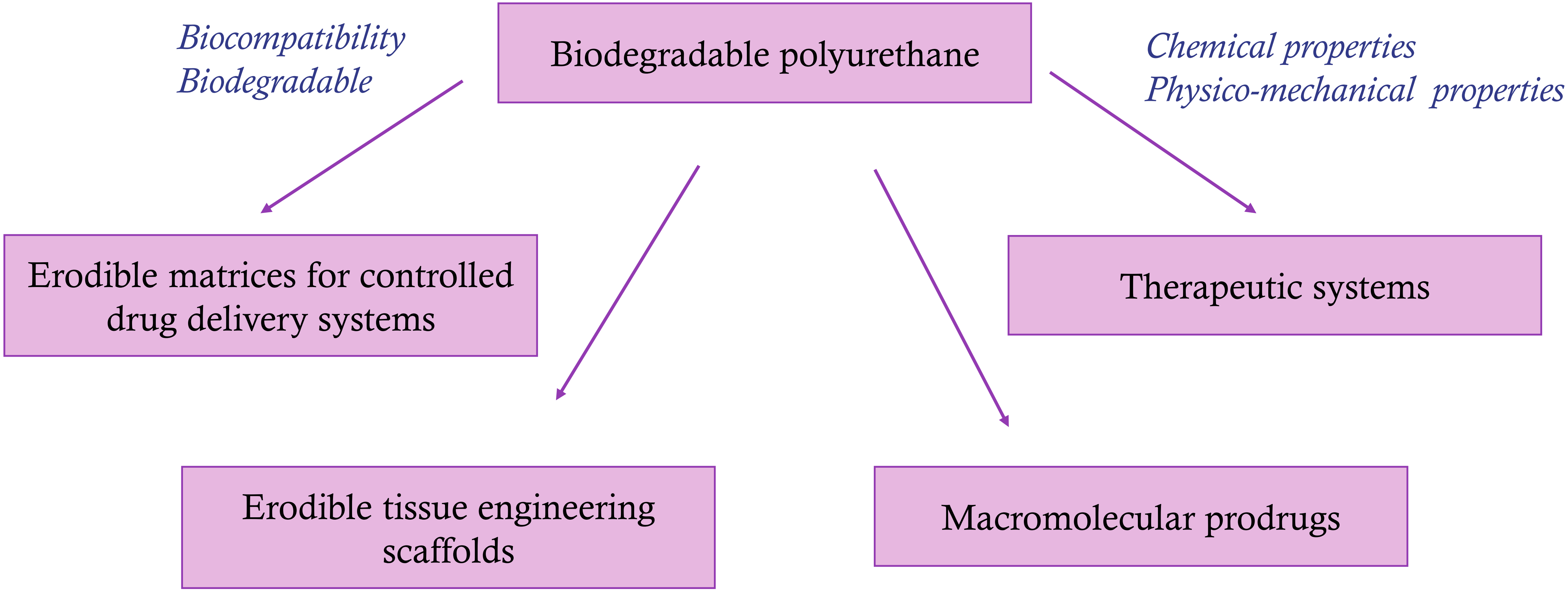
주제:
BIO 분야에서의 POLYURETHANE의 응용

2회: 생분해성 폴리우레탄의 연구 동향

화학공학소재연구정보센터IP(Information Provider) 연구분야 보고서

- **Biodegradable polyurethanes**

: 생분해성 폴리우레탄은 그 물리화학적 그리고 생리적 기능 덕분에 제약과 의학분야에 사용되는 biomaterial로써 중요한 물질이다.



Polymer-Plastics Technology and Engineering, 54: 155–172, 2015

- **Biodegradable polyurethanes in biomedical application**

Table 2. Typical commercial polyurethane products for biomedical applications.

Name	Company	Polyol	Isocyanate	Chain extender
Pellethane® 2363-80A; 55D; 75D; 90A	Lubrizol	PTMEG	4,4-MDI	1,4-BDO
Elasthane™ 80A	DSM	PTMEG	4,4-MDI	1,4-BDO
Tecothane™ 80A; TT1074A	Lubrizol	PTMEG	4,4-MDI	-
Tecoflex™ EG-80A	Lubrizol	PTMEG	4,4-H_{12}MDI	-
Biomer®	Ethicon	PTMEG	4,4-MDI	EDA
Elast-Eon™ E2A (80A; 90A)	Aortech	PDMS/PHMG 80/20	4,4-MDI	1,4-BDO
Corethane 80A; 55D	Corvita	PHEC	4,4-MDI	1,4-BDO
Bionate® 80A; 55D	DSM	PHMC	4,4-MDI	1,4-BDO
ChronoFlex® AL 80A; AR	AdvanSource Biomaterials	PC-1122 (An aliphatic PC glycol)	4,4-H_{12}MDI	1,4-BDO
Carbothane™ PC-3575A	Lubrizol	-	Aliphatic	-
Coremer™	Corvita	PHEC	4,4-MDI	EDA + DACH
Carbosil® 20 90A	DSM	PHMG 80% / PDMS 20%	4,4-MDI	1,4-BDO

Abbreviations: 1,4-BDO, 1,4-butanediol; DACH, 1,4-diaminocyclohexane; EDA, ethylene diamine; 4,4-H12MDI, 4,4-dicyclohexylmethane iisocyanate; 4,4-MDI, 4,4-diphenylmethane diisocyanate; PC, polycarbonate; PHEC, poly(1,6-hexyl 1,2-ethyl carbonate); PHMC, Poly(hexamethylene carbonate); PTMEG, poly(tetramethylene ether)glycol.

• Hydrolytic degradation of polyurethane

: 새로운 생체적합성 및 생분해성 폴리우레탄의 합성은 의료용 재료로서 큰 의의를 지닌다. 특히 재생의학에서 고분자 지지체 (scaffold)의 가수분해는 중요한 필수 조건 중 하나이다.
폴리우레탄은 합성 시 사용된 화학물질에 따라 그 가수분해 산물의 세포 독성이 크게 다르며, 특히 방향족 (aromatic) diisocyanate가 사용된 경우 그 가수분해 물질이 독성을 보이나 지방족 (aliphatic) diisocyanate가 사용된 경우 유의성을 지니는 독성을 보이지 않음이 보고 되고 있다.

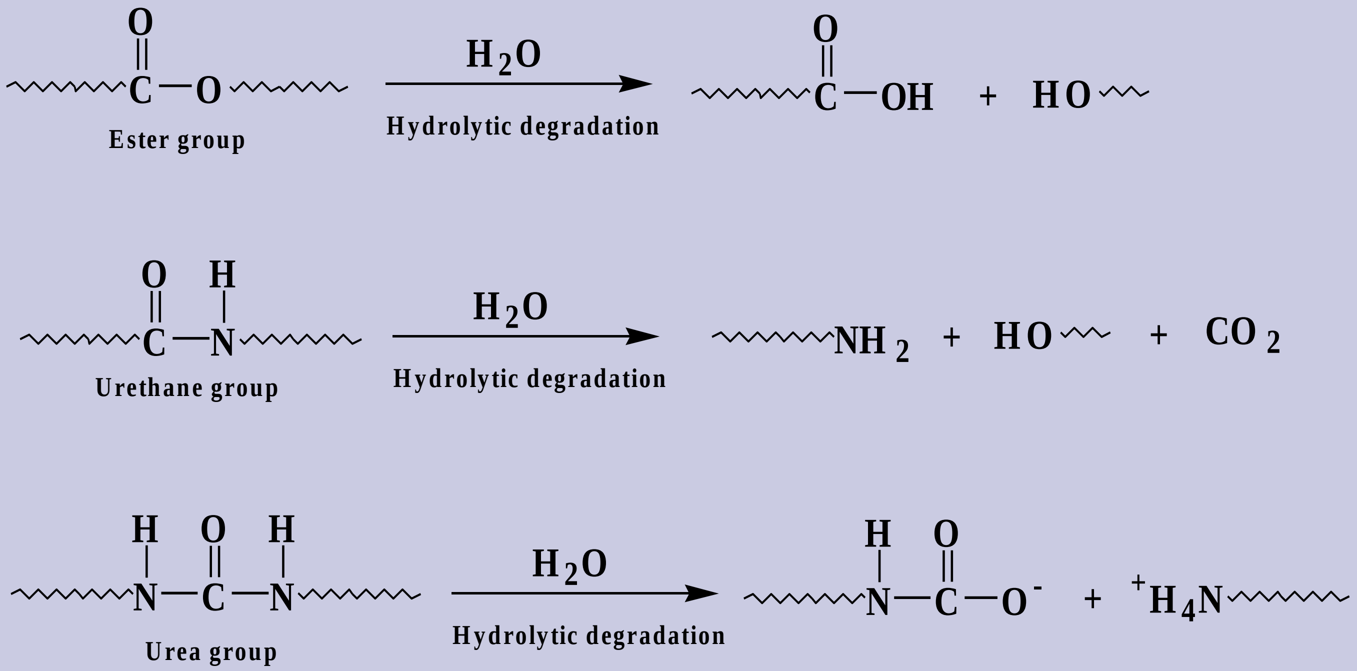


Figure 1. Typical hydrolytic degradation of Polyester-based polyurethane urea

: 폴리우레탄의 가수분해적 거동은 재생의학에서 지지체로서 사용되고 인체내에 무해하게 흡수되는 것으로 이용될 뿐만 아니라, 약물전달체로써 하이드로젤 (hydrogel) 에 응용한 서방성 (sustained) 약물 방출, 나노운반체 (nanocarrier)로써 약물 전달, injectable hydrogel 로써 세포 및 단백질의 전달에서 생체적합성에 중요한 요소로서 적용되어진다.

- **Enzymatic degradation of polyurethane**

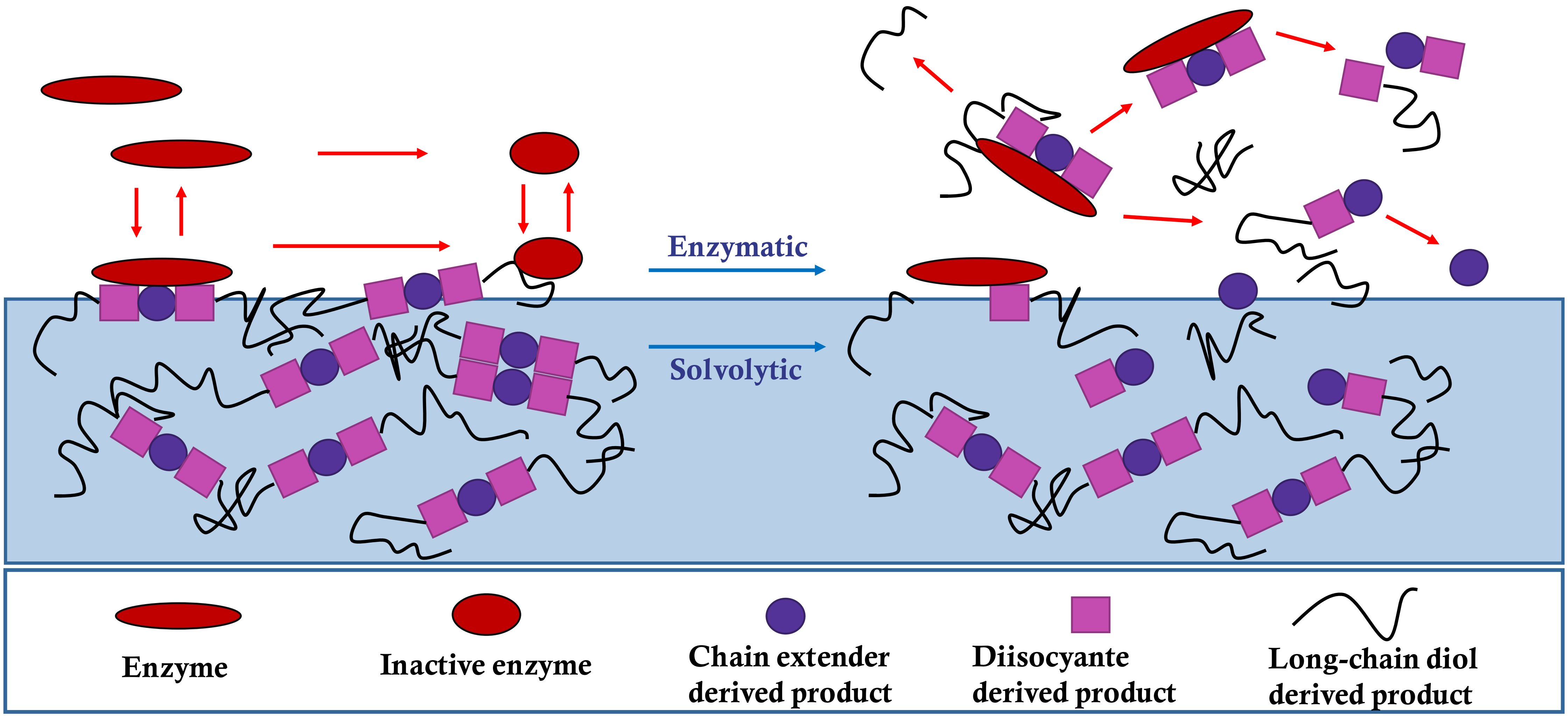


Figure 2. Schematic representation of complete in vitro enzymatic degradation process of polyester-based polyurethanes.

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• Degradation of Polyester Polyurethane by Bacterial Polyester Hydrolases

: Polyester-based polyurethane (anionic aliphatic polyester-polyurethane dispersion)의 polyester hydrolases enzyme (LC cutinase (LCC), TfCut2, Tcur1278 그리고 Tcur0390) 에 의한 분해도 test 결과 rapid PU degradation이 확인 됨.

Table 2. Kinetic parameters of the enzymatic hydrolysis of polyester based polyurethane determined by the kinetic model proposed by Mukai et al (Equation 1).

Enzyme	k (μg^{-1})	k^{s} (s^{-1})	R^2
TfCut2	0.188 ± 0.024	0.026 ± 0.001	0.972
LCC	0.038 ± 0.009	0.022 ± 0.002	0.955
Tcur0390	0.023 ± 0.007	0.026 ± 0.003	0.954
Tcur1278	0.004 ± 0.001	0.020 ± 0.002	0.938

Equation 1. kinetic model proposed by Mukai et al.

$$\left(\frac{(E)}{R}\right)^{\frac{1}{2}} = \frac{k[E]}{\alpha} + \frac{1}{\alpha}$$

$$\alpha = (k_s k)^{\frac{1}{2}}$$

R: hydrolysis rate
[E]: enzyme concentration
k: adsorption equilibrium constant
k_s: rate constant of the surface reaction

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• Degradation of Polyester Polyurethane by Bacterial Polyester Hydrolases

: polyester hydrolases from actinomycetes are able to degrade the thermoplastic polyester PU (TPU) Elastollan B85A-10 and C85A-10.

Table 3. Weight loss of TPU Elastollan B85A-10 and C85A-10 cubes with an initial weight of approximately 80 mg after hydrolysis by LCC, TfCut2, Tcur0390 and Tcur1278 for 100 h at 60–70 °C.

Enzyme	Temperature (°C)	Weight loss (%)	
		B85A-10	C85A-10
TfCut2	60 70	1.0 ± 0.1 1.9 ± 0.3	1.1 ± 0.2 1.5 ± 0.2
LCC	60 70	1.2 ± 0.2 3.2 ± 0.5	1.2 ± 0.2 2.5 ± 0.4
Tcur0390	60	0.3 ± 0.1	0.4 ± 0.0
Tcur1278	60	0.6 ± 0.1	0.8 ± 0.1

Table 4. Molecular weights of Elastollan B85A-10 and C85A-10 determined by GPC following hydrolysis by LCC at 70 °C for 200 h and of negative control samples without enzyme. The polydispersity index (PDI) is the quotient of Mw and Mn.

Polyurethane	Weight loss (%)	Mn	Mw	Mp	PDI
B85A-10	0 (negative control) 4.9	57,355 ± 1284 57,635 ± 891	132,425 ± 1948 108,873 ± 2688	97,559 ± 1011 77,501 ± 3176	2.31 1.89
C85A-10	0 (negative control) 4.1	49,061 ± 1514 49,009 ± 1613	109,264 ± 1024 88,956 ± 1530	73,335 ± 3426 66,288 ± 2846	2.23 1.82

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