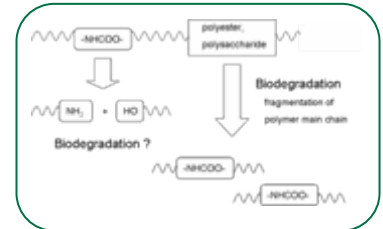


# Biodegradation of Urethane

Astuyoshi Nakayama, Noboru Yamamoto, and Norioki Kawasaki

Bio-based Polymers Group, Research Institute for Innovation in Sustainable Chemistry,  
National Institute of Advanced Industrial Science and Technology (AIST), JAPAN

Several biodegradable polyurethanes have been developed. However, the biodegradation has only been discussed in terms of molecular weight, weight loss, and mechanical deterioration. These phenomena do not show the biodegradation of urethane bonds in a polymer backbone directly because the common polyurethanes contained other segments, such as polyester, polyether, or saccharide units. On the other hand, if urethane compounds can be shown to maintain mechanical properties, they could lead to the development of a biodegradable elastomer. We have, therefore, been studying the biodegradability of urethane compounds, including model compounds and polymers. In this paper, we describe the biodegradation of oligomers and polymers which contain only urethane as a possible biodegradable bond.



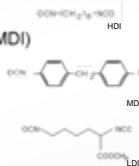
## (1) Experimentals

Urethane model compound, oligomers and polymers, were prepared from diisocyanates and diols. Biodegradation test was mainly carried out by an activated sludge method with determination of CO<sub>2</sub>. As for hydrolysis test, the enzymes used were *Rhizopus delemar* lipase, hog liver esterase, etc. Urethane-degraders were isolated from activated sludge and identified.

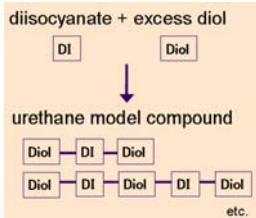
### Preparation of model compounds (oligomers)

Diisocyanate :

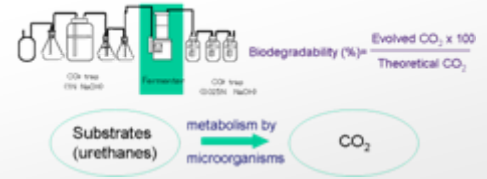
- hexamethylene diisocyanate (HDI)
- 4,4'-diphenylmethane diisocyanate(MDI)
- L-lysine diisocyanate (LDI)



- Diol : ethylene glycol (EG)  
1,4-buthane diol (BD)  
diethylene glycol (DEG)

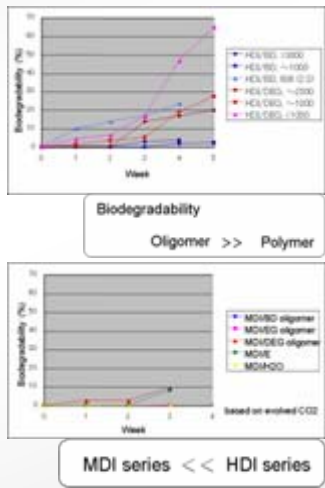
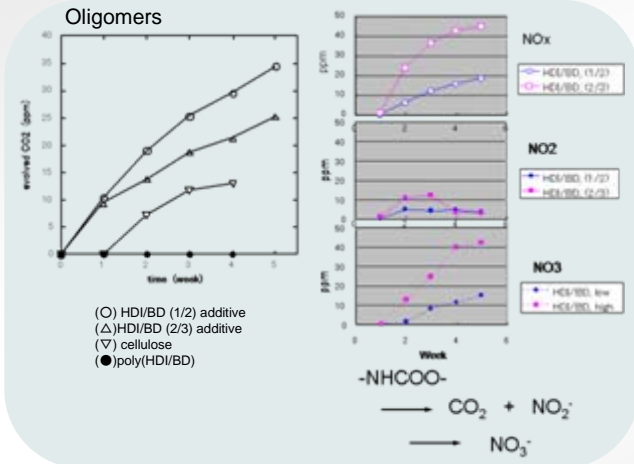


### Biodegradation by an activated sludge test

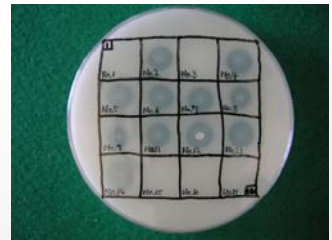


## (2) Biodegradation results and discussion

The biodegradation of the polymer by activated sludge was rather slow compared to that of the oligomer. The oligomers based on HDI and LDI showed higher degradation than those based on MDI.



### Urethane-degrading microorganisms



Isolated microorganisms from activated sludge  
substrate: BD-HDI-BD

## (3) Enzymatic hydrolysis

The LDI-based polyurethanes degraded more readily compared with HDI- and MDI-based polyurethanes and show potential as biodegradable elastomer, plasticizer and compatibilizer for biodegradable plastics. Urethane degrading-microorganisms were also isolated from the activated sludge.

### Enzymatic hydrolyses of several urethanes

	MW	I	II	III	IV	V
HDI/BD(1/2)	~350	○	○	○	○	○
HDI/BD(2/3)	~600	○	○	○	○	○
HDI/BD(5/6)	>1000	×	○	-	-	×
HDI/BD(1/1)	>2000	×	○	×	×	×
HDI/EG(1/2)	~290	○	○	-	-	×
HDI/EG(2/3)	~530	○	○	-	-	×
HDI/EG(5/6)	>1000	×	×	-	-	○
HDI/EG(1/1)	>2000	×	-	-	-	-
HDI/DEG(1/2)	~380	○	○	×	×	-
HDI/DEG(2/3)	~600	○	○	×	×	×
HDI/DEG(5/6)	>1000	×	○	○	-	×
MDI/DEG(1/2)	~460	○	-	○	○	-
MDI/DEG(2/3)	~670	○	○	×	-	-

I : hog liver esterase, II : *Rhizopus delemar* lipase  
III : proteinase, IV : papain , V : trypsin

### Effect of molecular weight (by esterase)

diol	NCO/OH	LDI	HDI	MDI
BD	92	○	○	○
	29	○	○	○
	56	○	×	○
	1011	○	×	○
DEG	91	○	×	○
	9	○	○	○
	29	○	○	○
	56	○	○	○
EG	91	×	×	○
	9	○	○	○
	29	○	○	○
	56	○	○	○
TEG	91	○	○	○
	91	○	○	○
PCL50	91	○	○	○

### Conclusions

- Urethane model compounds and oligomers were degraded by an activated sludge as an inoculum.
- Lysin diisocyanate based oligomers and polyurethanes were more readily degraded compared to 4,4-diphenylmethane diisocyanate based ones, and hexamathlene diisocyanate based ones.
- A microbe degrading an urethane model compound was isolated from the activated sludge.
- Urethane bond in low molecular weight of the oligomers was readily hydrolyzed by hog liver esterase.
- It is possible to use with limited content aliphatic diisocyanate as a chain extender or modifier for biodegradable polymers and plastics.