

Water-Blown Polyurethane Rigid Foam Modified with Maleate

SATOSHI MURAYAMA, KENJI FUKUDA, TADASHI KIMURA and TOSHIAKI SASAHARA

Nippon Polyurethane Industry Co.,Ltd.

Central Research Laboratory

440 Akiba-cho, Totsuka-ku, Yokohama, JAPAN

ABSTRACT

Water-blown polyurethane rigid foam has serious disadvantages, i.e. friability and resulting lower adhesion strength. In order to resolve the problems, maleate was added to polyol-premix containing water or to polyisocyanate, with both of which maleate does not react.

In spite of high stability of the maleate-containing polyol-premix or polyisocyanate, when the polyol-premix and the polyisocyanate were mixed, maleate reacted immediately with primary amine, generated by the reaction of isocyanate and water, to secondary amine. Then the secondary amine reacted with another isocyanate to "substituted-urea linkage" having moderate cohesive property related with bulky maleate residue.

By the addition of maleate, the friability and the adhesiveness were considerably improved. Furthermore, dimensional stability of the modified rigid foam did not deteriorate by addition of enough maleate to improve the friability. Computer simulation substantiated that the reactions started from maleate and primary amine were reasonably occurred during the foam preparation.

Thus, water-blown polyurethane rigid foam of which friability and adhesiveness is improved can be provided by only mixing of inexpensive maleate.

INTRODUCTION

In order to prevent the ozone layer from destruction, production of HCFC-141b has already been abolished, despite its useful properties as blowing agent for polyurethane (PUR) rigid foam manufacture. Hydrofluorocarbons (HFCs), hydrocarbons (HCs) and water are nominated for promising alternative blowing agent [1]. However, each of these blowing agents suffers at least one disadvantage compared with HCFC-141b, e.g. cost for HFCs and combustibility for HCs.

Water-blown PUR rigid foam has serious defects. Among all these problems, friability that leads to lower adhesiveness is the most important. On the other hand,

water as a blowing agent has many advantages, such as low cost, easy handling, low global warming effect, incombustibility, etc. Therefore, if solution to the problems is discovered, there is no doubt that water becomes the best blowing agent for PUR rigid foam. However, supposing a solution is found, there is no sense in a complex or an expensive solution.

Many approaches have ever been investigated from the variety of viewpoint [2-5]. Nevertheless, properties of water-blown PUR rigid foam are still inferior to the foams blown with HFCs or HCs.

In general, friability of water-blown PUR rigid foam is prominent at surface layer, and tends to bring about destruction of the surface layer. As a result, adhesiveness of the foam to another material is remarkably deteriorated. The origin of friability is immoderate cohesion of urea linkage created by the reaction of isocyanate and water, both of them is essential for the formation of water-blown PUR foams. On the other hand, the strong cohesion property of urea linkage is helpful to the strength of rigid foams.

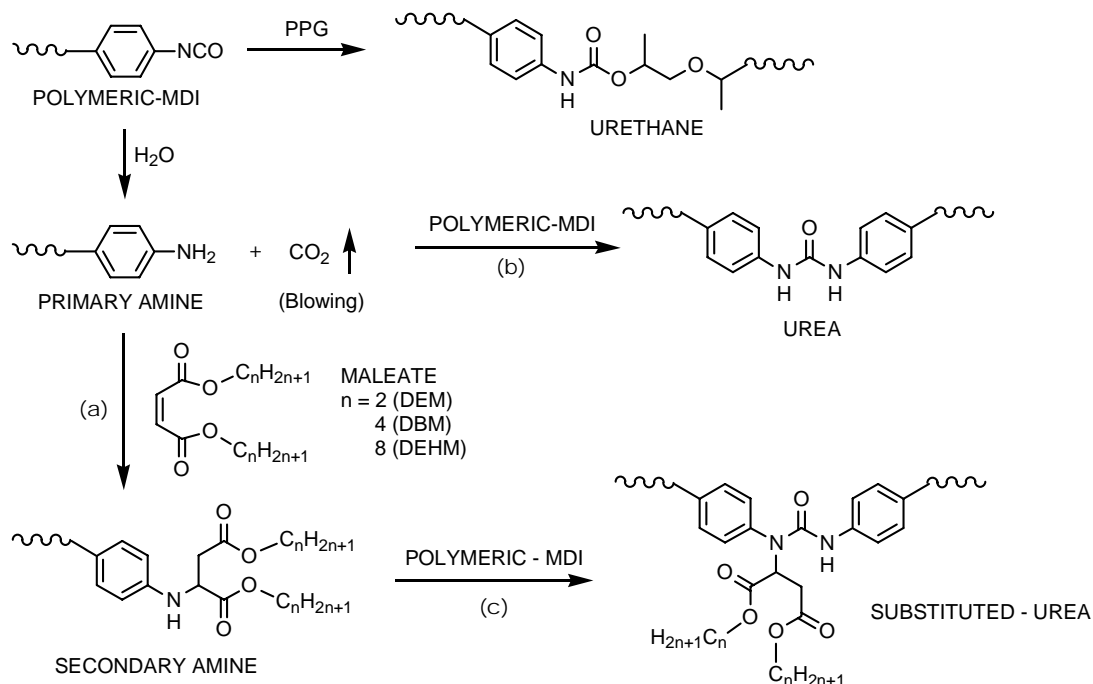
A simple, easy and novel approach based on maleate additives to solve the friability and the lower adhesiveness of water-blown PUR rigid foams is reported here.

EXPERIMENTAL

Materials and Formulation

Polyol-premix was prepared by mixing of polypropylene glycol (PPG), water as blowing agent, flame retardant, surfactant, and catalyst. One of maleate was selected among diethyl maleate (DEM), dibutyl maleate (DBM) or di-2-ethylhexyl maleate (DEHM), and mixed with the polyol-premix.

Maleates do not react with hydroxyl compound, water, and any other compound included in the polyol-premix. If necessary, maleate can be mixed with polyisocyanates because it does not react with isocyanate as well.



Scheme 1. Reaction paths of the water-blown PUR rigid foams modified with maleates.

A Polymeric-MDI (Millionate MR-200, Nippon Polyurethane Industry Co.,Ltd.) was used as polyisocyanate.

Table 1. Formulations

System-A	Polyol-premix		
	PPG (OHV=350)	100	pbw
	Water	6	pbw
	Flame Retardant	10	pbw
	Surfactant	3	pbw
	Catalyst	0.1	pbw
	DEM	0 – 9.6	pbw ¹⁾
Polyisocyanate			
MR-200 INDEX = 100			
System-B	Polyol-premix		
	PPG (OHV=400)	100	pbw
	Water	6	pbw
	Flame Retardant	8	pbw
	Surfactant	3	pbw
	Catalyst	0.8	pbw
	Maleate (either DEM or DBM)		
DEM	0 – 9.6	pbw ²⁾	
DBM	0 – 15.2	pbw ²⁾	
Polyisocyanate			
MR-200 INDEX = 100			
System-C	Polyol-premix		
	PPG (OHV=400)	100	pbw
	Water	7	pbw
	Flame Retardant	10	pbw
	Surfactant	2	pbw
	Catalyst	2	pbw
	Maleate (either DBM or DEHM)		
DBM	0 – 10	pbw ³⁾	
DEHM	0 – 10	pbw ⁴⁾	
Polyisocyanate			
MR-200 INDEX = 100			

1) 0 – 20 mol% of water

2) 0 – 20 mol% of water

3) 0 – 11.3 mol% of water

4) 0 – 7.6 mol% of water

Typical formulations of polyol-premix and polyisocyanate are shown in Table 1. System-A is a

semi-continuous-cell foam system, and System-B and -C are closed-cell system. Closed-cell content of System-A was 65-75%, and of System-B and -C were 92-97%. System-C contained more water than system-B. Therefore, system-C tends to friable compared to system-B without any invention.

Foam Preparation

A polyol-premix containing maleate and MR-200, both of which temperatures was adjusted at 20°C, were mixed and vigorously stirred for 5 sec with hand mixer. Then the mixture was immediately pored into an upright aluminum mold (height = 500 mm, width = 500 mm, thickness = 60 mm), which temperature was adjusted at 40°C. Over pack ratio of all the foams were controlled at 120%. After 10 min of curing period, PUR foam prepared was taken out of the mold.

Measurement

Steel plate (100 mm × 100 mm) was previously attached to the inner face of the aluminum mold in order to measure adhesion strength. The steel plate had attached to a foam surface during the formation of the foam. Adhesion strength was defined as peeling strength between the steel plate and the foam. Compression strength and dimensional stability were measured according to ASTM D 1621 and ASTM D 2126, respectively. FT-IR spectra were measured by ThermoNicolet AVATER-360 attached with ATR apparatus.

Computer Simulation

In order to understand each of the chemical reaction involved in the foam preparation, computer simulation was employed. Molecular orbital calculations were carried out

using MOPAC 2002 included in CAChe Worksystem Pro 5.5 [6] and Gaussian03W [7].

Reactions (a), (b) and (c) represented in Scheme 1 were simulated by MOPAC with PM5 Hamiltonian. Model structures of polymeric-MDI, primary amine and maleate used in MOPAC calculations were 4,4'-MDI, 4,4'-MDA and DBM, respectively. In the first place transition state structures were detected, then the respective intrinsic reaction coordinate were calculated. Each energy values of reactants, transition states and products were determined. Activation energy (E_a) and heat of formation (ΔH) were determined as differences of these energies.

By using the structures optimized by MOPAC as initial structures, density functional theory (DFT) calculations with B3LYP/6-31+G were executed to optimize to precise structures. In order to reduce CPU time to practical, however, small molecular models such as phenyl isocyanate, phenyl amine and dimethyl maleate were used in DFT calculations. Reaction (c) could not be calculated by using DFT method because the model is too large to calculate within practical CPU time. Precise energies of the reactants, transition states, and products were estimated and corrected by thermal and zero-point energy with B3LYP/6-311+G(d,p). Precise E_a and ΔH were determined in a similar manner as MOPAC.

RESULTS AND DISCUSSION

Foam Preparation

All the foams containing maleate were successfully prepared.

Maleate acted as a viscosity-decreasing agent for polyol-premix according to its low viscosity and excellent miscibility, resulting a good mixing of the polyol-premix and the polyisocyanate.

Adhesion strength

Figure 1 shows the effect of DEM content on the adhesion strength of the System-A foams. The adhesion strength of the foam to metal plate increases with increasing of DEM content. Excess amount of DEM, however, impairs the adhesion strength.

Amount of DEM, abscissa of Figure 1, was determined according to the molar ratio to the amount of water as blowing-agent. As shown in Scheme 1, maleate reacts with equivalent primary amine, which produced by reaction of isocyanate and water. Molar quantity of water, primary amine and maleate is equal. Consequently, supposing all the secondary amine formed converts quantitatively to "substituted-urea", it can be assumed that the proportion of "substituted-urea" compared to un-substituted urea equals to that of DEM compared to water.

The adhesion strength of the foams was spoiled by the excess amount of DEM. It appears that the moderate amount of maleate is present.

Figure 2 shows the effects of DEM or DBM content on the adhesion strength of the foam System-B. The foams do not adhere to the metal plate without containing of maleate. The surface layer of the foam was quite friable and easily collapsed. Thus measuring of the adhesion strength was impossible.

As shown in Figure 2, the adhesion strength of the foams is distinctly improved by the addition of DEM. With increasing of DEM content, the adhesion strength increases within the DEM content less than 15 mol%. This phenomenon was similar to the System-A.

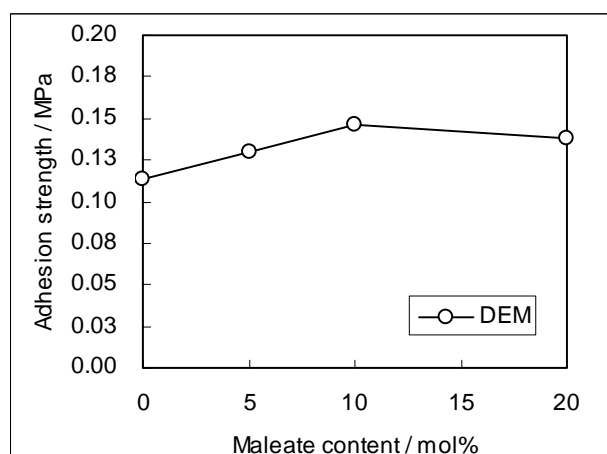


Figure 1. Effect of maleate content on the adhesion strength of System-A foams.

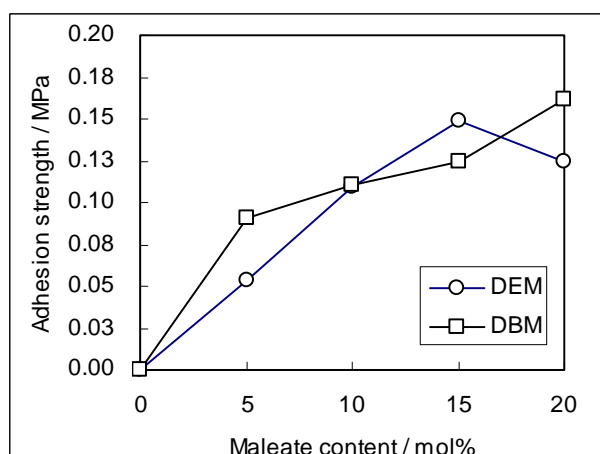
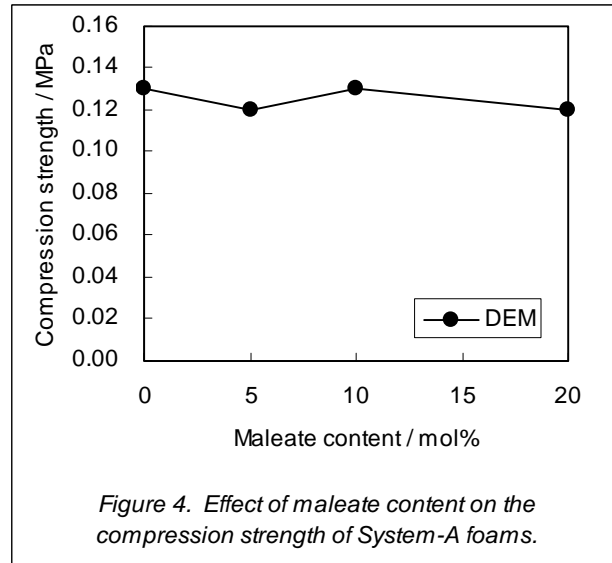
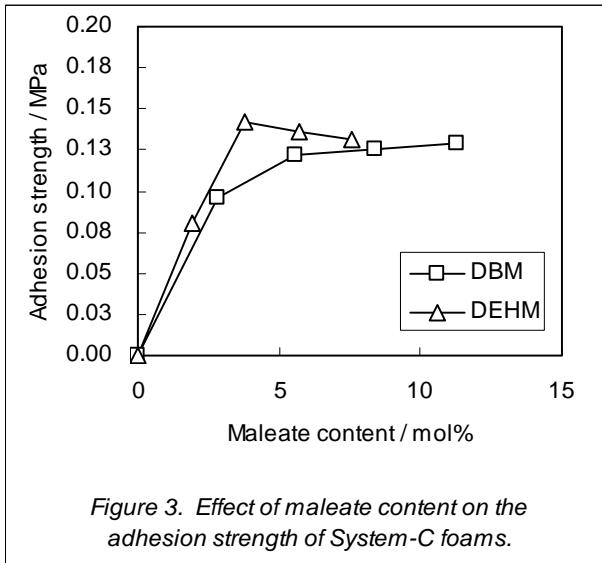


Figure 2. Effect of maleate content on the adhesion strength of System-B foams.



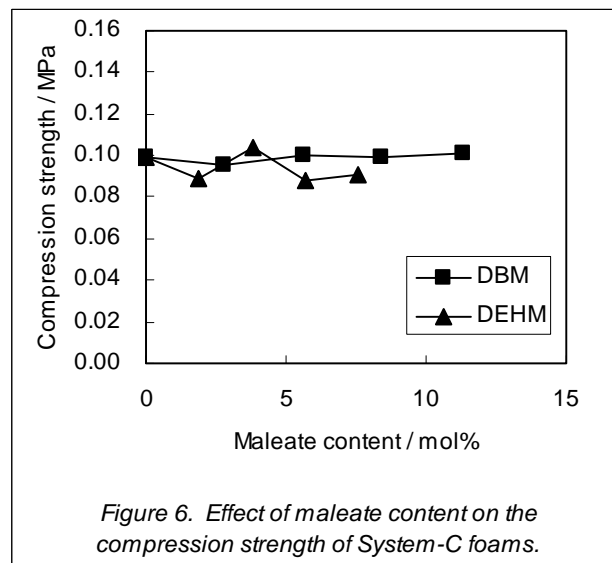
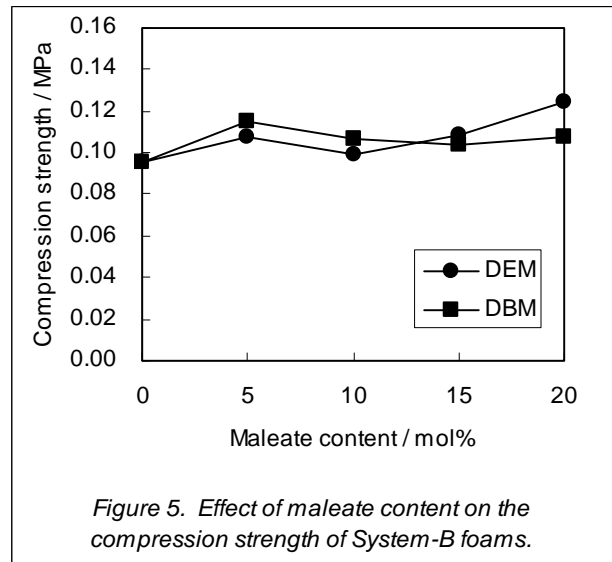
DBM exhibits the same effect to DEM on the adhesion strength of foam System-B. However, DBM has no limitation to the content within 20 mol%.

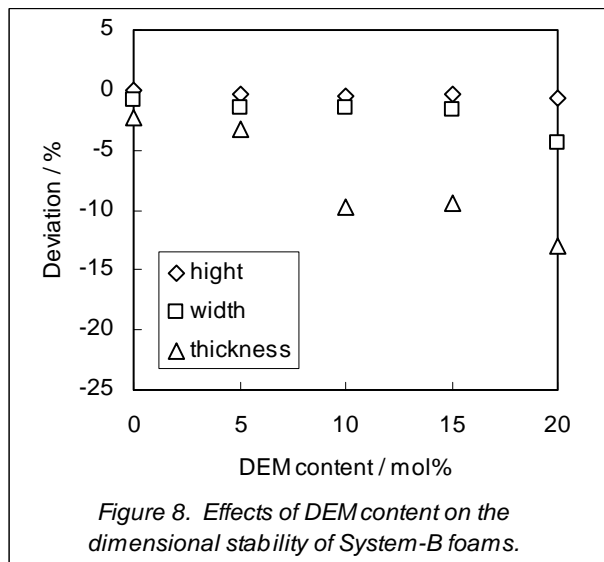
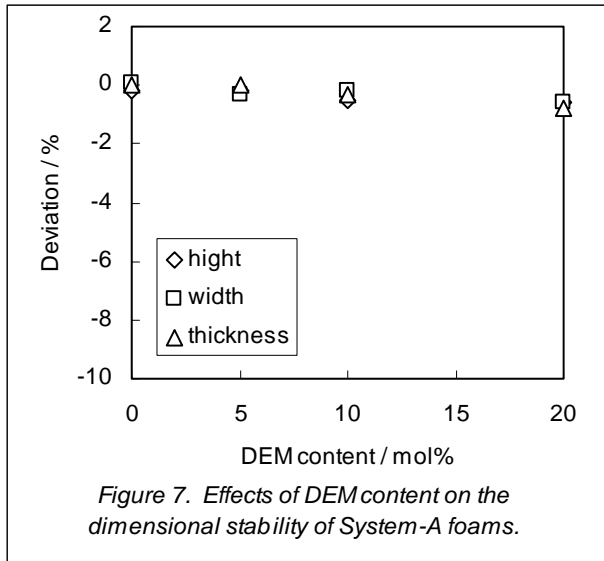
Figure 3 shows the effects of DBM or DEHM content on the adhesion strength of the foam System-C, containing more water compared with System-B. The surface layer of the foams without maleate was quite friable, resulting the foams did not adhere to any materials. In the System-C, maleates enhance the adhesion strength too. DBM has no limitation similar to System-B. On the other hand, DEHM indicates a peak at 3.8 mol%. It is considered that DEHM inhibited excessively the coagulation property of urea linkage because it has a particular bulky alkyl chain. In other words, DEHM has a potential effect to improve friability and adhesion at a small amount of addition to a foam formulation.

There is no general solution that which maleate should be selected or how much maleate should be used. Nevertheless, all the maleates used in this study had obvious effect on the improvement of the adhesiveness.

Compression strength

Figures 4, 5 and 6 show the compression strength of the System-A, -B and -C foams, respectively, modified with various maleates. The compression strength of all the Systems is scarcely changed with maleate content. Therefore, it is concluded that maleate does not affect on compression strength at least in the range experimented in this study. It can be easily presumed that excess amount of maleates leads to deterioration of compression strength. The adhesion strength has been satisfactorily intensified, as shown in Figures 1, 2 and 3, within the range that the compression strength has not been deteriorated.



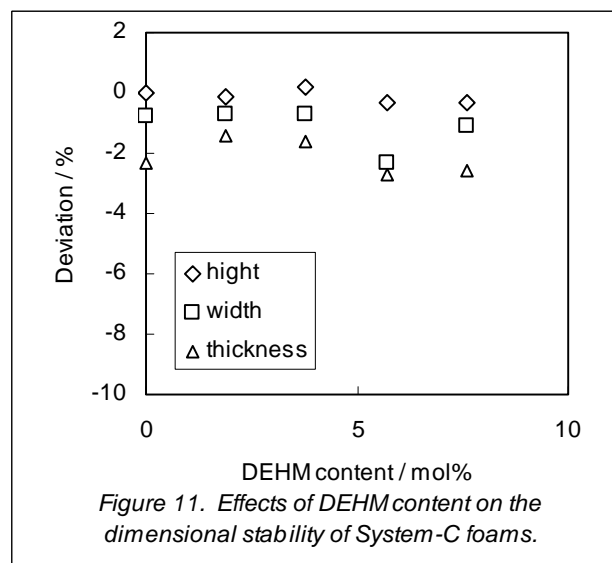
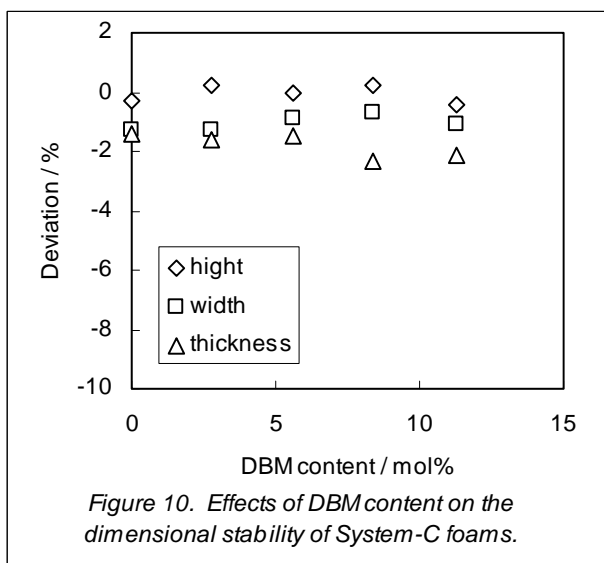
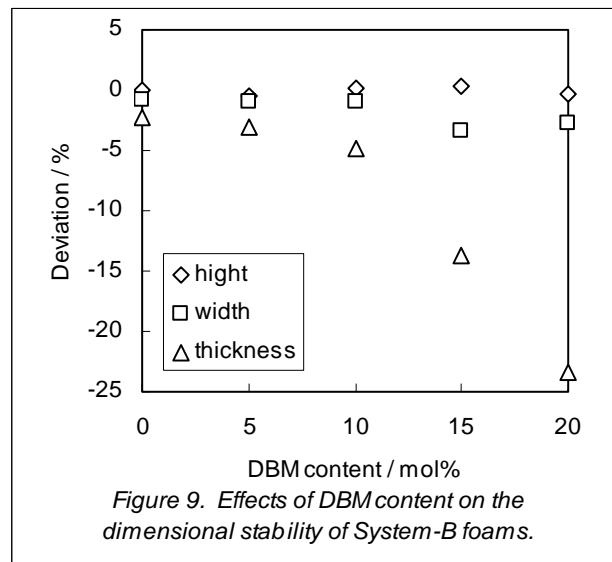


Dimensional stability

Figures 7-11 show the dimensional stability at high temperature (80°C, 48 h). It should be noted that the ordinate of these Figures are distinct in each case.

Effects of DEM content on the System-A are shown in Figure 7. The deterioration of dimensional stability by the addition of DEM is not serious, because the System-A was a semi-continuous-cell system.

As shown in Figures 8 and 9, the dimensional stability of System-B is seriously deteriorated by the addition of DEM or DBM, especially in the thickness direction. It was suggested that the glass transition temperature of PUR itself consisting the framework of the rigid foam decreased by the addition of maleates, which is the origin of bulky side-chain located in hard segment. However, within 5 mol% of DEM or DBM content, the adhesion strength was increased as shown in Figure 2, in spite of the dimensional stability is



kept below 4 %. Consequently, through the moderate content of maleates, the dimensional stability can be compatible with the adhesion strength.

Figures 10 and 11 show the dimensional stability of System-C foams by the addition of DBM or DEHM. In this system, the dimensional stability is kept below 2 % in the range that the adhesion strength was enough improved, as shown in Figure 3.

Spectral and Model Chemistry

Figure 12 shows the FT-IR absorbance of the surface of the System-A foams. Two peaks can be detected in the range of 1750 to 1610 cm^{-1} . The absorption bands centered at 1710 and 1640 cm^{-1} are assigned to C=O stretching vibration of urethane and urea linkage, respectively. As increasing in the DEM content, absorbance of the urea linkage decrease although the absorbance of the urethane linkage does not change. This phenomenon implies that the urea linkage existed at the surface of the foams was decreased with the increasing of DEM content. It appears that the decrease of urea leads to improvement of friability at the surface of the foams. On the other hand, excess amount of maleate leads to softening of the bulk foam and to deterioration of dimensional stability or even adhesion strength

The result of FT-IR measurement suggests that both of the reactions (a) and (b) assumed in Scheme 1 were really occurred. In order to support the assumption, computer simulation was carried out. The reaction paths of these reactions were successfully simulated, thus the assumption that amine reacts with both isocyanate and maleate is proved.

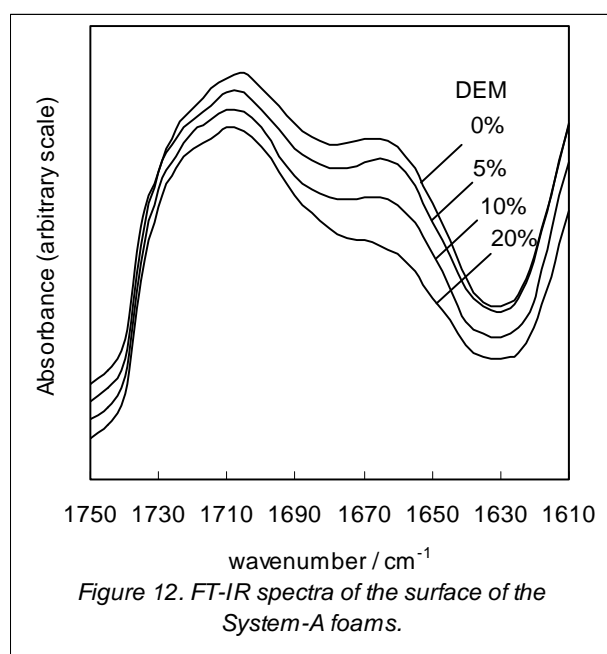


Figure 12. FT-IR spectra of the surface of the System-A foams.

Table 2. Calculated E_a and ΔH value of the reactions

Reaction	E_a (kcal/mol)		ΔH (kcal/mol)	
	DFT	MOPAC	DFT	MOPAC
(a)	42.058	19.595	-10.305	-20.086
(b)	31.577	15.855	-10.466	-19.239
(c)	-	21.163	-	-13.755

Table 2 shows the calculated E_a and ΔH of the reactions (a), (b) and (c). E_a of the reaction (b) calculated with DFT is 31.577 kcal/mol, which is low enough to occur the reaction without any catalyst or extra heating. On the other hand, E_a of reaction (a) is 42.058 kcal/mol, indicating the barrier of the reaction (a) is high compared to (b). Nevertheless, the value of 42.058 kcal/mol is enough low to the reaction occur spontaneously. Consequently, it is reasonable that the reactions (a) and (b) could occur simultaneously during the foam preparation. In addition, ΔH values of these reactions are -10.305 kcal/mol and -10.466 kcal/mol, respectively, representing there is no significant difference between these values.

These results suggest that the maleate was consumed during foam preparation resulted in secondary amine formation.

The E_a and ΔH values of reactions (a) and (b) calculated with MOPAC have the same tendency to that with DFT, although the absolute values are not consistent. Therefore, it is still significant that the value calculated with MOPAC is used to be indication of reactivity. E_a of reaction (c) is close to the reaction (a). Consequently, it is reasonable that the reaction (c) occurred successively after the reaction (a), resulting "substituted-urea linkage".

CONCLUSIONS

The water-blown PUR rigid foam modified with maleate was successfully prepared. The friability of the foam surface was improved through the modification with maleate. As a result, the adhesion strength of the foam was considerably improved. Compression strength was not affected by the addition of maleates. Dimensional stability did not deteriorated by the addition of enough maleate to improve the friability.

Computer simulation and spectral studies suggest that the maleate reacted with primary amine, which was generated by the reaction of isocyanate and water, resulting secondary amine. The secondary amine reacted with isocyanate to bulky "substituted-urea linkage", which acts as inhibitor for the excess coagulation of the ordinary urea linkage.

Maleates are inexpensive chemical products, and the direction of use is only mixing into polyol-premix or polyisocyanate. Thus, water-blown PUR rigid foam of which friability and adhesiveness is improved can be provided at a reasonable price.

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Satoshi Murayama



Satoshi Murayama received his Doctor of Engineering degree from Gunma University in 1993, and joined Nippon Polyurethane Industry Co.,Ltd. He worked on elastomers, adhesives, coatings and rigid foams. Currently he is a technical manager of Basic Research Group at Central Research Laboratory.

Kenji Fukuda



Kenji Fukuda received his B.S. degree from Akita University, Department of Mining Science in 1992, and joined Nippon Polyurethane Industry Co.,Ltd. He worked on process engineering at TDI plant of Nanyo Factory and currently on rigid foams at Central Research Laboratory.

Tadashi Kimura



Tadashi Kimura graduated from Akita national college of Technology in 1991, and joined Nippon Polyurethane Industry Co.,Ltd. He worked on binder and currently on rigid foams at Central Research Laboratory.

Toshiaki Sasahara



Laboratory.

Toshiaki Sasahara received his B.S. degree from Kyoto University, Department of Hydrocarbon Chemistry in 1979, and joined Nippon Polyurethane Industry Co.,Ltd. He worked on rigid and flexible foams, adhesives and coatings. Currently he is a manager of Rigid Foam Group at Central Research

BIOGRAPHIES