

# High performance polyurethane flexible foam for heavy-duty gasket

Takeshi Nagaoka , Hiroyuki Ito, Naoya Yoshii

*Nippon Polyurethane Industry Co., Ltd.*

*Central Research Laboratory*

*440 Akiba-cho, Totsukaku*

*Yokohama 245-0052*

*JAPAN*

## ABSTRACT

In recent years, polyurethane flexible foam (PUF) has been applied to polymer gasket field because it meets fundamental requirements for its purposes as waterproof, dustproof, airtight and so on. However, in Japan, the PUF occupies only a small part of the total production of polymer gaskets.

This minor position in the conventional PUF gasket is mainly ascribable to its poor weatherability and low productivity.

In this situation, in order to expand the application areas of the PUF gasket, we investigated a new PUF gasket technology that can achieve high degrees of both the weatherability and the productivity.

## INTRODUCTION

The essential requirements for polymer gasket are watertightness, airtightness, and durability in the severe ambient condition. Nowadays, PUF is being applied to this field because it meets these fundamental requirements. However, in Japan, the PUF gaskets are very small quantity in the total production of polymer gaskets.

The reasons for this minor production of the PUF gaskets are the followings.

1. Since conventional PUF gaskets are easily deteriorated by direct sunlight, its application is limited to indoor use only.
2. The production of the PUF gaskets generally requires many processes, such as foaming, slicing, punching out, attaching on their works and so on. Furthermore, the residual PUF after punching out will be industrial waste.

Instead of the PUF, other materials such as silicone gum and ethylene-propylene-diene gum (EPDM) are being applied to the major part of this field. However, these materials also have some defects. For example, the silicone gum, which generally includes volatile impurities, spoils electronic interface. Hence this type of gaskets cannot be used around electronic devices. On the other hand, due to its poor adhesiveness, the production of EPDM gasket requires a lot of handworks, such as conditioning a surface to attach, laying adhesive, placing the gasket on their works and so on.

Under these situations, in order to expand the application area of the PUF, a new PUF gasket technology that can achieve high degrees of both durability and productivity was investigated in this study.

This paper provides our newly developed in-place PUF gasket technology showing excellent performance. The in-place foaming technology allows us to automate the production line and to obtain complicated shape products without extra processes. Again, the incomparable weatherability makes the application areas of the PUF gasket expand.

Control of both reactivity of the PUF and cross-section shape of the gasket is also discussed in this paper. Furthermore, the results about weatherability modification and the best composition of isocyanates for gaskets will be described, too.

The PUF gaskets with the newly developed technology are expected to take the major position in polymer gasket applications.

## EXPERIMENTAL

### Raw Materials

The raw materials listed in Table 1. were employed to prepare the test samples.

PUF systems based on Methylene-bis-(4-phenylisocyanate)(MDI) were applied in this study. Why the MDI base gasket systems have a lot of advantages is described as follows.

1) The reactivity of the MDI is higher than that of Toluene diisocyanate (TDI), so the MDI based PUF systems can improve the productivity.

2) Because of the low vapor pressure of the MDI, better condition can be provided to the working area.

3) As mentioned in previous papers [1-3], the MDI based PUF systems have excellent dynamic and static durability. The excellent performance of thickness change rate and hardness change rate at longtime durability test were certified in these papers. (Some typical data are described in Table 2)

All polyols described in Table3 are common polyether polyols and co-polymer polyols in Japan. Some additives were used for the purpose of the improvement of weatherability and coloring.

Incidentally, because of silicone-based surfactants spoils electronic interface, they were not used in this study.

**Table 1. Raw Materials**

Category	Name	Description
Isocyanates	CES-063	All-MDI prepolymer
	CES-064	Monomeric MDI /Polymeric MDI
	CES-066	All-MDI prepolymer
	CES-067	All-MDI prepolymer
	CES-068	All-MDI prepolymer
Polyols	Polyol-A	Polyether polyol
	Polyol-B	Polyether polyol
	Polyol-C	Polymer polyol
Thickeners	Thickener-a	Colloidal silica
	Thickener-b	Hydrogenation castor oil
	Thickener-c	Stearic acid

**Table 2. Comparison of various Systems of Seat Cushion**

Systems			TDI	T/M	MDI base	All-MDI
Density	Over-all	kg/m <sup>3</sup>	55.0	54.6	54.7	56.3
Hardness	25%ILD	N/314cm <sup>2</sup>	211	213	210	212
50%Compression set	Dry condition	%	4.6	4.4	4.6	4.2
	Wet condition	%	17.1	14.6	10.7	6.4
Creep value after dynamic creep test of 32400cycles		mm	24.2	21.9	16.4	16.1

### Conditions for Basic Examination

For the basic examinations such as optimization of density, hardness, physical properties, and reactivity, small-scale hand-mixed examinations with square block molds and free-rise buns were performed. The detailed conditions are shown in Table 3.

The gasket samples in this study were prepared by using a low-pressure dispensing machine. The details are shown in Table 4.

**Table 3. Conditions for Basic Examinations**

Mixing condition	7sec. at 7000rpm
Cups and Mold size	Cup : 500ml Mold : 200×150×50mm(aluminum)
Components temp.	25±1°C
Mold temp.	60±1°C
De-mold time	5min.
Crashing condition	Once after de-mold in 10sec. 5 stage rollers (in:40mm/out:20mm)
Conditioning before testing	23°C, 50% RH for 24hrs

**Table 4. Conditions for Gasket Sample Preparation**

Total components output	1.5 ~ 2.0g/s
Stirrer type	Spiral type
Mixing speed	3000rpm
Conditioning before testing	23°C, 50% RH for 24hrs

### Foam Property Measurements

Basic physical properties of the PUF were determined in accordance with JIS K-6400. Gasket samples were evaluated in accordance with below descriptions.

Appearances	: By sight	Hardness	:CSC2 type durometer
Weatherability	:JIS K-5600 7-7	Density	:JIS K-6268 A.

### Foam System Evaluation

To evaluate the gaskets as an enclosure for instruments of precision, a steel box was used as a holder. Constituent parts of the box are a main body, a lid and hinges. The main body and the lid can be tightly closed by a latch.

Along edges of the lid, PUF gaskets were applied using the low-pressure dispensing machine. Height of the gasket was controlled precisely, as the gasket layer to be 3mm constricted in thickness when the box is closed in place.

Examinations of damp proof and opening/shutting durability after 24hrs cure are done under following conditions.

\*The cure condition is described in Table2.

Opening/shutting durability evaluation

: Inspect the gaskets surface by sight after 10,000 times repeated operations of opening and shutting of the lid.

Damp proofing evaluation

: Inspect inside of the box by sight and touch after 1week exposure to 50°C, 70%RH.

## RESULTS AND DISCUSSION

### Viscosity Optimization

Since gaskets exert their abilities when they are at reversible deformation between the body and the lid of the box, they have to have enough thickness to reduce against given width. In the case of PUF gaskets, it is necessary to restrain horizontal expanse of poured isocyanate/polyol mixture to obtain enough height of the gasket. Since increasing viscosity of the raw materials seemed effective for this issue, a lot of thickeners applied as ingredients for polyol mixtures.

According to the viscosity measurements, it was confirmed that Thickener-b worked effectively. (Table 5) However, because the Thickener-b was solid in low temperature, it was necessary to heat the polyol mixture up to 90°C to obtain homogeneous liquid. Furthermore, the effects of the Thickener-b sometimes became unstable depending on mixing conditions.

Accordingly, some other methods to optimize the viscosity of the polyol mixtures were examined. Results of these are described in Table.6. In this study, a co-effect of the Thickener-a and specific catalyst was observed. When the Thickener-a was combined with the Catalyst-c, viscosity of the polyol mixture was increased to same level with the case of Thickener-b. In addition, the viscosity of the polyol mixture include these additives was stable in any mixing conditions.

Consequently, the combination of Thickener-a and Catalyst-c was adopted as indispensable ingredients in later experiments.

**Table 5. Examination of Thickeners**

Polyol-A	30		
Polyol-B	20		
Polyol-C	50		
H <sub>2</sub> O	1		
Thickener-a	2.5	0	0
Thickener-b	0	2.5	0
Thickener-c	0	0	2.5
Viscosity (mPa·s at 25°C)	2500	23100	2100

**Table 6. Examinations of Thickeners 2**

Polyol-A	30			
Polyol-B	20			
Polyol-C	50			
H <sub>2</sub> O	1			
Thickener-a	2.5			
Catalyst-a (trimerization)	0	1	0	0
Catalyst-b (strong base compound)	0	0	1	0
Catalyst-c (general amine)	0	0	0	1
Viscosity (mPa·s at 25°C)	2500	3400	28000	29700

## Control of Reactivity

Shortening its cycle time in a product line is one of the most important issues for the gaskets and it is directly affected by PUF reactivity. However, in order to accelerate the reaction of the PUF, both using active catalysts and adding some amount of the catalysts activate all stages of the PUF foaming reaction. Especially, acceleration of early stage of the reaction generates a projection, which causes deterioration of the caulking ability of the gasket, at the point where the gasket is jointed by start-to-end of their pouring. This phenomenon is brought by the different degrees of the PUF reaction between start and end of the pouring.

Therefore examinations to achieve both extension of the cream time (C.T.) and reduction of the total reaction time (tuck-free time) were done by hand-mixed cup-foaming. (Table 7)

**Table 7. Control of Reaction Rate**

Polyol-A	30					
Polyol-B	20					
Polyol-C	50					
H <sub>2</sub> O	1.5					
Thickener-a	2					
Extender	0	0	0	1.0	2.0	3.0
Catalyst-c	0.5	0.7	1.0	0.7	0.7	0.7
Cream Time (sec.)	42	20	4	38	53	83
Rise Time (sec.)	150	101	59	109	127	158
Tuck-free Time (sec.)	890	650	500	290	280	210

In this study, a co-effect of the catalyst and the specific extender was observed. When the extender was combined with the Catalyst-c, contradictory reactivity was integrated, namely, low initial reactivity consists with fast tuck-free time.

It was understood that the phenomenon originated from different reactivity of multiple hydroxyl groups of the extender.

In the first reaction stage, outward hydroxyl groups react with isocyanates, but hydroxyl groups located in midmost of the extender molecules remain owing to their steric hindrance. In this stage, reaction is progressing favorably but the reactants have enough low molecular weight to maintain the low viscosity of the mixture. And seemingly the reaction rate was delayed.

When inside temperature of the PUF reaches high enough, the reaction progress to next stage then residual hydroxyl groups react with isocyanates. In this stage the formation of the cross-linkage rapidly takes place then tuck-free time is reduced in spite of the slow C.T.

According to these results, the Thickener-a, the Catalyst-c and the Extender were adopted in later examinations.

## Weatherability

In case of panelboards and switchboards, a considerable number of them are located outdoors. And gaskets for these purposes are required superior weatherability than the indoor use.

Generally, to improve the weatherability, addition of light stabilizers is effective. Therefore at first, various kinds and quantities of the light stabilizers for weatherability modification are examined. (Table 8)

The CES-066 was used as an isocyanate component and gasket samples were formed by low pressure dispensing machine. The weatherability test was carried out by a xenon weathometer WEL-SUN-HC (SUGA Test Instruments Co., ltd)

By inspection of gaskets surface, the degrees of color change and presence of cracks were evaluated. The results are expressed by three phases described below. (Table 9)

- ++ : There is no change of color and no crack.
- + : Slightly change of color to white and there is a few cracks of very small size.
- : White colored and there are many cracks.

**Table 8. Additives for Weatherability improvement**

Name	Description
Additive-a	Mixture product of UVA
Additive-b	Benzotriazole type UVA
Additive-c	Low Molecular Weight type HALS
Additive-d	Mixture product of AO and High Molecular Weight type HALS
Additive-e	High Molecular Weight type HALS
Additive-f	Chyanoacrylate type UVA

**Table 9. Comparison of Stabilizers**

	Ref	A	B	C	D	E	F	G	H	I
Additive-a	0	5	0	0	0	0	0	0	0	0
Additive-b	0	0	5	0	0	0	0	2.5	0	2.5
Additive-c	0	0	0	5	0	0	0	2.5	2.5	0
Additive-d	0	0	0	0	5	0	0	0	0	0
Additive-e	0	0	0	0	0	5	0	0	0	2.5
Additive-f	0	0	0	0	0	0	5	0	2.5	0
Result	-	-	-	+	+	+	-	+	+	+

From results of 200 hours irradiation, an effects of ultraviolet rays absorbents (UVA) were confirmed as not sufficient. It is considered that a toner, which was added for the coloration, adsorbed UV rays. So the performances of UVA were not exerted [3-4].

On the other hand, hindered amine type light stabilizers (HALS) showed a good result. For further optimization we decided to compare them in 500 hours in irradiation time (Table10).

From this examination, the Additive-d performed the best and an excellent effect was observed in 15pbw. So the Additive-d was hired in later study. Besides, we were later informed the Additive-d was the mixture of high molecular weight HALSs and the antioxidants (AO). It is not yet cleared about detailed mechanism of co-effect of a HALS and an AO, but it is being accepted in a lot of cases. [4]

**Table 10. Comparison of HALS**

	Ref	K	L	M	N	O
Additive-c	0	0	0	0	0	15
Additive-d	0	0	0	0	15	0
Additive-e	0	5	10	15	0	0
Result	-	-	++	++	+++	-

## Composition of Isocyanate

With a hand-mixed preparation of PUFs into square block molds, optimization of a composition of an isocyanate was examined. (Table 11)

When a PUF is used as a gasket of switchboard and a weather strip, it is forced to be under compression state by those opening and shutting operations. Under these situations, a compression set and mechanical properties are regarded as important properties for the gaskets. It is well known that the properties are influenced by changes of the number of average functional groups (functionality) of isocyanate.

**Table 11.** Comparison of Isocyanate Compositions

Polyol mixtures	Polyol-A		30				
	Polyol-B		50				
	Polyol-C		20				
	Catalyst-c		1.0				
	H <sub>2</sub> O		2.5				
	Extender		3				
	Thickener-a		2.5				
	Additive-d		15				
	Toner		1				
NCO Index		60	59	60	57	53	
Isocyanates	CES-066	47					
	CES-067		38				
	CES-068			36			
	CES-063				34		
	CES-064					30	
Number of the average functional groups of Isocyanate		2.16	2.25	2.28	2.31	2.51	
Density	Over-all	kg/m <sup>3</sup>	159	160	158	160	159
Hardness	25%ILD	N/314cm <sup>3</sup>	230	233	231	232	230
Mechanical properties	T B	kPa	143	114	89	85	64
	EB	%	164	129	105	102	97
	TR	N/cm	8.5	5.6	4.8	4.2	3.2
50% Compression set	50% dry set	%	41.1	25.9	8.0	7.5	5.5

It was effective to obtain excellent mechanical properties to choose the isocyanates with low functionality. On the contrary, the isocyanates with high functionality were effective to improve the value of compression set.

The detail is later described but we chose the isocyanate with relatively high functionalities, because improving the compression set had the priority comparing with improvement of physical properties as a gasket.

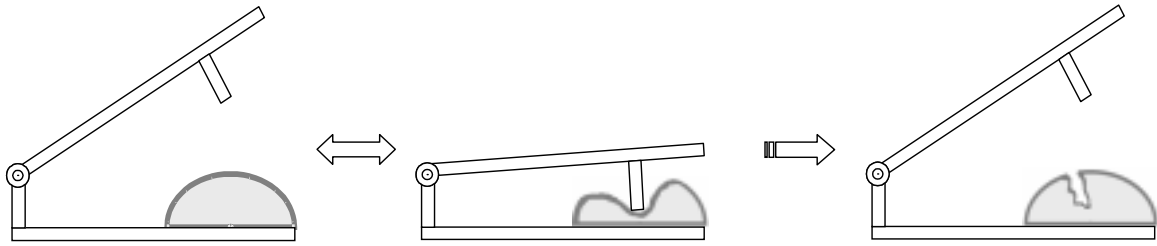
## Evaluation as Precision Instrument Enclosure

By forming a gasket on a precision instrument container directly, some important properties were evaluated. The main evaluations were 10,000 times of opening/shutting examination and dampproofing examination.

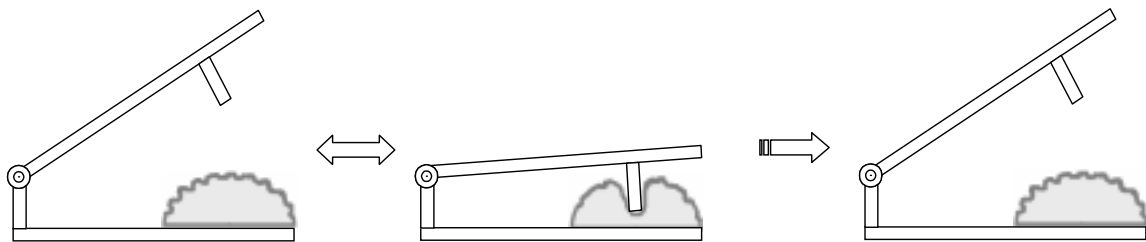
Even if dampproofing performance was good soon after forming, when cracks occur in the skin layer by an opening/shutting examination, the performance will deteriorate remarkably.

Thus, the opening /shutting durability was regarded as the most important issue. In the beginning, regardless of high mechanical properties of isocyanate CES-066, the result of the opening/shutting test was not enough.

During the examination, the skin layer is expanded many times by a member of the lid. Because a skin layer of general PUF was thin and smooth, it was supposed that a degree of expansion of the skin layer were too extreme, so that a crack was taken place easily. (Figure 1)



**Figure 1.** Transformation schematic view of a gasket made with CES -066 of opening/ shutting examinations



**Figure 2.** Transformation schematic view of a gasket with some wrinkles on its surface

Therefore, we tried to make some wrinkles on the skin layer like images in Figure 2. When the skin layer was expanded, the formed wrinkles would act as a growth margin and the gasket was able to avoid crack on their skin layer.

As an effective manner to form wrinkles on the skin layer, making cell structure coarse was expected from past experiments. The following techniques are generally applied to make cell structure coarse in PUF.

- : Use small amount of ethylene-oxide-capped polyols
- : Add some cell openers
- : Increase blowing catalyst
- : Increase foaming agents(water)
- : Add some fillers

The results of emergence of the wrinkles on the skin and opening/shutting examinations are shown in Table 12.

In the case of , because of severity of formability, it was thought that control of forming conditions were difficult. In the case of , and , inside cell structure of the gasket was observed as coarse slightly, but no wrinkle was observed on the skin layer.

When a hydrophobic colloid silica was applied as a filler, in the case of , obvious wrinkles were formed on the skin layer. After an opening/shutting examination, the skin layer was not damaged in case of , and this gasket passed a dampproofing examination after the opening/shutting test.

It is quite interesting that two types of colloid silica acted as different roles in the system.

**Table 12. Results of Modification of the Skin Layer**

	Ref.					
Polyol-A	30	30	30	30	30	30
Polyol-B	20	0	20	20	20	20
Polyol-C	50	50	50	50	50	50
Extender	3	3	3	3	3	3
Thickener-a	2.5	2.5	2.5	2.5	2.5	2.5
Additive-d	15	15	15	15	15	15
Catalyst-c	1.0	1.0	1.0	1.0	1.0	1.0
Toner	1.0	1.0	1.0	1.0	1.0	1.0
Low ratio of Ethylene-oxide-capped Polyol	0	20	0	0	0	0
Cell opener	0	0	5	0	0	0
Blowing catalyst	0	0	0	0.2	0	0
H <sub>2</sub> O	2.5	2.5	2.5	2.5	3.0	2.5
Filler	0	0	0	0	0	0.5
Presence of some Wrinkles on the skin layer	None	-*	None	None	None	positive
State of the Skin Layer after an Opening and Shutting Examination	Crack	-*	Crack	Crack	Crack	No Change
Dampproofing examination	Failure	-*	Failure	Failure	Failure	Pass

\* In the case of i, because the foam sank at the time of foaming, gasket shape was not provided.

In this study, we found a way to improve seemingly the strength of the gasket without improvement of the mechanical properties of the PUF. The fact allowed us to use relatively high functional isocyanates as CES-063 in the gasket system. Finally all-important properties for precision instrument enclosure were achieved in this study.

We established the newly developed PUF gasket system that could endure through severe conditions as a polymer gasket and shows good caulking performances.

## CONCLUSIONS

In this study, we investigated viscosity of raw materials, reactivity control, weatherability modification, composition of isocyanate and evaluation as a precision instrument enclosure. The discussion summarized as follows.

The viscosity of polyol mixture was optimized by a combination of colloidal silica with specific catalyst. And it made the gasket system to obtain enough thickness even if the initial reaction rate was delayed.

We found that some extender was effective to delay reaction in early stage only. This effect allowed us to increase a catalyst in quantity for improving cure characteristics, without the projection on the gasket.

In weatherability modification, we confirmed that it was effective to add a mixture product of AO and high molecular weight type HALS.

The number of the average functional groups of isocyanate influences both the mechanical properties and the compression set, which is important performance for gasket.

The mechanical properties and compression set are contradicting performance. But, when some wrinkles were foamed on the skin layer of gasket, strength as a gasket seemingly turned into strong.

The gasket system, which we developed, has high degrees of both weatherability and productivity. And it will be adopted to a Japanese manufacturer in a few days.

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## BIOGRAPHIES

### Takeshi Nagaoka



Takeshi Nagaoka joined Nippon Polyurethane Industry Co., Ltd. in 1999 after receiving B.S. and M.S. degree in Material Science and Engineering from Yamagata University in 1997 and 1999, respectively. He has engaged in the R&D of flexible polyurethane foam and he currently works for R&D of new MDI flexible polyurethane foams at Central Research Laboratory in Yokohama.

### Hiroyuki Ito



Hiroyuki Ito joined Nippon Polyurethane Industry Co., Ltd. in 1982. He has worked on developments flexible polyurethane foam for 24 years. He is currently a team reader of the flexible polyurethane foam group at Central Research Laboratory in Yokohama.

### Naoya Yoshii



Naoya Yoshii joined Nippon Polyurethane Industry Co., Ltd. in 1990 after receiving B. S. degree in Industrial Chemistry from Kyushu University. He has worked on developments of TPU, MDI production, and flexible polyurethane foam. He is currently a reader of the flexible polyurethane foam group at Central Research Laboratory in Yokohama.