol, and toluene, as well as with cation-curable epoxy resin and other oxetanes, making them easy to blend in various ways.

Table 1: Liquid physical properties of the new monofunctional oxetanes

	OXT-211 (POX)	OTX-213 (CHOX)
Molecular weight	192.3	198.4
Appearance	Colorless, transparent liquid	Colorless, transparent liquid
Purity 1)	98% or more	98% or more
Boiling point	130°C/0.67 kPa	125°C/1.33 kPa
Melting point	< -20°C	< -20°C
Flash point 2)	145°C	122°C
Viscosity 3)	13.8 mPa·s	6.7 mPa·s
Surface tension 4)	37.2 mN/m	33.6 mN/m
Specific gravity	1.046 (25°C)	0.954 (25°C)
Refractive index 5)	1.514	1.460

1) GC area %
2) Cleveland open cup method
3) E-type viscometer (25°C)
4) Platinum plate method (23°C)
5) D line (25°C)

Next, the solubility in typical photocationic initiators is shown (**Table 2**). OXT-211 (POX) with an aromatic ring shows better solubility in sulfonium salt-based initiators.

Table 2: Solubility of initiators in the new monofunctional oxetanes

Initiator	OXT-211(POX)	OXT-213(CHOX)
UVI-6992[1]	＞10wt%	＜2wt%
SP-152[2]	＞10wt%	＞10wt%
Irgacure250[3]	＞10wt%	＞10wt%
Rhodsil2074[4]	＞10wt%	＞10wt%

1) Manufactured by Dow Chemical (triarylsulfonium salt)
2) Manufactured by ADEKA (triarylsulfonium salt)
3) Manufactured by Ciba Specialty Chemicals (diaryliodonium salt)
4) Manufactured by Rhodia (diaryliodonium salt)

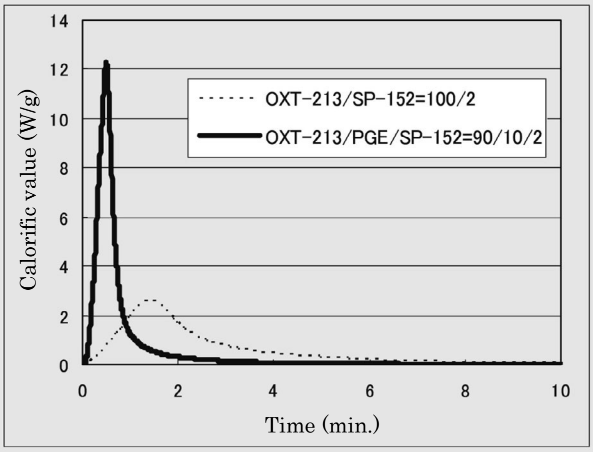

Figure 4: Photo-DSC measurement results (OXT-213 and PGE)

3. UV curability

We confirmed the UV curability of each oxetane monomer using Photo-DSC. As the photocationic initiator, we used SP-152 (triarylsulfonium salt, manufactured by ADEKA), which dissolves well in both monomers.

We measured Photo-DSC by irradiating approximately 1 mg of sample on an aluminum pan with UV light (0.18 mW/cm^2) using a Q100 instrument (manufactured by TA Instruments). The measurement was performed at 25°C under dry air flow.

When we added 10 parts by weight of epoxy monomer (1,2-Epoxy-3-phenoxypropane, hereafter "PGE") to each monomer, the time to reach maximum calorific value under UV irradiation was shortened, and the calorific value per unit time increased (**Figs. 3** and **4**). It is assumed that this was because the initiation reaction was accelerated by the addition of epoxy, which also accelerated the subsequent growth reaction, as reported by Sasaki et al.[1].

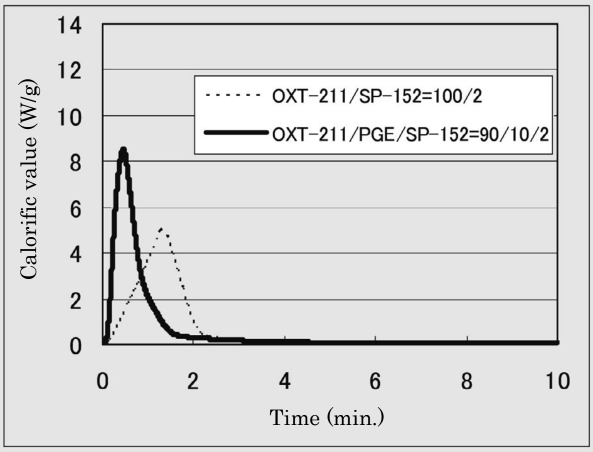

Figure 3: Photo-DSC measurement results (OXT-211 and PGE)

4. Properties of the cured products

Next, we prepared cured products of OXT-211 (POX) and OXT-213 (CHOX), and measured their properties. We prepared a mixture with oxetane/alicyclic epoxy (UVR-6110, manufactured by Dow Chemical) and thermal cationic initiator (ratio = 90/10/0.5), and formed the cured product by heating it at 125°C for 30 minutes and then at 150°C for 1 hour under nitrogen flow. As the thermal cationic initiator, we used CP-66 (trialkylsulfonium salt, manufactured by ADEKA).

4.1 Viscoelasticity

We measured the viscoelasticity spectra of the resulting cured products. **Fig. 5** shows the OXT-211 (POX) composition system, and **Fig. 6** shows the OXT-213 (CHOX) composition system.

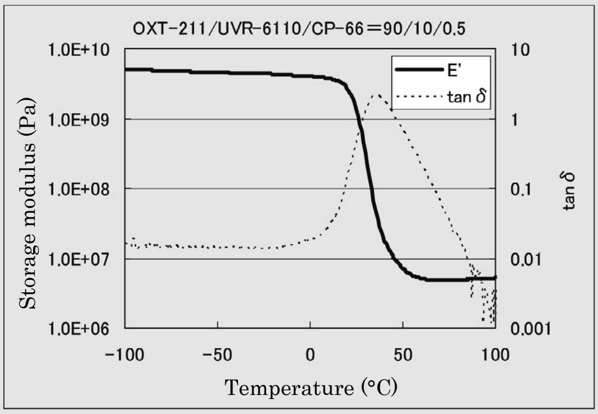

Figure 5: Viscoelastic spectrum (OXT-211/UVR-6110)

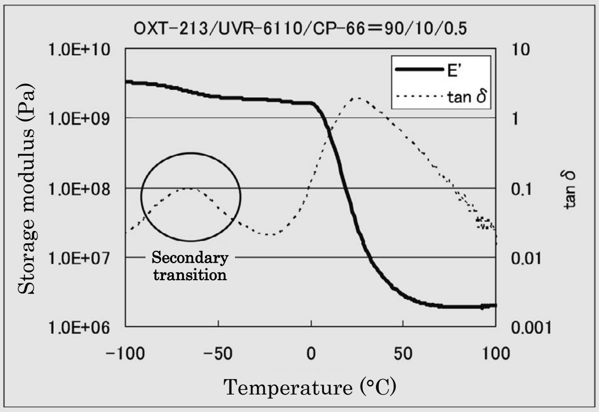

Figure 6: Viscoelastic spectrum (OXT-213/UVR-6110)

We observed the maximum value of tanδ around room temperature in all of the formulations, and confirmed that the cured products had excellent flexibility. It is also noteworthy that OXT-213 (CHOX) showed a secondary transition around -70°C, which is presumed to be due to β relaxation. This suggests that the cyclohexyl group contributes to stress relaxation at high frequencies and that it can impart toughness.

4.2 Tensile properties

We conducted tensile tests on each cured product and measured the breaking strength and elongation at break (**Table 3**). The composition containing bisphenol A diglycidyl ether (YD-128, manufactured by Tohto Kasei) showed an elongation of approximately 300%, indicating that a flexible cured product with high extensibility was obtained.

Table 3: Tensile test results

OTX-211 (POX)	90		90	
OXT-213 (CHOX)		90		90
UVR-6110 1)	10	10		
YD-128 2)			10	10
CP-66 3)	0.5	0.5	0.5	0.5
Viscosity (mPa·s/25°)	17	8	20	10
Curing shrinkage (%)	3.7	4.8	3.5	4.5
Tensile strength (MPa)	4.0	1.8	1.4	0.9
Elongation (%)	120	130	270	310

1) Alicyclic epoxy (manufactured by Dow Chemical)
2) Bisphenol A diglycidyl ether (manufactured by Tohto Kasei)
3) Trialkylsulfonium salt (manufactured by ADEKA)

5. Applications

5.1 Improvement in adhesion

OXT-211 (POX) and OXT-213 (CHOX) have good compatibility with bisphenol A diglycidyl ether (YD-128, manufactured by Tohto Kasei), which enables reduction in viscosity while maintaining curability.

Although curing shrinkage after UV curing increases with the addition of more OXT-211 (POX), it has been reported that the film substrate generates no curling at all even after UV curing, and that it has excellent adhesion to plastic substrates such as PC, PMMA, and PET[2]. **Table 4** shows the test results for adhesion.

Table 4: Adhesion with OXT-211 (POX) and OXT-213 (CHOX) compositions

YD-128 1)		100	80	60	40	20	80	60	40	20
OXT-211(POX)			20	40	60	80				
OXT-213(CHOX)							20	40	60	80
UVI-6992 2)		3	3	3	3	3	3	3	3	3
Compatibility		OK	OK	OK	OK	OK	OK	OK	OK	NG
Viscosity (mPa・S/25℃)		10,700	1,600	350	110	37	950	180	52	-
Curability 3)		2	2	4	6	9	2	4	7	-
Adhesion 4)	Steel	○	○	○	○	○	○	○	○	-
	Al	△	○	○	○	○	○	○	○	-
	PC	×	△	○	○	○	○	○	○	-
	PMMA	×	×	○	○	○	×	○	○	-
	PET	○	○	○	○	○	○	○	○	-
Curl test 5)		×	△	○	○	○	△	○	○	-

1) Bisphenol A diglycidyl ether (manufactured by Tohto Kasei)
2) Triarylsulfonium salt (manufactured by Dow Chemical)
3) Tack-free time, high pressure mercury lamp (160 W, H = 10 cm), conveyor speed: 5 m/min.
4) Cross-cut test. ○: No peeling, △: Partial peeling, ×: Total peeling.
Steel: Zinc phosphate treatment, Al: Chromium chromate treatment, PC: Iupilon Sheet NF-2000, PMMA: Acrylite #001, PET: Takiron 6010G
5) Coated on PET film (50 μm thickness) at 25 μm thickness. Evaluated by visual inspection after UV curing.
○: No curling, △: Slight curling, ×: Clear curling

This favorable adhesion has been attributed to low residual stress between the coating film and the substrate. Due to the difference in reactivity between oxetane and epoxy, the crosslinking reaction of the bifunctional epoxy resin (YD-128) proceeds during the later stages of polymerization, relieving stress from curing shrinkage [2].

Furthermore, its potential as a high-adhesion hard-coating agent through hybridization with inorganic fillers has been proposed [3].

5.2 Improvement in brittleness

As described previously, OXT-213 (CHOX) shows β relaxation ascribed to the cyclohexyl group. This relaxation is thought to be capable of imparting toughness to the cured product.

The curability and cured-product properties of a silicate oligomer containing an oxetanyl group (**Fig. 7**, hereinafter "OX-SC"), which is an organic-inorganic hybrid, cationically curable material, using an aluminum complex catalyst, have already been reported[4]. In this article, we investigated whether mixing OXT-213 (CHOX) into OX-SC could impart toughness to the cured product. We prepared the cured product by thermal curing with 1000 ppm aluminum trisacetylacetonate added as a catalyst. The heating conditions were 60°C (4 h) → 120°C (2 h) → 150°C (2 h).

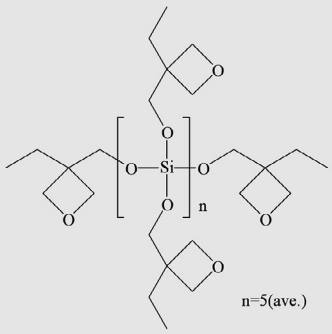

Figure 7: Model structure of OX-SC

We measured the viscoelastic spectrum of the cured product obtained from a 90/10 formulation of OX-SC and UVR-6105 (manufactured by Dow Chemical), and found that the cured product broke at approximately 80°C, and that it was difficult to measure at higher temperatures. **(Fig. 8).**

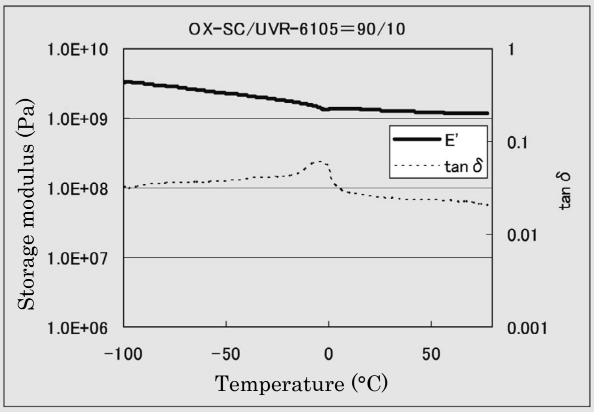

Figure 8: Viscoelastic spectrum (OX-SC/UVR-6105)

We therefore added OXT-213 (CHOX), and observed a secondary transition at around -70°C in the viscoelastic spectrum of the cured product, and confirmed that the addition of OXT-213 (CHOX) reduced brittleness (**Fig. 9**).

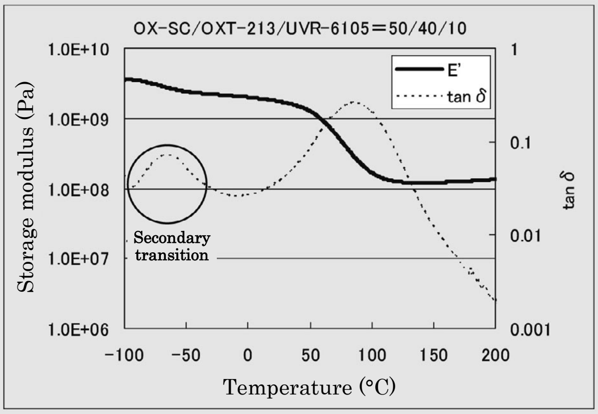

Figure 9: Viscoelastic spectrum (OX-SC/OXT-213/UVR-6105)

Although the addition of OXT-213 (CHOX) resulted in the development of a distinct glass transition point (Tg), the storage modulus above Tg showed a high value at 10^8 Pa. Furthermore, this high elastic modulus did not decrease up to 200°C, suggesting excellent heat resistance.

Therefore, we conducted heat resistance tests at 150°C on the cured products (2 mm thickness) using OXT-213 (CHOX), OX-SC, and alicyclic epoxy. The thermal curing conditions were 60°C (4 h) → 120°C (2 h) → 150°C (2 h). We measured the changes in transmittance at 400 nm (1 mm thickness equivalent) over time, and obtained relatively favorable results with approximately 70% being maintained even after 1000 hours (**Fig. 10**). Regarding coloration under heating, we believe further improvement is possible by reviewing the resin composition and optimizing the antioxidant.

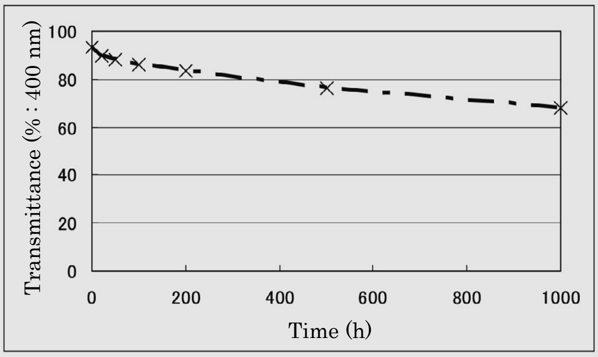

Figure 10: Change in transmittance over time (150°C)

6. Safety

One of the characteristics of oxetane is its high safety profile. Epoxy, which is a three-membered ring ether with one fewer carbon than oxetane, is often mutagenic. On the other hand, oxetane is considered less mutagenic than epoxy, and both OXT-211 (POX) and OXT-213 (CHOX) tested negative in the Ames test, which is a measure of mutagenicity. It also has a low value for a low molecular weight monomer with respect to primary skin irritation (Table 5).

Table 5: Safety test results

	Mutagenicity	Skin irritation
OTX-211 (POX)	Ames negative	P.I.I = 1.9
OXT-213 (CHOX)	Ames negative	P.I.I = 2.5

7. Regulatory compliance

Both OXT-211 (POX) and OXT-213 (CHOX) have been notified as low-production-volume chemicals (up to 10 tons per year) under Japan's Act on the Regulation of Manufacture and Evaluation of Chemical Substances. Going forward, we plan to continue to acquire various safety data in response to demand and to comply with the Act on the Regulation of Manufacture and Evaluation of Chemical Substances.

8. Conclusion

We found that the two monofunctional oxetanes introduced in this article exhibit very high flexibility and that they are capable of imparting toughness to multifunctional cured products. Since they also have favorable adhesion to various substrates, we expect that they will be particularly useful in the fields of coatings and adhesives for various plastic films.

We believe that addressing the performance gaps in existing cationic materials will significantly expand the applications of cation-curable materials going forward.

Reference

1) H. Sasaki, et al., *J. Polym. Sci. Part A-Polym. Chem.,* 33, 1807(1995).
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4) H. Sasaki, Toagosei Annual Research Report, 7, 29 (2004).