■ 總 說 ■

우레탄 탄성체의 고무롤 적용

오 택 수

1. 고무롤 산업의 종류와 재질 및 그 적용

1.1 고무 Roller 관련 산업의 종류

Paper, printing, steel, textile, wood, tanning, business machine, and plastics.

1.2 고무 Roller의 역할

Feed, squeeze, protect, isolate, insulate, conduct or dissipate an electric charge.

1.3 고무 Roller 산업의 특징과 사용재질

1) Graphic Art

Resistance of printing ink, resistance of dampening solutions, roller washed.

NBR and PVC/NBR blends.

2) Pulp and Paper Making Rollers

Resistance of chemicals, excellent dynamic characteristic under high pressure and speed, long life time.

NBR, NBIR, EPDM, CSM, CR, NR, SBR, HNBR, and polyurethane.

3) Steel Processing

Cost, squeegee, wipe and stretch steel during processing.

NBR, EPDM, CSM, CR, NR, SBR, XNBR, HNBR and polyurethane.

4) Textile Industry

Dying, bleaching, mercerizing and slashing applications.

Resistance of chemicals, excellent dynamic characteristic under high pressure and speed.

NBR, EPDM, CSM, XNBR, HNBR and limited use of polyurethane.

5) Industrial Rollers

Feed, squeeze, protect, isolate, insulate, conduct or dissipate an electric charge.

Coating rollers, the furniture industry, the plastic industry, the food industry, the leather industry, the circuit board industry, the glass industry, etc..

NBR, EPDM, CSM, CR, NR, SBR, XNBR, HNBR, silicone, and polyurethane.

6) Business Machine Rollers

Copy machine, offect duplicators, lazer printers,

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dot matrix printer, film processors, label presses, plotters, Fax machine, etc..

Chemistry, heat, coefficient of friction and abrasion resistance.

NBR, EPDM, CSM, CR, NR, SBR, XNBR, and silicone.

1.4 고무 Roller Manufacturing Processes

1) Casting

Polyurethane and liquid silicone에 사용.

The mold degassed to remove trapped air and placed in an oven for curing.

Offest printing roller, steel mill roller, pulp and paper making rollers, and general industrial rollers.

2) Molding

Compresson, transfer, injection molding process.

Small offset printing rollers and business machine rollers.

3) Strip-Building

1970년대 초에 개발된 공정.

This process was a take-off of the orbitread method of building tires, where rubber is fed into cold feed extruder, a thin ribbon is wound around a mandrel and pressure is applied to the rubber with an applicator head to insure trapped air is removed in the fabrication process.

Graphic arts rollers, pulp and paper rolls, steel mill rollers, textile rolls and general industrial.

4) Calender Building

대표적인 roller제조 방법으로 전반적으로 이 방법으로 제작되어짐.

Table building process.

Three roll building.

1.5 고무 Roller에 사용되는 각종 재질의 특성 및 적용산업

1) NBR

Nitrile rubber, 전체 roller산업의 60%를 차지.

① Resistance to aliphatic hydrocarbons.

② Compounding versatility in order to meet a variety of end use applications.

③ Cost effective material.

④ Ease of manufacturing rollers.

Applications : Coating roll, flexography, paper making and converting, offset printing, textile, wood, and steel.

2) NBR/PVC

① Resistance to aliphatic hydrocarbons.

② Improved ozone resistance over straight nitrile.

③ Improved abrasion resistance over straight nitrile.

④ Enhanced grinding characteristics.

Applications : Coating roll, flexography, converting, offset printing, and steel.

3) XNBR

화학적으로 NBR과 유사하며 내마모성은 Buna N, Neoprene, EPDM, Hypalon, NBR보다 우수하며 화학적 특성이 우수하다.

① Resistance to aliphatic hydrocarbons.

② Abrasion resistance.

③ Cost effective material as compared to alternative abrasion resistant type.

④ Ease of manufacturing rollers.

Applications : Paper making and converting, wood, and steel.

4) HNBR

1970년대에 개발되었으며 내열특성, 내유성이 우수하다.

① Improve abrasion resistance.

② Excellent dynamic properties and low hysteresis.

③ Improve tear and chunk out resistance.

④ Retention of roll geometry.

Applications : Paper and converting, steel, and general industrial rollers.

5) EPDM

Ethylene, propylene, diene의 공중합체로서 내오존성, 내화학성이 우수하다.

① Resistance of polar solvents(i. e, esters and ketones)

② Compounding versatility for an extensive variety of end use application.

③ Resistance to temperatures up to 177℃/350°F.

④ Resistance to acids and caustics.

Applications : Coating roll, flexography, paper making and converting, offset printing, textile, wood, and steel.

6) CSM

화학적으로 chlorosulfonated polyethylene으로 Hyplaon으로 잘 알려져 있다.

① Resistance to ozone attack.

② Outstanding abrasion resistance.

③ A board range of chemical resistance.

④ Withstands temperature up to 140℃/300°F

⑤ Outstanding tensile/tear strength over the entire hardness range.

Applications : Coating roll, flexography, paper making and converting, offset printing, textile, wood, and steel.

7) CR

Polychloroprene rubber로서 Neoprene으로 잘 알려져 있으며 고무롤에 사용되는 대표적인 고무이다. 내유성이 NBR과 유사하며 내오존성과 내열성이 우수하다.

① Ease manufacturing rollers.

② Compounding versatility in order to meet a variety of end use applications.

③ Balance of physical properties.

Applications : Coating roll, flexography, paper making and converting, offset printing, textile, wood, and steel.

8) ECO

Epichorohydrin rubber, or polyepichlorohydrin.

① Resistance to aliphatic hydrocarbons.

② Outstanding ozone resistance.

③ Excellent dynamic properties.

Applications : Offset printing, business machine, and gravure.

9) AU, EU

Polyurethane수지로서 liquid cast technology로 roll 제작.

① Excellent abrasion resistance.

② Outstanding resiliency even in extreme hardness(i. e. 75 Shore D).

③ Polyesters have excellent solvent resistance.

Applications : Coating roll, paper making, steel, gravure, and industrial rollers.

10) NR

Natural rubber로 화학적으로 polyisoprene임.

① Resistance of polar solvents(i. e, esters and ketones).

② Outstanding resiliency.

③ Cost effectiveness.

④ Abrasion resistance.

Applications : Flexography, paper making and converting, and steel.

11) SBR

Styrene과 polybutadiene의 공중합체이며 천연고무와 유사한 내화학성을 가짐.

① Cost effectiveness.

Applications : Paper making and converting, steel, and industrial rollers.

12) MQ

Silicone이며 화학적으로 polydimethylsiloxane이며 식용으로 사용가능.

① Outstanding resiliency.

② Low coefficient of friction(i. e. good release).

③ Heat resistance up to 260℃/500°F.

Applications : Flexography, paper making and converting, general industrial rollers.

13) MQ/EPDM

MQ와 EPDM의 좋은 성질을 나타내고 있음. 고온에서의 특성이 우수함.

① Enhanced toughness over silicone compounds.

② Enhanced release properties over straight EPDM.

③ Improved heat resistance over straight EPDM up to 204℃/400°F.

Applications : Paper and industrial rollers.

14) FKM

Fluoroelastomers이며 상품명으로 Viton, Fluorel로 알려져 있으며 내화학성, 내용제성, 내열성이 우수하다.

① Enhanced toughness over silicone compounds.

② Resistance to a broad range of solvents.

③ Heat resistance up to 500°F.

Applications : Paper, steel, textile, and industrial rollers.

15) T

Thiokol 혹은 polysulfide rubber임.

① Resistance to a wide range of solvents.

② Poor physical properties.

③ Objectionable odor.

Applications : Wood, coating roller, and industrial rollers.

16) IIR

Butyl rubber로서 isobutylene과 isoprene의 공중합체이다. 내화학성이나 내용제성은 EPDM과 유사하다.

Applications : Coating rollers and general industrial.

1.6 고무 Roller 산업의 미래

고무 Roller 산업은 다음과 같은 관점에서 앞으로의 영업 및 연구개발을 진행하여야 한다. 즉, 현재의 산업이 점차로 고도화 함에 따라서 전에는 요구하지 않았던 각종 성질을 요구하게 되었으며, 국내의 고무롤 산업은 업체의 난립에 따른 치열한 경쟁시대에 부딪치게 되므로서 신기술의 개발 및 새로운 고성능 소재의 고무 roller에 적용, 그리고 환경정책에 따른 새로운 기업문화의 변화가 이루어져야 한다.

- Environment scrutiny.
- New equipment design.
- Competitive pressure has led to evaluation of alternative production technology.

Application of high performance material.

Polysulfide, FMQ, HNBR, FKM, Vamac, PO, ECO, and ACM.

Table 1. Roller market segmentation in USA

Item	Percentage(%)
Graphic Arts :	35.30
Offset printing	85.35
Flexographic printing	6.66
Gravure printing	6.66
Letter press	1.33
Pulp and paper	42.40
Steel and aluminum industries	3.50
Textile industry	2.35
General industrial	7.05
Business machine	9.40

*This market segmentation is based on roller sales dollars.

New technological development.

Rotational cast polyurethane.

Alternative technologies that eliminate rollers completely, like indigo.

2. Polyurethane

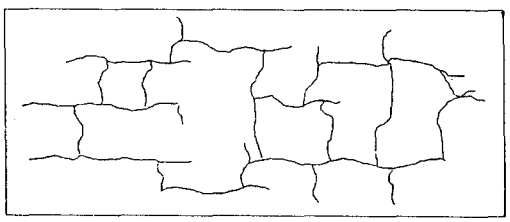
Vinyl이나 diene의 중합에 의해서 합성고무나 PS, PVC와 같은 고분자의 합성은 1930년대 중반부터 시작되었으며, 같은 시기에 DuPont의 Carothers는 adipic acid와 hexamethylene diamine의 축합반응으로 부터 Nylon 66의 합성하였다.

$$HOOC(CH_2)_4COOH + H_2N(CH_2)_6\text{-}NH_2 \xrightarrow{-H_2O} \left[NH(CH_2)_6\,NH\,CO\,(CH_2)_4\,CO\,NH(CH_2)_6\,NHCO(CH_2)_4\,CO\right]_n$$

Otto Bayer는 1937년에 diisocyanate의 부가중합반응에 의해서 고분자량의 polyurethane을 만들 수 있다고 제안하였으며, diisocyanate와 diol을 이용하여 다음과 같은 물의 제거가 필요없는 polycondensation반응을 발견하였다.

$$nOCN\text{-}(CH_2)_6\text{-}NCO + nHO\text{-}(CH_2)_4\text{-}OH \longrightarrow \left[OC\text{-}HN\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}O\text{-}(CH_2)_4\text{-}O\right]_n$$

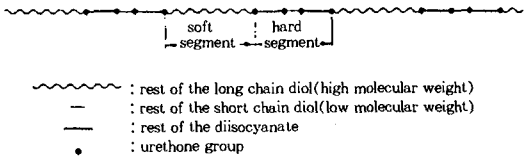
1982년에 사망한 Otto Bayer에 의하여 이루어진 polyurethane은 그 당시 전세계적으로 300만 톤의 생산량과 6조 달러의 매출을 이루었으며, 1995년에는 6.6백만 톤을 생산하였다.



Wide-meshed network

Otto Bayer는 고분자량의 가지 달린 polyester polyol로 만든 polyurethane의 탄성이 크다는 것을 발견하였으며, 이것은 고무상의 탄성체 모델로서 생각할 수 있다.

이러한 분자간에 network의 형성은 여분의 diisocyanate의 crosslinking에 의한 것이다. 그리고 polyurethane elastomer는 형태학적으로 분자 network이 segment로 구성되어 hard segment와 soft segment가 교대로 구성되는 형상을 가지고 있다.

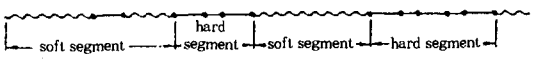


The ideal structure of segmented polyurethane

그리고 polyurethane elastomer는 다음과 같은 3가지 요인에 의해서 형성된다.

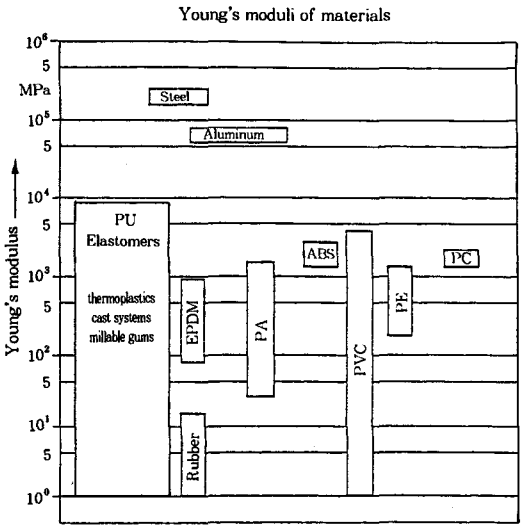
- an oligomeric polyether or polyester glycol
- a short chain glycol or diamine
- a diisocyanate

Soft segment는 coil과 같이 움직임이 자유로우나, hard segment라고 하는 딱딱한 oligourethane은 diisocyanate와 chain extender(glycol and diamine)의 반응에 의해서 생성된다. 그리고 Flory의 분산에 의해서 이론적인 hard segment의 양보다 실제적으로는 더 많이 존재하게 된다.

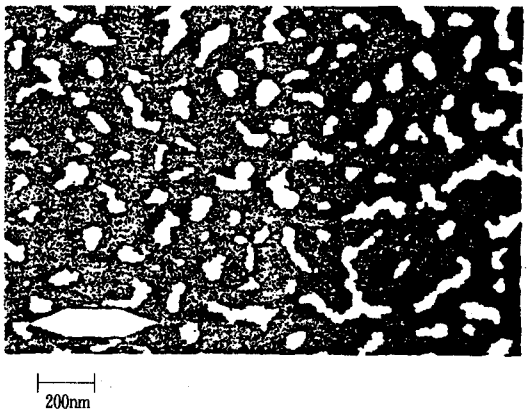


The realistic structure of a segmented polyurethane

polyol과 glycol의 diisocyanate 반응에 의해서 생



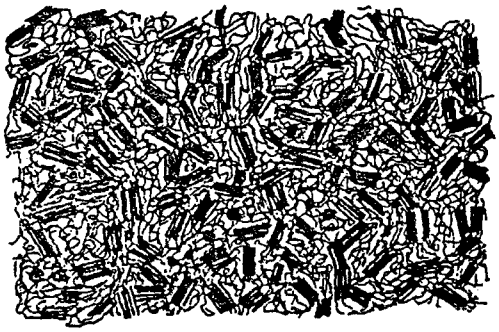
The Young's modulus of PU elastomers(including glass fiber reinforced products)

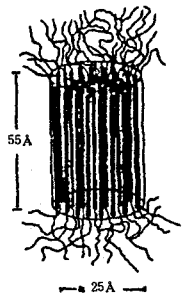


TEM of a film of a segmented PU elastomer. The cylinder shaped hard domains are represented by the white ares(bars)

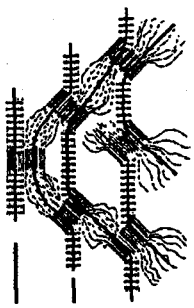
긴 nonpolar soft segment와 고융점의 hard segment의 비상용성으로 인하여 낮은 융점을 가진 거대분자가 형성이 된다. 따라서 domain사이에 상분리가 형성된다.

선형의 polyurethane segment의 열적, 기계적 성질은 화학적으로 crosslink 되어 있는 것과는 아주 다르다. hard segment domain의 용융범위가 열안정성을 나타낸다. 용융온도 범위 위의 온도에서는 열가소성수지이다. 잡아 당겼을 경우에 soft segment는 풀리며, hard segment는 stress 방향으로 배열된다.





Schematic superstructure for the segment outlined in the TEM and cylinder model of the hard domains



Stretching

Upon stretching, a portion of the soft segments are stressed by uncoiling, hard segments are oriented in the stress direction.

Reorientation

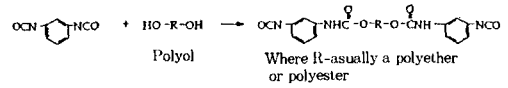
Reorientation after stress and thermofixation.

Hard segment를 250℃(urethane의 열분해온도) 이상으로 가열하여 주면 선형의 polyurethane은 열가소성의 거동을 나타내지 않는다.

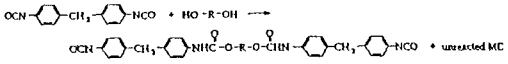
가역적인 탄성체의 거동은 soft segment의 분자사슬의 움직임에 기인한다. Polyurethane elastomer의 Tg, resilience, 신율은 soft segment의 길이와 형상에 의존하며, hard segment의 용융온도는 내열성을 좌우한다.

Prepolymer는 수분이 없는 상태에서 가열(80℃/176°F) 분위기에서 여분의 diisocyanate와 polyether-diol이나 polyester-diol의 반응에 의해서 만들어진다. 그리고 prepolymer의 isocyanate 함량은 약 4-10%이며, 분자량은 840에서 2,100 사이이다.

상온에서 대부분의 prepolymer는 고체나 고점도의 액체로 되어 있다. 이것을 60-100℃의 온도로 가열하여 점도가 낮은 액체상태로 만든 후에 chain extender인 glycol이나 diamine과 섞어준다.



TDI prepolymer



MDI prepolymer

Polyurethane prepolymers

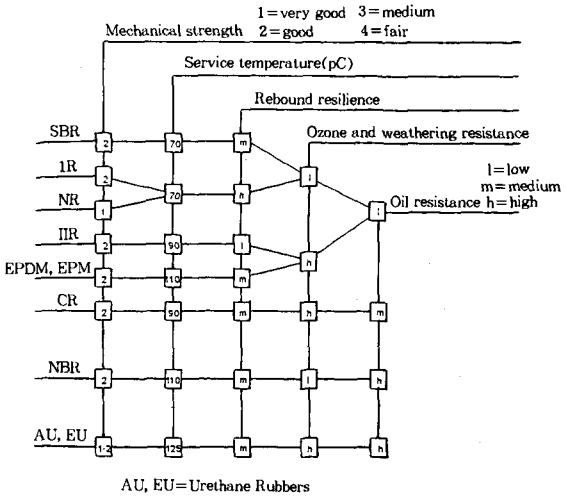
대부분의 경우 chain extender는 MDI prepolymer는 1,4-butane diol이며, TDI prepolymer는 MOCA를 사용한다.

3. 우레탄 탄성체의 고무롤 적용

Polyurethane elastomer는 고무분야에 사용되는 Polyurethane 탄성합성물질의 총칭이며, 1940년대 초기 유럽에서 특히 독일과 영국에서 발전하여, Vulkollan(I. G. Farbenwerke), Vulcaprene A(ICI) 등의 열경화성이 있는 것이 시판되었고, 그 후 미국에서도 Adiprene L, B, C series(DuPont)를 위시하여 Chemigum SL(Good Year Tire and Rubber), Genthane S(General Tire and Rubber), Daycollan (American Latex Product), Elastothane(Thiokol Chemical) 등이 속속 시장에 출현하게 되었다.

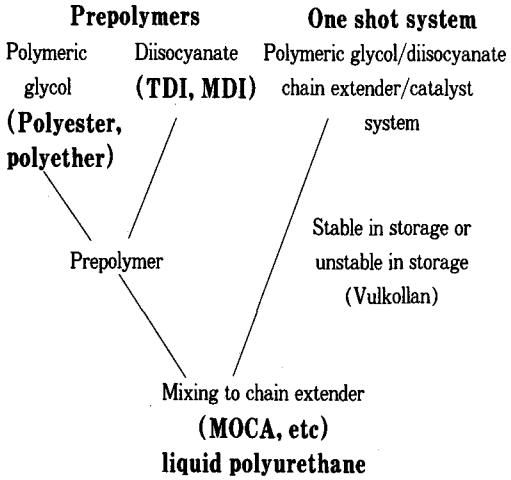
Polyurethane elastomer를 액상주형법의 상품으로 처음 세상에 소개한 것은 E. Müller이며, 그는 각종 polyester와 1.5 나프탈렌디이소시아네이트(Desmodur 15)를 주원료로 하는 elastomer가 "Vulukollan"의 명칭으로 시판되었다. K. A. Pigatt, C. S. Schollenbeger 등은 열가소성 Polyurethane elastomer를 소개하였고, 그 후 많은 연구자에 의해 사출, 압출성형법이 개발되었다.

Polyurethane elastomer는 화학적으로 분류하면 망상구조형과 직쇄구조형으로 구분된다. 전자는 열경화성이며, 성형 전에 경화제(가교제)를 배합하여 수지를 만들고 주형법 또는 혼련법으로 성형한다. 후자는 열가소성으로 일단 고형수지를 성형에 있어서 가열용융하여 사용하는 것으로 주로 사출성형이나 압출성형에 의해 가공한다.



AU, EU=Urethane Rubbers

Urethane rubbers in comparison with other rubbers



Alterinative processing routes for liquid polyurethane elastomers

Fabrication techniques

1. Casting : cast into hot moulds until dimensionally stable.
   Hot air post-cure for 3-24 h at 100℃
2. Centrifugal casting.
3. Rotational casting.
4. Compression moulding from plastic gum.
5. Transfer moulding from plastic gum.
6. Spray coating either reaction or solvent techniques.
7. Reaction injection moulding at low pressure specially microcellular products e. g. 2-3 min demold time.

Table 2. Property comparison of ether and ester polyurethane rubber

	Eher	Ester
Coefficient of friction	High	Medium
Wet traction	F	G
Dry traction	E	F
water resistance	E	P(unprotected)
Oils	G	E
Fuels	F	G
Heat resistance	F	E
Compression set	G	G-E
Low Durometer	F-G	G-E
Abrasion	G	E
Bonding to metal	E	E
Rebound	E	G
Solvents	High	Low or High

E=Excellent, G=Good, F=Fair, P=Poor

Table 3. Selection of a cure system for a specific durometer

Cure	Peroxide	Sulfur	Isocyanate
Durometer			
25A		VG	
30A		VG	
40A	C	VG	
50A	G	G	
60A	G	G	
70A	G	G	C
80A	VG	C	G
90A	VG		G
50D			G
60D			G
70D			G

C=Common, G=Good, VG=Very good

The PU-elastomers are divided into three groups of products :

- the castable liquids
- the thermoplastic resins
- the millable gums

Table 4. Typical properties of poly urethane elastomer

Property	Cast elastomer	Millable gum	Thermoplastic elastomers
Hardness, Shore A	A65-D70	A45-95	A82-D60
Tensile strength, MPa	31-48	20-39	34-43
Elongation, %	350-650	300-600	400-500
Modulus 300, MPa	4-20	10-22	7-20
Tear strength, Graves N/mm	7-12	5-25	25-45
Compression set*, 24h/RT%	10-25	5-15	20-30
Compression set*, 24h/100℃%	100	20-45	100

*DIN 53517

Reference

1. M. Chase, "Overview of the roller industry", Rubber Division 151 st Spring Technical Meeting, Paper #57, Anaheim, Cal. May 6-9, 1997.
2. R. Cunningham, "Sulfur, peroxideand isocyanate curable polyurethane rubber for demanding roll applications", Rubber Division 151 st Spring Technical Meeting, Paper #58, Anaheim, Cal. May 6-9, 1997.
3. M. Gozdiff and J. C. Laurich, "Influence of temperature on properties of vulcanized NBR & XNBR rubber", Rubber Division 151 st Spring Technical Meeting, Paper #59, Anaheim, Cal. May 6-9, 1997.
4. T. L. Jablonowski and R. J. Scribner, "Acrylonitrile-butadiene rubber for used in roll application", Rubber Division 151 st Spring Technical Meeting, Paper #61, Anaheim, Cal. May 6-9, 1997.
5. D. N. Jasinski, "Practical compounding of millable polyurethane mixtures", Rubber Division 151 st Spring Technical Meeting, Paper #73, Anaheim, Cal. May 6-9, 1997.
6. T. Lapsley and S. Dickson, "The advantages of silicone elastomer in the construction of roller", Rubber Division 151 st Spring Technical Meeting, Paper #74, Anaheim, Cal. May 6-9, 1997.
7. M. Chase, "Offset roller technology requirements", Rubber Division 151 st Spring Technical Meeting, Paper #75, Anaheim, Cal. May 6-9, 1997.
8. W. R. Randall, "EPDM and neoprene for the roller industry", Rubber Division 151 st Spring Technical Meeting, Paper #76, Anaheim, Cal. May 6-9, 1997.
9. A. Schroeter, "Development of polyurethane rubbers, vulcanizable via dimerized TDI, for the production of wear and tear resistant rubber roll coverings in a very high hardness", Rubber Division 151 st Spring Technical Meeting, Paper #77, Anaheim, Cal. May 6-9, 1997.
10. P. H. markusch and H. G. Schmelzer, "Synthesis of polyurethane elastomer", Rubber Division 151 st Spring Technical Meeting, Paper #7, Anaheim, Cal. May 6-9, 1997.
11. C. Hepburn, "Polyurethane Elastomer", 2nd Ed., Elsevier Sci. Publishers Ltd., England, 1991.
12. 金弘在譯, "폴리우레탄樹脂", 플라스틱材料講座 2, 대광서림, 1976.