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NIPPON SHOKUBAI

2021.12

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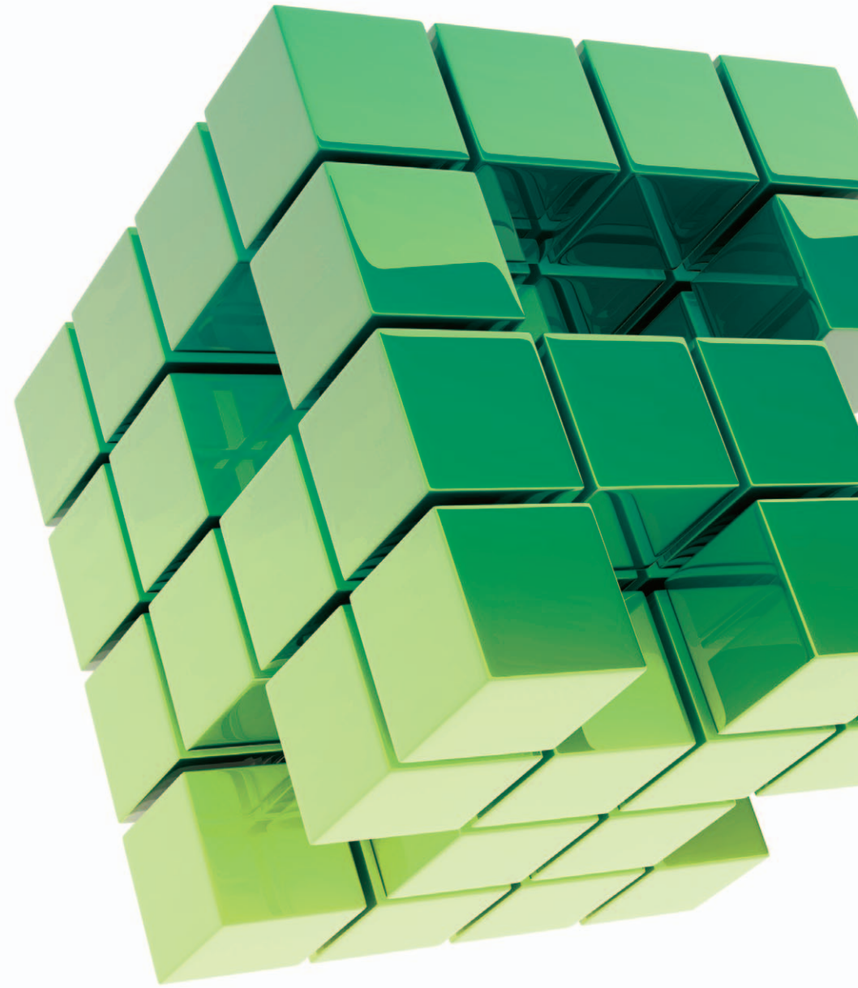
Oxazoline functionalized reactive copolymers

EPOCROS

Novel Low toxic Polymer Crosslinker and
Adhesion Promoting agent for waterborne



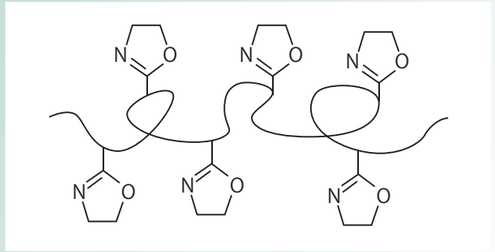
Introduction

Epocros has been introduced to the market by Nippon Shokubai as world's first commercialization of Oxazoline related product built on the basic technique of Dow Chemical Company USA as well as the accumulated knowledge of Nippon Shokubai on synthetic organic chemistry and polymer science.
Recently, worldwide expectation for developing environmentally safe product is becoming prevalent and the trend is being accelerated toward the waterborne product against VOC and solvent. With those background, Epocros is accepted and utilized by variety of customers.
Especially, as Epocros is realized on polymer structure which is quite rare for the crosslinkers, the market is recognizing it as a crosslinker with extremely high safety.
This document provides the characteristics of each Epocros series with supplementary technical data which can be used for examples. If you need detailed technical information, contact our sales division.

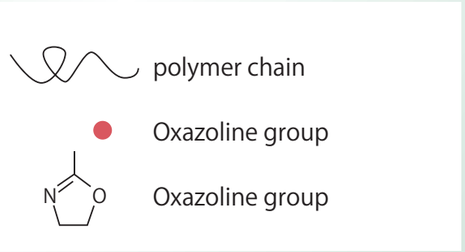
Aplication areas of EPOCROS

Table of contents

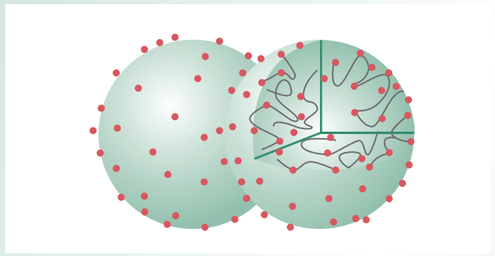
General Information of EPOCROS



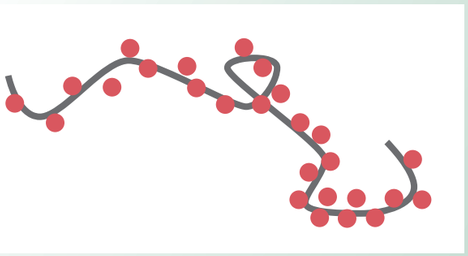
Oxazoline functionalized reactive copolymer



Oxazoline functionalized reactive copolymer

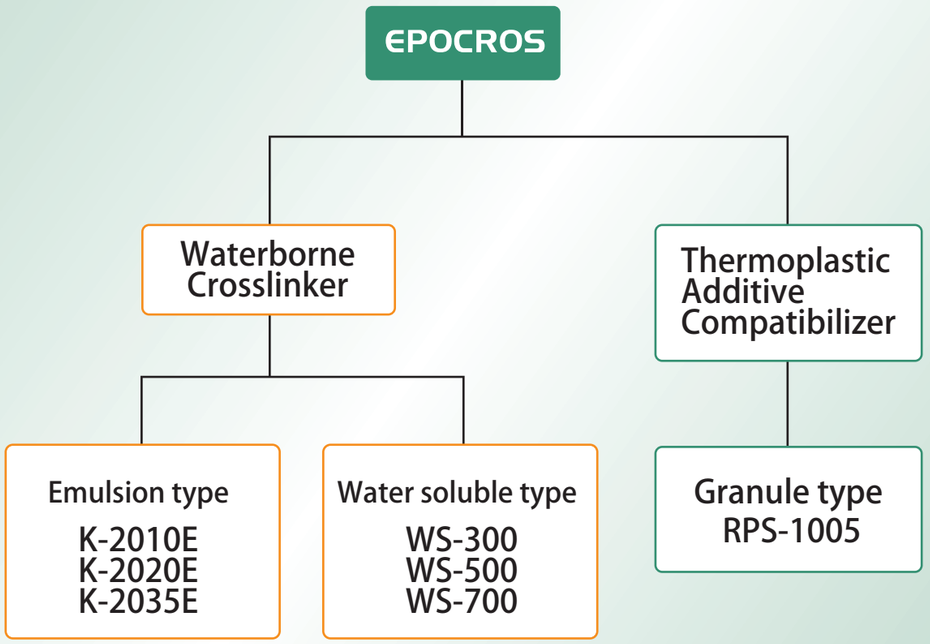


Emulsion type (K-series)



Water soluble type (WS-series)

Classification of EPOCROS



Product line-up, properties and characteristics

Product Type		Emulsion			Water soluble		
Series name		K-2000 Series			WS Series		
Product No.		K-2010E	K-2020E	K-2035E	WS-300	WS-500	WS-700
Appearance		Milky white emulsion			None～Clear Red Liquid	Clear yellow liquid	
Type		Soft	Middle	Hard	High oxazoline VOC free	Standard	VOC free
Nonvolatiles(wt%)		40			10	39	25
Solvent		Water			Water	Water/PM*7	Water
pH		7-9			7-10	8-10	7-10
Main components		Styrene/Acrylic			Acrylic		
WPO*1		550			130	220	
Oxazoline groups amount*2		1.8			7.7	4.5	
Tg(℃)		-50*3	0*3	50*3	90*3	50*4	50*4
Molecular Weight*5	Mn	N/A*6			4×10^4	2×10^4	2×10^4
	Mw	N/A*6			12×10^4	7×10^4	4×10^4
Common characteristics		・VOC free, Long Pot life for one packaging ・Controllable appearance by Tg adjustment ・Improve water resistance, heat resistance and film properties ・Adhesion promoting particularly to polyester ・Fast drying ・Low-toxicity			・Long Pot life one packaging ・Higher reactivity in comparison with emulsion type ・Improve water resistance, heat resistance and film properties ・Adhesion promoting for PET, OPP, PVC etc. ・Fast drying ・Low-toxicity		

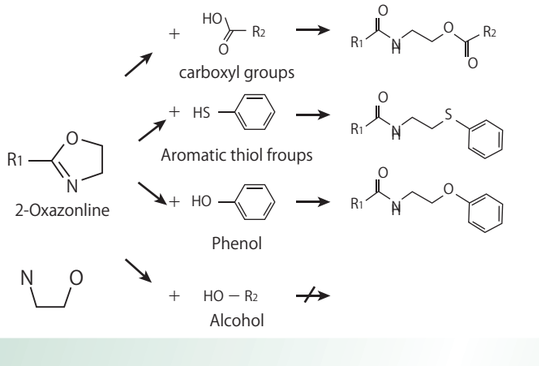
Figures shown in the above table are representative values ; these are not to be considered product specification

＊1 Equivalent Weight (Weight per oxazoline equivalent: nonvolatiles g/eq.) ; Theoretical value
＊2 Oxazoline groups amount (mmol/g, nonvolatiles) ; Theoreticalvalue
＊3 Calculated value
＊4 Actual measurement
＊5 Molecular weight (HPLC, g/mol)
＊6 N/A: not available
＊7 1-Methoxy-2-propanol

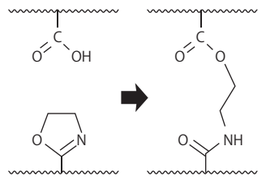
Reactivity of the Oxazoline groups

Reaction with the carboxyl groups

1. Reaction with carboxyl groups which is contained in most of waterborne polymers is regarded to have the highest reactivity.
2. After the reaction with the carboxyl groups, stable amid ester bonding is formed. Any by-product will not be generated.
3. Reaction with carboxyl groups proceeds rapidly at elevated temperature 80℃ to 100℃
4. Reaction with carboxyl groups proceeds slowly at room temperature.
5. Oxazoline groups have better reactivity with carboxyl groups than with epoxy groups.
6. Oxazoline groups also react with aromatics such as thiol groups as well as phenol groups, but oxazoline groups cannot react with alcoholic hydroxyl groups.

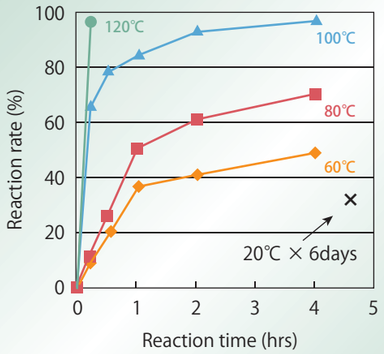


Schematic reaction between
Carboxyl groups and Oxazoline groups

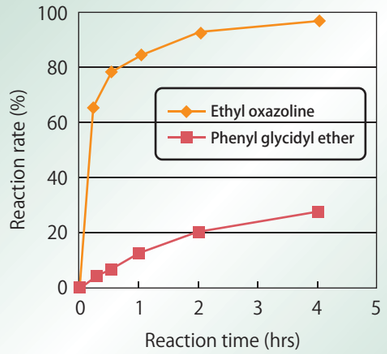


Crosslinked structure (Amide ester bonding)

Model reaction of Oxazoline groups (Ethyl Oxazoline / Propionic acid)



Model reaction of Oxazoline / Carboxyl groups
(Ethyl Oxazoline / Propionic acid)



Comparison between the reactivity of
Oxazoline groups and Epoxy groups
(Reaction with Propionic acid, 100℃)

Conditions on Reactivity : Ethyl oxazoline / Propionic acid = 1/1 (mol/mol), solvent-free reaction
Phenyl glycidyl ether / Propionic acid = 1/1 (mol/mol), solvent-free reaction
Method of analysis : Gas chromatography analysis

Safety and worldwide Regulatory

EPOCROS is a low toxic and highly safe crosslinker

● Safety data

	Ames test	Skin temporaty irritant test (Rabbit)	Acute toxicity (Oral, Rat, LD50)	Fish toxicity (Killfish, LC50, 96hr)
K-2010E	Negative	None	＞2000mg/kg	＞1000mg/L
K-2020E	Negative	None	＞2000mg/kg	＞1000mg/L
K-2035E	Negative	None	＞2000mg/kg	＞100mg/L
WS-300	Negative	Slight irritation PII＝0.2	＞2000mg/kg	N/A
WS-500	Negative	None	＞2000mg/kg	＞1000mg/L
WS-700	Negative	None	＞2000mg/kg	＞1000mg/L

N/A : not available

● Legislation and Regulations (as of August 2021)

Law / Inventory Country / regions	Law concerning the Examination and Regulation of Manufacture,etc,of Chemical substances JAPAN	TSCA USA	REACH EU (EEA)	KECL KOREA	IECSC CHINA
K-2010E	○	○	○*	Pre-registration	contact us
K-2020E	○	○	×	×	contact us
K-2035E	○	○	○*	Pre-registration	contact us
WS-300	○	○	contact us	○**	contact us
WS-500	○	○	○*	Pre-registration	○
WS-700	○	○	○*	Pre-registration	○

○ : Registered
○* : Registered under limited tonnage
○** : Registered (need importer registration)
× : Not Registered

References

General formulating consideration:

If we could suppose that the reaction proceeds just like the theory, optimum quantity of Epocros as an additive is 100mol%. However, under the effects of reacting conditions as well as the effects of other additives, 20 to1OOmol% is considered to be recommended in actual usages.

● Amount of the Oxazoline group contained in the EPOCROS (per g.NV*)

	K-2000 Series	WS-300	WS-500	WS-700
Amount of the Oxazoline group (mmo/g,NV*)	1.8	7.7	4.5	4.5
Nonvolatiles(wt%)	40.0	10.0	39.0	25.0

Caution: Each value is theoretically calculated, not to be considered as specification.

● Calculating method of the amount of Epocros additive regarding the amount of the base resin (Calculation of mol to be added)

Before the calculation, prepare the acid value and g,NV* of the base resin as well as the amount of the Oxazoline and g,NV* in the crosslinking agent.
First. get the COOH mol amount from the acid value of the base resin by using formula A. Then substitute the variables in formula B.

Formula A: COOH mol amount (mmol/g,NV*) = Acid value / 56.1 (Molecular weight of KOH:g/mol)

Acid value: Amount (mg)of the KOH potassium hydroxide which is required to neutralize the COOH groups contained in 1g of NV* base resin.

COOH mol amount: Number of COOH mols contained in 1 g of NV* base resin.

Formula B (Calculating method of the adding amount of Epocros):

Amount of the ading Epocros (g) = (Weight of the base resin (g) x (NV* ratio of the base resin (%) / 100) x (Amount of COOH mol (mmol/g) / (Amount of Oxazoline group in the Epocros (mmol/g)) / NV* ratio of the Epocros (%) / 100)

For example, suppose the main acid value of the base resin is to be 30(mg KOH/g NV*) and the NV* ratio is to be 40.0%;

By using the formula A. COOH mol amount of the base resin is decided to be 0.54(mmol/g, NV*). (Calcullation: 30/56.1 = 0.53(mmol/g , NV*)

Amount to be added for K-2000 series (g) = (100 x (40 / 100) x 0.54) / 1.8 / (40 / 100)) = 29.4

Amount to be added for WS-300(g) = (100 x (40 / 100) x 0.54) / 7.7 / (10 / 100)) = 27.5

Amount to be added for WS-500(g) = (100 x (40 / 100) x 0.54) / 4.5 / (40 / 100)) = 12.1

Amount to be added for WS-700(g) = (100 x (40 / 100) x 0.54) / 4.5 / (25 / 100)) = 18.8

Example: Maximum and minimum values of recommended amounts (wt%) of Epocros to be added when each of them is used for the base resin with acid value30.

EPOCROS to be added	K-2000 Series	WS-300	WS-500	WS-700
20mol%	5.9wt%	5.5wt%	2.4wt%	3.8wt%
100mol%	29.4wt%	27.5wt%	12.1wt%	18.8wt%

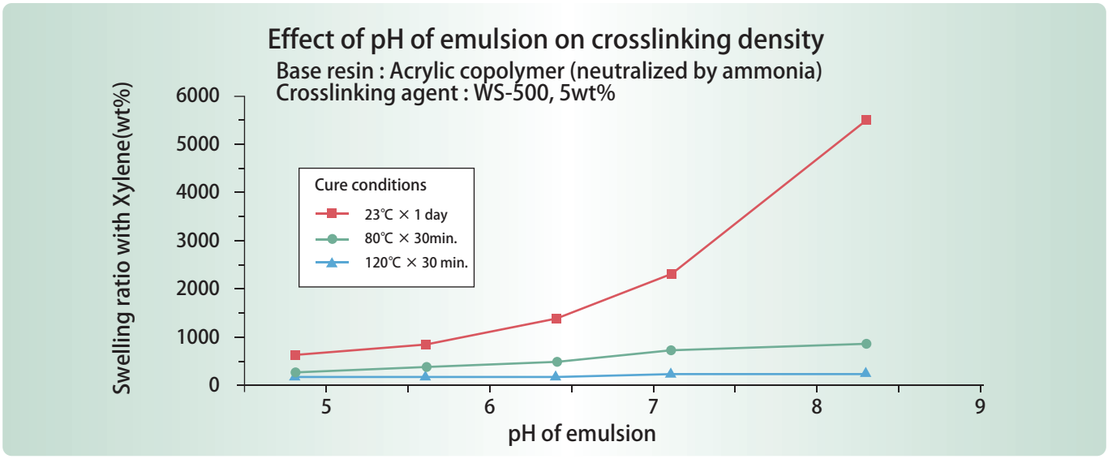
* NV:Nonvolatiles

Effect of the neutralization agent on reactivity

As Oxazoline group has quite low reactivity with Carboxylate, it has good pot life when mixed with waterborne resin which has neutralized carboxyl groups. While it is drying, as the neutralizing agents (such as ammonia or amine etc.) are being evaporated, the reaction occurs. Crosslinking speed is tend to be affected by the neutralizing agents for Carboxyl group. Therefore, when you need to harden it at low temperature, combination with the waterborne resins which have highly evaporative ammonia as its neutralizer is recommended.

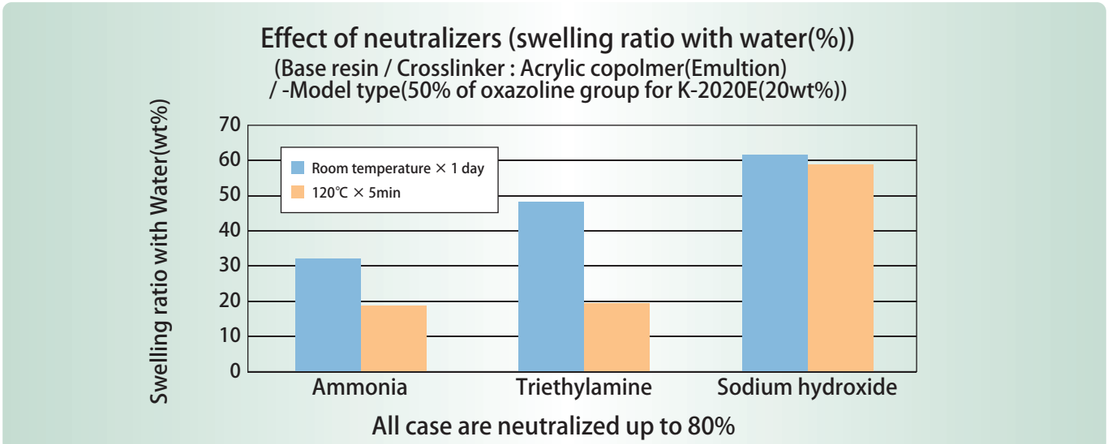
● Effect of pH

- Crosslinking density is inversely related to swelling ratio. As ammoniacal neutralizers have high evaporation rate, it is rarely affected by pH at elevated temperature (80℃ and 120℃).
- At room temperature (23℃), as ammoniacal neutralizer can not evaporate well, it is highly affected by pH.



● Effect of depending on types of neutralizer

- Reactivity of Epocros is affected by evaporation of neutralizer.
- At elevated temperature (120℃), neutralization by ammonia and triethylamine has similar reactivity



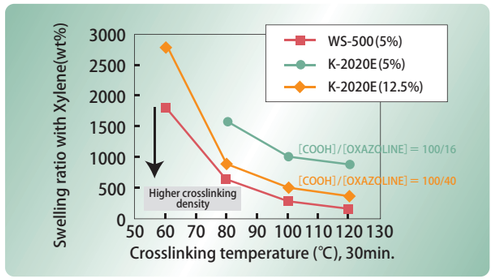
References

Reactivity

● Measuring swelling ratio with Xylene ① (Observing the heating condition to be hardened)

- By adding Epocros. swelling ratio with Xylene is suppressed, therefore solvent resistance is increased.
- Hardening performance is significantly increased at 80℃ and above.
- WS-500 demonstrated better hardening performance than K-2020E when same amount of additives were provided.

Base resin : Acrylic copolymer (emultion)

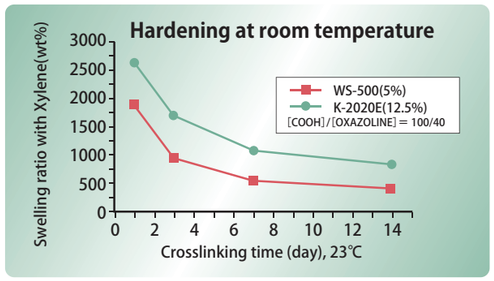


Crosslinking of emulsion with carboxyl groups

● Measuring swelling ratio with Xylene ② (Crosslinking at room temperature)

- By adding Epocros. swelling ratio with Xylene decreased, therefore solvent resistance increased.
- It can be hardened under the room temperature. However, significantly long curing time is required to get enough performance.
- WS-500 demonstrated better hardening performance than K-2020E when same amount of additives were provided.

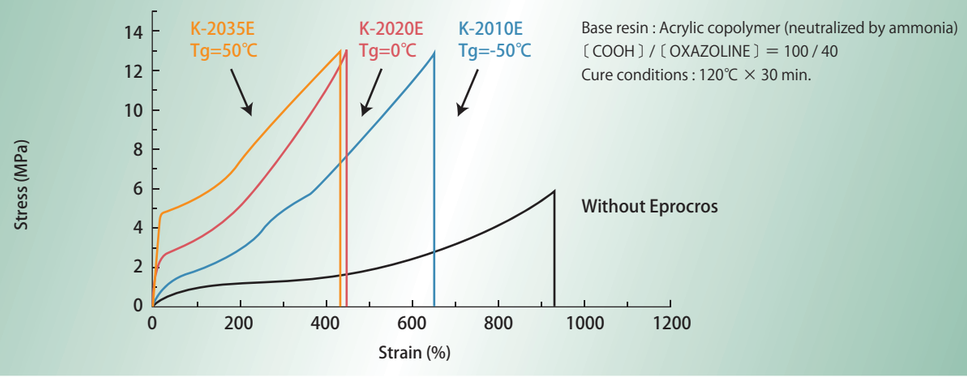
Base resin : Acrylic copolymer (emultion)



Crosslinking of emulsion with carboxyl groups at room temperature

● Film tensile strength test

- By adding Epocros, film tensile strength of the base resin is increased.
- Suitable Stress-Strain performance for each application can be obtained by selecting polymer Tg of K-series.

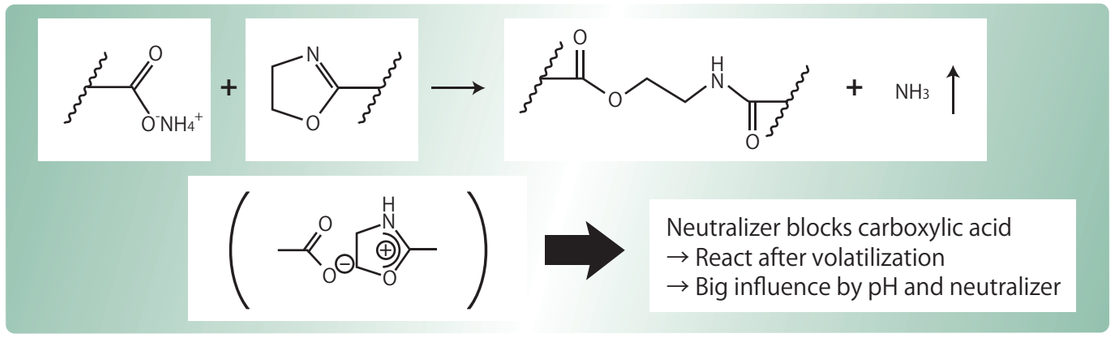


Base resin : Acrylic copolymer (neutralized by ammonia)
〔COOH〕/〔OXAZOLINE〕= 100 / 40
Cure conditions : 120℃ × 30 min.

Result of film tensile strength test

Reaction mechanism of storage stability

- The mixture of carboxylated resin and Epocros shows excellent storage stability under ambient conditions. This is attributed to blocking effect of neutralizers.
- As the neutralizer volatilizes, for example during the drying, the reaction is accelerated.
- The product can be prepared as one packaging



■pH : Low←→High
- Pot life : Short (two packaging) ←→Long(one packaging)
- Hardening temp : Low(room temp.) ←→Midle・High(than 80℃～100℃)

■Neutralizer :
- NH3 : Oxazoline group can react at low temperature
- Amine with high boiling temperature : Oxazoline group can react at elevated temperature
- NaOH etc : Oxazoline group needs acid catalist to react with carboxyl group

● Stability data of one packaging condition ①

Base resin : Acrylic copolymer (Emultion type, Acid value: 31mgKOH/g, nonvolatiles)
Storing condition: 50℃ × One month after mixing

- There is no significant difference on pH, viscosity, and MFT performance when stored for one month after mixing at 50℃. The tensile strength of films formed from these mixture show almost same value in this test.

	WS-500		K-2020E		Control
Added ratio(phr)*	5		5		0
Functional ratio of [COOH] / [OX]	100/40		100/16		
Storage period	Initial	1month	Initial	1month	Initial
pH	7.6	7.4	7.5	7.3	7.3
Viscosity(mPa.s)	39	40	32	28	35
MFT(℃)	10	11	14	13	12
Crosslinking Characteristics					
Swelling ratio(Xylene : wt%)	180	115	880	820	Dissoived
(Water : wt%)	7	6	8	8	9
Tensile strength					
Dry(MPa)	12.7	13.2	7.8	8.0	5.9
Wet(MPa)	11.8	12.7	6.4	6.3	4.9

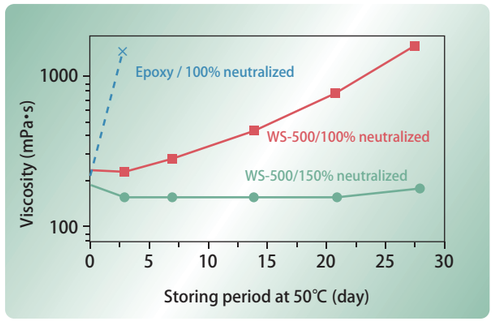
＊ phr : Parts per hundred resin (nonvolatiles)

References

● Stability data of one packaging condition ②

Base resin: Acrylic copolymer on the market (Emulsion
Acid value: 195 mgKOH/g nonvolatiles)
Storing condition: 50℃ x One month after mixing
・Epocros shows longer pot life in comparison with that of water-soluble epoxies.
・Pot life can be longer when base resin is over neutralized

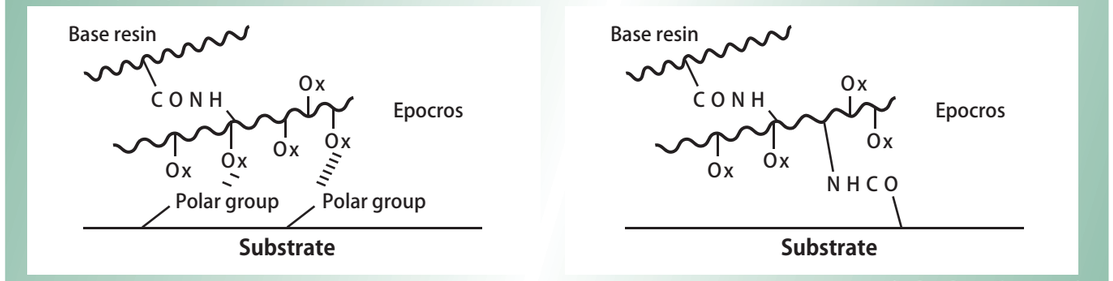
Storing stability (Viscosity change)



Improvement of Adhesion properties

・By adding Epocros, adhesion properties to various plastic substrates can be improved.
・The interaction between oxazoline group and hydrophobic group on surface promotes adhesion properties. Furthermore, formation of covalent bond with carboxyl group on substrate surface results strong bonding.

Imaginary diagram



(－Ox : Oxazoline group)

● Data of improving adhesion properties ①

Base resin: Acrylic copolymer (Emulsion type, Acid value: 26mg KOH/g, NV)
Substrate: PET film (100 μm)
Drying condition: 150℃ x one min.
Evaluation method: Peel test with pressure sensitive adhesion tape (at room temperature)

Crosslinker	Amount of addition	Adhesion*1	Water resistance of adhesion*2
No crosslinker	0%	－	－－
K-2020E	5%	＋	＋/－
Water soluble melamine	3%	－	－－
Water soluble epoxy	3%	＋/－	－
K-2020E itself	100%	＋	＋/－

＋: No peeling　＋/－: Partly peeled　－: Peeled almost entirely　－－: Entirely peeled

＊1 at room temperature
＊2 at room temperature after immersed in water for one day

● Data of improving adhesion properties ②

Base resin: Chlorinated Polypropylene (Emulsion type, Acid value:13 mgKOH/g, NV)
Subtrate: Polypropylene test panel
Drying condition: 80℃ x 30 min.
Evaluation method: Peel test with pressure sensitive adhesion tape (at room temperature)

Crosslinker	Amount of addition	Adhesion*1	Water resistance of adhesion*2
No crosslinker	0%	＋/－	－－
K-2035E	10%	＋	＋/－
WS-500	3%	＋	＋/－
Water soluble epoxy	3%	－－	－－

＋: No peeling　＋/－: Partly peeled　－: Peeled almost entirely　－－: Entirely peeled

＊1 at room temperature
＊2 at room temperature after immersed in water for one day

● Data of improving adhesion properties ③

Base resin: Acrylic copolymer (Emulsion, Acid value: 39 mgKOH/g, Acryset EMN-260E(Nippon Shokubai Co., Ltd.))
Formulation: Crosslinkers are added to provide 0.5mol of each functional groups against carboxyl groups in the base resin.
Substrate:PP (Polypropylene)
ABS (Acrylonitrile - Butadiene - Styrene) resin
PC (Polycarbonate)
PMMA (Polymethylmethacrylate)
Drying condition: 150℃ x one minute

Crosslinker	Amount of addition	Substrate			
		PP	ABS	PC	PMMA
No crosslinker	0%	－	－	＋	＋
WS-500	8%	－	＋	＋	＋
WS-700	8%	－	＋	＋	＋
Water soluble epoxy	6%	－	－	－	＋

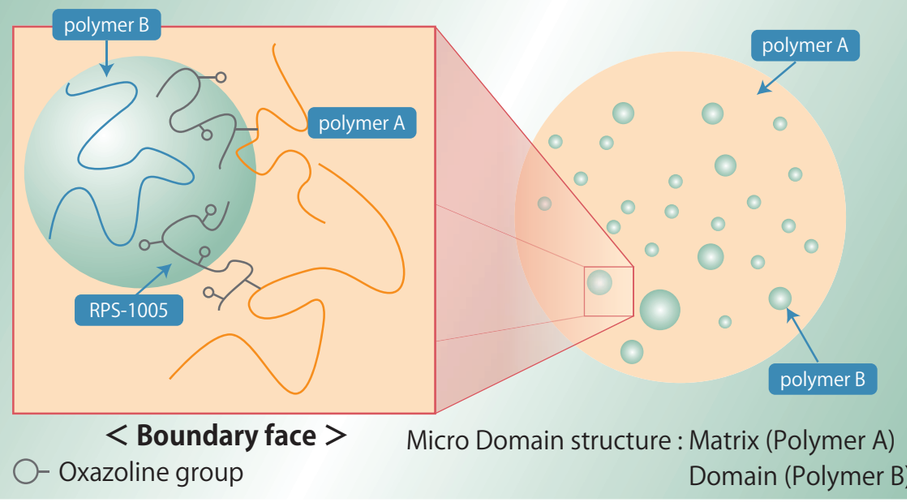
＋: No peeling　＋/－: Partly peeled　－: Peeled almost entirely　－－: Entirely peeled

PP (Polypropylene)
ABS (Acrylonitrile - Butadiene - Styrene) resin
PC (Polycarbonate)
PMMA (Polymethylmethacrylate)

EPOCROS RPS-1005

Epocros RPS-1005 is an amorphia type reactive polymer which has oxazoline groups as its pendant. By utilizing the characteristics of oxazoline groups as polar functional groups and high reactivity they have with carboxyl groups, Epocros is expected to have wide variety of application fields in thermoplastic area as compatibilizer and dispersing agent.

Imaginary diagram



Characteristics

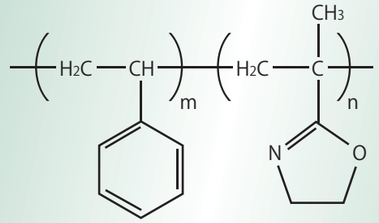
① Oxazoline groups have high reactivity with carboxyl groups. Being melted and kneaded with melt polymers with carboxyl groups, they can quickly generate graft polymers.
② It has highly stable viscosity when melted and kneaded under high temperature.
③ Customers can utilize polarity and ionic interaction arisen from oxazoline groups.

Examples of uses

・Compatibilizer
By utilizing the reactivity of the oxazoline groups, Epocros can realize micro dispersion of dispersing phase as well as improving physical characteristics of moldings (especially improvement on impact strength)
・Auxiliary agent for dispersing
Epocros can improve the dispersing status of pigments, fire retardants and bulking agents which are added into thermoplastic resins.
・Acid trapping agent
Epocros can improve heat stability of the moldings by trapping free acids generated in thermoplastic resins.
・Polymer chain extending agent
Epocros can improve viscosity of melting resins by introducing brunch structure using oxazoline groups as the reactive sites.
・Extruded laminated body
Laminated structure and laminated films can be generated without inserting adhesive layers between each layer by utilizing the reactivity between oxazoline groups and carboxyl groups contained in thermoplastic resins (ex. PET and / or Acid altered polyolefin)
・Dielectric constant reducer
The oxazoline group is used as a reaction point, and the dielectric constant is lowered by introducing a styrene unit.

Physical property basics of RPS-1005

● Structural formula



● Properties

Items		Property	Unit	Testing method
Main structure		Styrene	—	—
Appearance		White granule	—	—
Density		1.05	g/cm3	JIS7112(B)
Amount of Oxazoline groups		0.27	mmol/g・solid	Calculated Value
Molecular weight	Mn	Approx. 70,000	g/mol	GPC (Corresponding value to standard polystyrene)
	Mw	Approx. 160,000	g/mol	
Glass transition temperature (Tg)		109	℃	DSC method
Thermal decomposition temperature		320	℃	TG-DTA method weight decreasing temperature (measured under air atmosphere)
Melt flow rate (MFR)		6-10	g/10min	200℃, load 5Kg

Figures shown in the adove table are representative values; these are not to be considered product specifications

● Regulations

	Registering status
CAS No.	30174-74-4
Law concerning the Examination and Regulation of Manufacture,etc,of Chemical substances	6-1961
Industrial Safety and Heaith Law	9-650
TSCA [USA]	Registered
REACH [EU]	Not Registered
KECL [KOREA]	Phase in substance
IECSC [CHINA]	Registered
Fire Service Law	Nominated as a flammable material,synthetic resin