EPOLEAD PB3600 and PB4700*

(*PB4700 is a developmental product.)

-Epoxidized polybutadiene-

Contents

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DAICEL Group

1. Introduction

The EPOLEAD PB series is epoxidized polybutadiene which DAICEL Corporation commercialized with its epoxidation technique with peracetic acid.

The series, which has a lower epoxy equivalent than conventional epoxidized polybutadiene, is characterized by being excellent in compatibility with bis-A-type and cresol novolac-type epoxy resins.

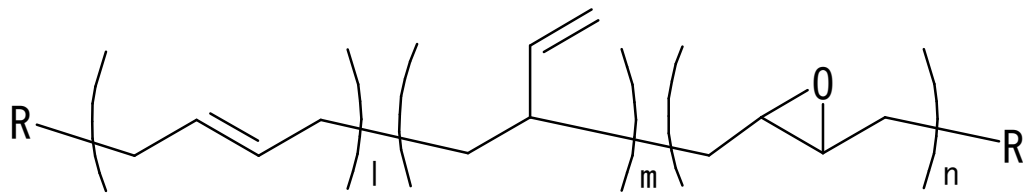
EPOLEAD PB is cured with a phenol resin or the like as a curing agent to provide cured product excellent in flexibility, and hence may be used for applications such as a can coating agent or the like.

Further, it may also be cured with an acid anhydride as a curing agent to provide cured product which is excellent in transparency and has reduced stress. It could be used in semiconductor sealant and similar applications.

EPOLEAD PB may also be used as a cationic electrodeposition paint or an aqueous paint through a reaction with an amine compound.

In addition, it is also applicable to a printed circuit board material and cationic coating.

Basic structure of EPOLEAD PB



R = H or OH

2. Products and general properties

2.1 General properties

EPOLEAD PB includes two kinds of products. Table 1 shows their general properties.

The two kinds of products have a major difference in terminal group.

PB3600, which has a hydroxyl group at the terminal and also has a hydroxyl group in the molecule, is characterized by having high polarity and a relatively high viscosity. PB4700 is characterized by having a lower viscosity and a lower epoxy equivalent than PB3600.

Table 1 General properties

	EPOLEAD PB3600	EPOLEAD PB4700
External appearance	Pale yellow liquid	Pale yellow liquid
Color (APHA)	25	15
Water (%)	0.01	0.01
Viscosity (mPa·s/45°C)	28,000	6,700
Acid value (KOHmg/g)	0.2	0.05
Terminal group	Hydroxyl group	Hydrogen
Epoxy equivalent	193	165

∗The numerical values described above are representative values and are not guaranteed values.

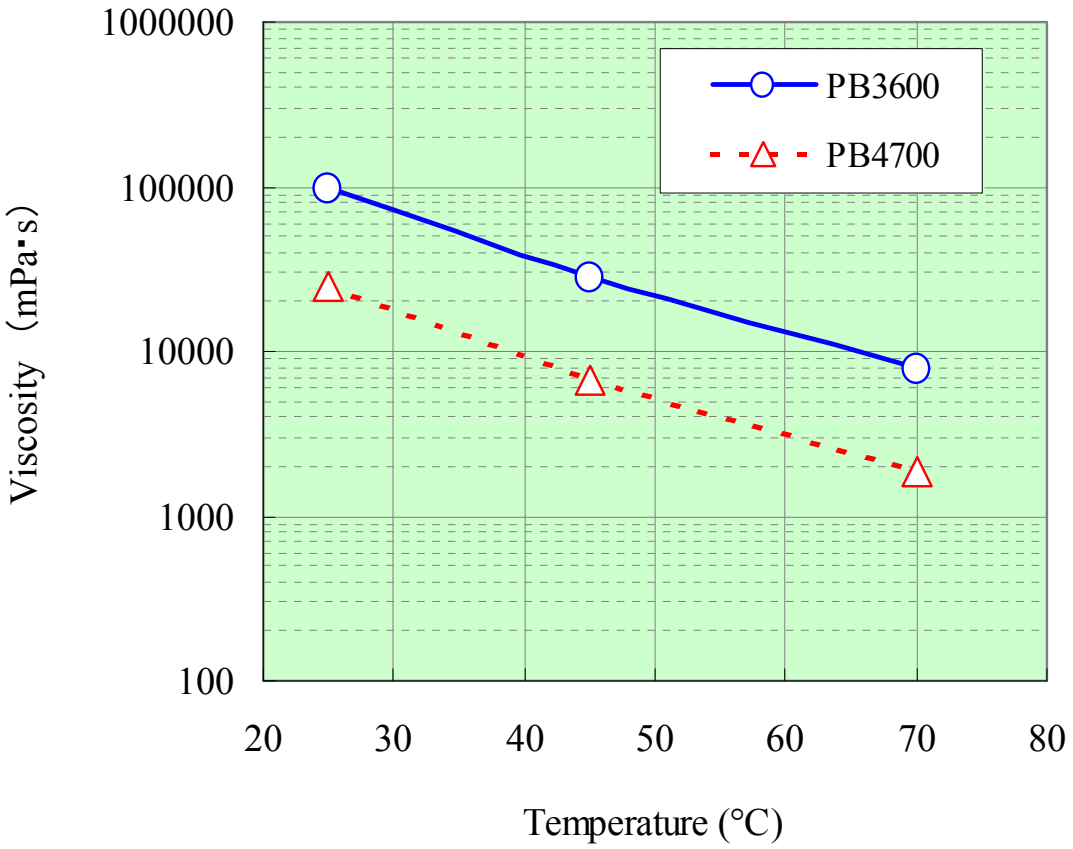
Characteristics of cured product

EPOLEAD PB is an epoxy resin which imparts rubber elasticity and can improve impact and bending resistance.

It should be noted that PB4700 has a low epoxy equivalent, and hence hard and brittle cured product tends to be obtained owing to an increase in cross-linking density when the blending ratio of EPOLEAD PB as an epoxy resin is set to 75% or more.

2.2 Temperature-viscosity curve

Fig. 1 Temperature-viscosity curve



2.3 Solubility in organic solvent

The EPOLEAD PB series has high solubility* in a number of organic solvents excluding aliphatic hydrocarbons and alcohols.

For example, the series is soluble* in ethyl acetate, butyl acetate, methyl ethyl ketone, methyl isobutyl ketone, toluene, xylene, tetrahydrofuran, chloroform, carbon tetrachloride, and acetone.

*Solubility (50 g or more/100 ml, at 30°C)

2.4 Compatibility with other epoxy resins

EPOLEAD PB is excellent in compatibility with other epoxy resins (bisphenol A-type and cresol novolac-type). Table 3 shows the results of an external appearance test.

Table 2 Tested resins

Product name	Epoxy equivalent g/eq	Softening point °C	Type	Manufacturer
jER 1009	2,400 to 3,300	144	Bisphenol A	Mitsubishi Chemical Corporation
Araldite ECN 1273	217 to 233	68 to 78	Cresol novolac	Huntsman Advanced Materials K.K.

Test method

1) An epoxy resin, a solvent*, and epoxidized polybutadiene are mixed with each other at a ratio of 50:50:140 (wt).

2) The mixture is applied onto a glass plate, dried, and then evaluated (coating film thickness: 100 μm, condition for drying: 24° C for 7 days).

Transparent: ○ Opaque: ×

Table 3 Properties of used epoxidized polybutadiene and results of external appearance test

Product name	Properties		Compatibility	
	Epoxy equivalent	Viscosity mPa·s/70°C	jER 1009	Araldite ECN 1273
PB-4700	168	1,850	○	○
PB-3600	198	8,000	○	×
E-1000-8.0[a)]	211	1,560	×	×
BF-1000[b)]	210	2,340	×	×

a) Manufactured by Nippon Petrochemicals Co., Ltd. (*old company name*)

b) Manufactured by ADEKA CORPORATION

* Diethylene glycol monobutyl ether was used as a dilution solvent for jER1009 and ethylene glycol monoethyl ether was used as a dilution solvent for Araldite ECN 1273.

EPOLEAD PB4700 is compatible with the above-mentioned epoxy resins irrespective of its blending ratio.

EPOLEAD PB3600 causes phase separation only when being mixed with jER 1009 in an equal amount [1:1 (weight ratio)] but shows compatibility when one of the resins is used in a larger amount than the other.

3. Curing of EPOLEAD PB with phenol resin

EPOLEAD PB is cured with a phenol resin as a curing agent to provide cured product excellent in impact resistance and bending resistance.

A metal alkoxide- or imidazole-based curing catalyst is effective as a curing catalyst.

A quaternary amine, a phosphate ester, toluenesulfonic acid, or the like exhibits little catalytic effect.

A variety of data are shown below.

3.1 Blending and curing methods

EPOLEAD PB and a bis-A-type epoxy resin (jER 1009) were used as epoxy resins and a phenol resin (RESITOP PS-2980: manufactured by Gunei Chemical Industry Co., Ltd.) was used as a curing agent.

Blending

The blending ratio of EPOLEAD PB in the epoxy resins was changed in the range of 0 to 100 wt% to examine physical property values of coating films.

Further, the curing agent was used in a 1/2 equivalent of an epoxy equivalent. In addition, $Al[OCH(CH_3)_2]_3$: aluminum isopropoxide as a curing catalyst was used in an amount of 1 part with respect to a resin solids content.

Conditions for curing

A test piece of SPTE: 50×150×0.3 (mm) was used and curing was performed on a plate heated to a temperature of 200° C for 10 minutes. The coating film thickness after the curing was 5 μm.

3.2 Physical properties of cured product

The physical properties of cured product obtained by curing a blend of EPOLEAD PB and a bisphenol A-type epoxy resin with a phenol resin as a curing agent are shown in the tables (EPOLEAD PB3600: Table 4, EPOLEAD PB4700: Table 5, E-1000-8.0: Table 6).

Table 4 Physical properties of coating films each including blend of jER1009 and PB3600

EPB blending ratio	External appearance	Rubbing test	Pencil hardness	Impact test (cm)	Tape peeling	T-bend
0	Transparent	○	H	30	10	2T
25	Transparent	○	H	40	10	3T or more
50	Transparent	○	H	45	8	1T
75	Transparent	○	3H	35	8	3T
100	Transparent	○	H	40	10	4T

When PB3600 is blended to prepare a coating film, impact resistance can be enhanced while adhesiveness is maintained at almost the same level. In addition, bending resistance (T-bend) can be imparted by setting the blending ratio to be 50%.

Table 5 Physical properties of coating films each including blend of jER1009 and PB4700

EPB blending ratio	External appearance	Rubbing test	Pencil hardness	Impact test (cm)	Tape peeling	T-bend
0	Transparent	○	H	30	10	2T
25	Transparent	○	H	50	10	4T or more
50	Transparent	○	2H	45	8	0T
75	Transparent	○	3H	30	6	4T or more
100	Transparent	○	2H	5	2	4T or more

When PB4700 is blended to prepare a coating film, the following tendency is observed. That is, a blending ratio of EPOLEAD PB in epoxy resins of 25 to 50% provides good impact resistance, whereas a larger blending ratio of EPOLEAD PB provides a hard film.

Bending resistance can be improved to 0T by setting the blending ratio to 50%.

Table 6 Physical properties of coating films each including blend of jER1009 and E-1000-8.0

EPB blending ratio	External appearance	Rubbing test	Pencil hardness	Impact test (cm)	Tape peeling	T-bend
0	Transparent	○	H	30	10	2T
25	Opaque	Δ	H	40	10	3T or more
50	Opaque	Δ	H	35	10	4T or more
75	Transparent	Δ	H	35	10	3T or more
100	Transparent	Δ	H	25	10	4T

In case of using another company's product, a cross-linking density is low and the coating film becomes opaque, although adhesiveness is satisfactory and impact resistance is also improved.

Description of terms in Tables 4 to 6

EPB blending ratio ..... Blending ratio of epoxidized polybutadiene in epoxy resins (wt%)

External appearance ..... The external appearance of a cured coating film was visually evaluated.

Rubbing test ..... Xylene/100 times

○: There was no or minor damage.

Δ: The entire rubbed portion became opaque.

×: A substrate was exposed.

Pencil hardness test (JIS K5400) ..... Measured with pencil scratching tester

Impact test (JIS K5400) ..... Measured with DuPont impact deformation tester

Tape peeling (JIS K5400) ..... Evaluated by cross-cut tape method.

T-bend ..... Measured in accordance with ASTM-D4145-83

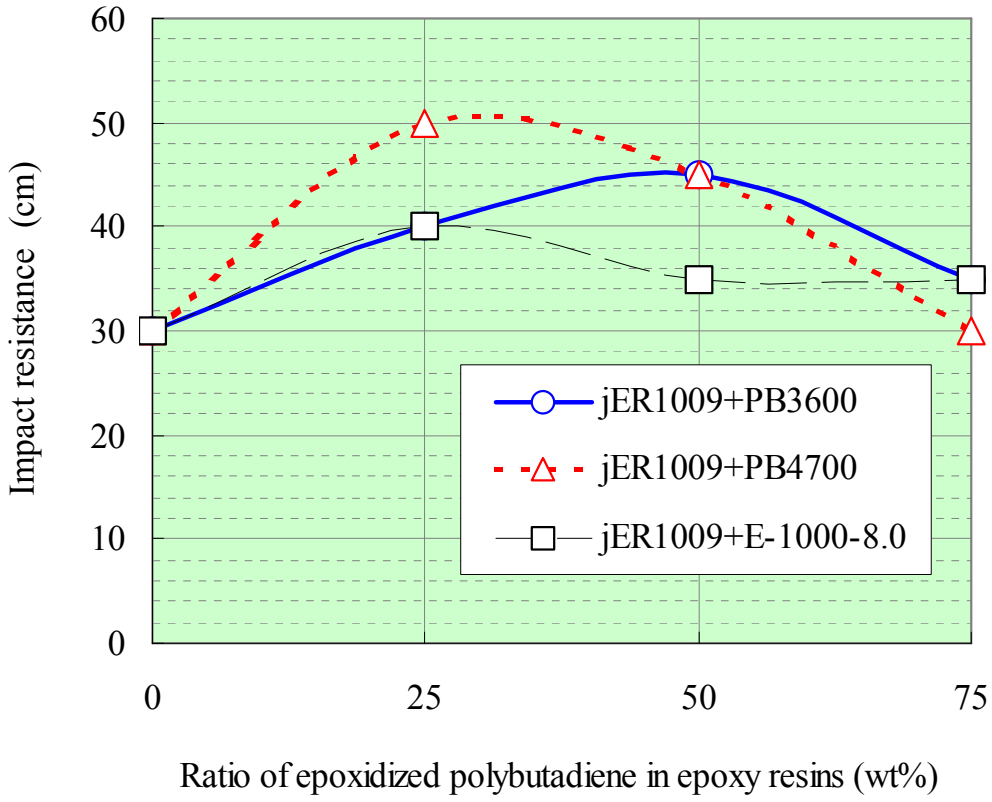
(the phrase "or more" means that measurement was not able to be performed owing to the absence of the residual substrate although rejection was made on the number of bending cycles of interest)

As illustrated in Fig. 2, coating films each including a blend of EPOLEAD PB show varying impact resistance.

An increase in blending ratio of PB4700 results in a reduction in impact resistance. This is probably because the cross-linking density was excessively increased to make the coating film hard.

EPOLEAD PB can be used at an appropriate blending ratio to impart rubber elasticity to a coating film.

Fig. 2 Impact resistance of coating films each including blend of epoxidized polybutadiene



Bending resistance was measured in order to confirm adhesiveness to a substrate and rubber elasticity of a coating film. As a result, as illustrated in Fig. 3, both of PB3600 and PB4700 showed improvements in performance to 0T to 1T only at a blending ratio of about 50 wt%.

A blend of the other company's epoxidized polybutadiene cannot be expected to make any further improvement in bending resistance in the case of using a bisphenol A-type epoxy alone. In contrast, EPOLEAD PB can be used at an appropriate blending ratio to remarkably improve bending resistance.

Fig. 3 Bending resistance of coating films each including blend of epoxidized polybutadiene

4. Application of EPOLEAD PB to UV cationic coating agent

EPOLEAD PB can be blended into a UV cationic coating agent to improve the bending resistance and impact resistance of a coating film.

Table 7 shows the physical properties of coating films in the case of blending EPOLEAD PB into Celloxide 2021P (alicyclic epoxy resin manufactured by DAICEL Corporation.

Conditions for curing

A test piece of Al H4000 (A5012P, thickness: 0.5 mm) was used and coated with a bar coater #8. Then, curing was performed at 80 W/cm (90 mJ/cm^2).

Table 7 Addition effect of EPOLEAD PB in UV cationic cured coating film

		EPOLEAD blend		Blank
		PB3600	PB4700	
Blend [a)]	Celloxide 2021P (wt%)	80	80	100
	EPOLEAD PB3600 (wt%)	20		
	EPOLEAD PB4700(wt%)		20	0
Physical properties of coating film	Pencil hardness (scratch/break)	2H/3H	2H/3H	2H/2H
	Rubbing test	○	○	○
	Adhesiveness (cut/tape peeling)	6/4	10/4	8/4
	Bending test (mm)	4	4	>10
	Impact test (cm)	35	40	<5

a) Containing a cationic catalyst: FX512 (manufactured by 3M Company) at 3 wt% and a leveling agent: FC430 (manufactured by 3M Company) at 0.3 wt%

Description of terms in Table 7

Pencil hardness test (JIS K5400) ・・Measured with pencil scratch tester

Rubbing test ・・・・・・Methyl ethyl ketone/10 times

○: There was no or minor damage, Δ: The entire rubbed portion became opaque, and ×: A substrate was exposed.

Adhesiveness (JIS K5400) ・・Evaluated by cross-cut method and cross-cut tape method

Bending test (JIS K5400) ・・The value is a diameter of a rod by which no crack or peeling is caused in a coating film.

Impact test (JIS K5400) ・・Measured with DuPont impact deformation tester (weight: 300 g).