

Incredible Polyurethanes: An old polymer with a breath of new life

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Introduction

Polyurethanes have attracted considerable attention as a class of interesting materials with outstanding physical and chemical properties. Polyurethanes are a unique class of addition polymers, which can behave as a thermoplastic, thermoset or an elastomer depending on its chemical composition. Such a combination of material attributes in one class of polymer is unprecedented in polymer science. Polyurethane was discovered in 1937 at the laboratories of IG Farben Industries in Germany by Professor Otto Bayer, a company which is now better known as Bayer [1]. However, due to the exigencies of war, the first scientific paper reporting the chemistry of polyurethane appeared only in 1947 [2]. Unlike the well-known and predominantly practiced chemical processes for making large macromolecules, such as chain-growth and step-growth reactions, polyurethanes are made by a unique chemistry, termed "addition polymerization". This class of polymerization is distinct from step-growth (or condensation polymerization) in the sense that no volatile by-products are formed during polymerization.

The characteristic chemical linkage in polyurethanes is the urethane linkage formed by the reaction of an isocyanate group with a hydroxyl group (Figure 1). The unique mechanical properties

of PU's arise mainly from two physico-chemical phenomena, that is, phase separation between hard and soft segments and hydrogen bonding between carbamate (or urethane) bonds.

Polyurethanes, since their

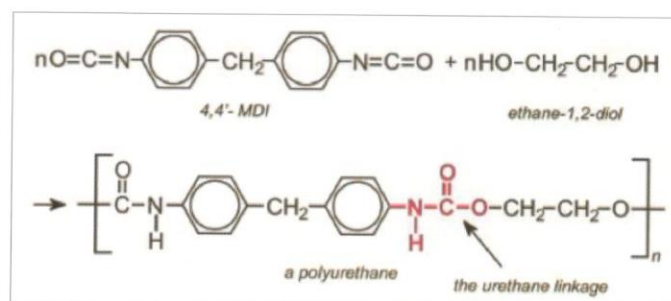


Figure 1: The urethane forming reaction

discovery, have made rapid strides in terms of both technology and applications. Some of the key events in the evolution of polyurethane materials are shown in Figure 2.

YEAR	EVENT
1937	Discovery of polyurethanes at IG Farben
1940	Rigid foams used first in aircrafts
1948	Use of PU foams in insulation
1953	PU shoe soles and foam cushions
1958	Spandex/ Lycra elastomeric fibers
1960	Sandwich building panels
1969	Automobile bumpers
1985	Energy absorbing foams
1993	Medical catheters
1995	Bicycle tyres
2001	Automotive tyres
2004	Artificial heart with PU Ventricles
2008	100% high speed swim suits
2011	PU manufacturing using polycarbonate diols

Figure 2: PU: Timelines in history

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It is evident that polyurethanes are continuing to grow into newer domains of applications with newer properties; their versatility arising largely due to wide options available for tailoring properties (Figure 3).

close to demand. The main growth driver for PU foams are regulation and energy efficiency (rigid foam insulation), an increasing population rising to the middle class in emerging markets (flexible foam), the transportation sector

The global capacity for PU is over 17 million tons per annum valued at over US\$ 55 million. The consumption in India is about 700,000 tons per annum. PU consumption is directly related to the disposable income of the consuming population; increasing standards of living is certain to push the demand for PU based products in India

**Polyurethanes:
Sustainability Issues**

As the consumption of polyurethane increase in volume issues of sustainability loom large and are a great driver of both regulations as well as innovation. There are many dimensions to sustainability, namely, resource base for building blocks, safety in manufacture and use by consumers, emissions propensity to generate hazardous waste and finally the manner in which the products after their use are disposed of. The current trends in technology evolution are significantly influenced by these

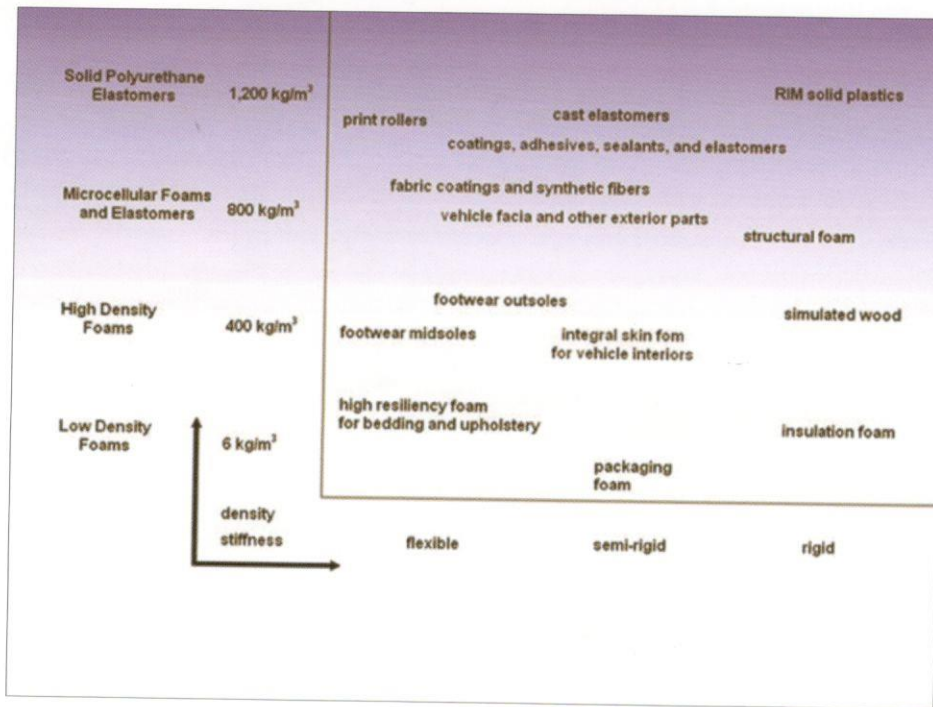


Figure 3: PU: Versatile materials with wide options for tailoring properties

(flexible foams) and increased use of refrigeration (rigid foams).

The world of polyurethanes comprise of flexible foams, rigid foams and resins (thermoplastics, elastomers, adhesives and coatings) [3]. A breakup of consumption in terms of application is shown in Figure 4. Largest amongst the category of cellular polymers are the PU foams, both, fflexible (cushioning) and rigid (insulation). PU foams are characterized by excellent mechanical properties, elasticity, aging and chemical resistance. Transportation of finished foam is not economical; so manufacturing facilities are located

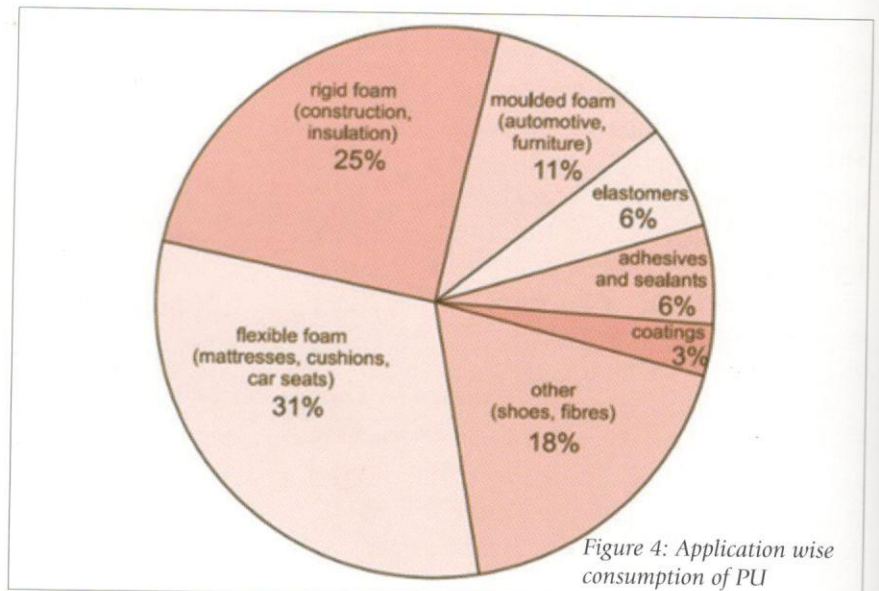


Figure 4: Application wise consumption of PU

sustainability imperatives. A broad sweep overview of technology trends indicates that the following are the major frontiers:

- Polyurethane building blocks from renewable plant based resources. Examples are polyols from edible and non-edible vegetable oils, lignin and polysaccharides;
- Use of carbon dioxide as a feedstock for polyols and for non-isocyanate polyurethane;
- Safe and environmentally benign adjuvants and additives for polyurethanes ((examples, blowing agents, catalysts and flame retardant);
- Recycling of polyurethanes.

A brief overview of current efforts in these areas is provided below:

Vegetable oils, such as soyabean, rapeseed and castor are excellent renewable raw materials for the preparation of polyols. Such polyols are used for rigid and flexible foams. Many methods are used for converting vegetable oils to derivatives useful for polyurethanes. They include, direct oxidation of oils, epoxidation followed by ring opening with diols, hydroformylation, ozonolysis, and transesterification of triglycerides with triethanolamine [4]. In spite of the competitive price and performance of such polyols, their market penetration is still small. This is due to two reasons. One, the large capacities already existing for petrochemical derived polyols, and two, the complexities of the chemistry that is needed to convert a vegetable oil to a feedstock suitable for polyurethane.

Polysaccharides and lignin have also been explored as substrates for preparing multifunctional polyols to be used for the preparation of PU foams [5]. Of this lignin is particularly interesting because of its abundant availability. Lignin and its derivatives have been used to partly replace petroleum derived polyols in PU foams. The total replacement, however, is still a challenge on account of poor compatibility between lignin and the PU matrix.

Use of carbon dioxide as a feedstock for making polyols has made significant inroads in recent years. Polycarbonate diols and polyether-carbonate diols have emerged as important polyols for PU (Figure 5).

functional and tri-functional diols can be used in all applications of PU where currently polyether polyols are used. 100% ether free polycarbonate diols with narrow polydispersity result in a 50 % increase in tensile strength, high energy absorbing property and slow recovery viscoelastic foams. The viscosity of the polyols is a little higher than that of standard products but processing on existing foaming machines is not a problem. Novomer's Converge Polyol RF-x polyols are utilized in polyisocyanurate (PIR) rigid foams and provide improved flammability performance. Depending on the amount of carbon dioxide incorporated, use of polycarbonate diols contribute

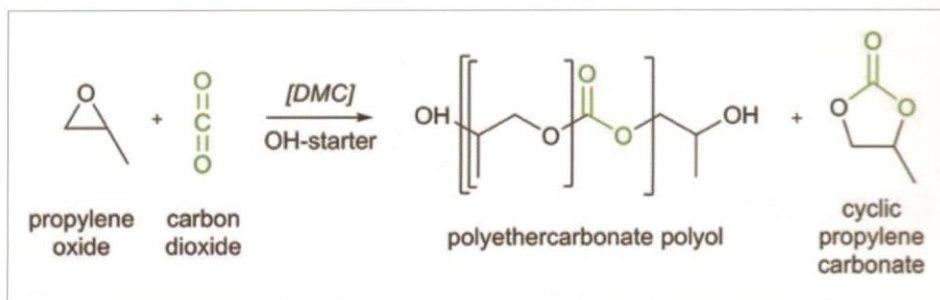


Figure 5 : Polyether-carbonate polyols from the reaction of an epoxide and CO₂

Depending on the catalyst and reaction conditions, polyether-carbonate diols with varying ether and carbonate linkages can be obtained. Major producers are Covestro, Perstrop (Oxymer, polycarbonate diols based on 1, 6-hexanediol) and 100% polycarbonate diols based on propylene oxide (Novomer). Other companies active in this field are, SK Energy, Korea (GreenPol Technology) Empower Materials, USA, Eonic Technologies and Huntsman Chemicals [6]. Di-

to improvement in sustainability metrics. The first commercial plant for polycarbonate diol has been commissioned by Covestro (formerly Bayer Advance Materials) in 2016.

The key to all technologies for the manufacture of polycarbonate diols are proprietary high efficiency catalysts that promote copolymerization of an epoxide with CO₂. Organometallic complexes of Zn and cobalt are widely employed [7]. Recently it

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has been shown that nonmetal activators can also be used which simplify the process by making catalyst removal from the product polymer redundant [8].

Another important use of CO₂ in polyurethane product technology is the development of non-isocyanate polyurethane (NIPU). Conventional method for PU elastomer production is based on the reaction of isocyanates with terminal hydroxyl groups. In this method, the water isolation of the reaction system is essential, because the free isocyanate groups undergo facile reaction with the moisture contained in the air or the substrate. Additionally, conventional PU is unsuitable for some applications like composite

matrix materials, because the hydrolytically unstable chemical bonds in polymer structure make it vulnerable to environmental degradation. Besides, exposure to isocyanates can cause adverse effects such as skin irritation and asthma. Thus, there is a need to develop processes for the preparation of non-porous

PU without isocyanate. NIPU can be prepared from cyclic carbonates and amine. Hydroxyl groups are generated during the reaction which leads to a linear or network structure of NIPU with intermolecular hydrogen bonds formed among hydroxyl groups at the β-carbon atom of the urethane moiety (Figure 6).

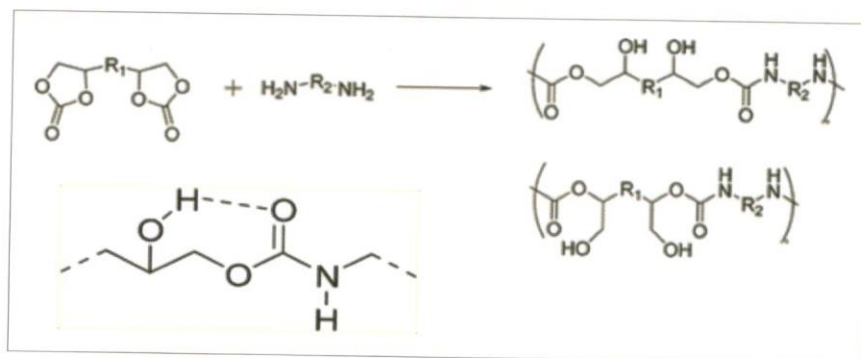


Figure 6: Structure of NIPU and the nature of intermolecular hydrogen bonds



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NIPU exhibits mechanical properties comparable with conventional PU. For example, NIPU prepared by reacting cyclic carbonate of soybean oil with 1, 2-ethylenediamine, 1, 4-butylenediamine, or 1, 6-hexamethylenediamine showed a tensile strength of 2.6 –6.9 MPa, an elongation at break of 163–232%, and a Shore A hardness of 84–93 (Figure 7).

[10]. Like other plastics, many polyurethane products can be recycled in various ways to remove them from the waste stream and to recapture the value inherent in the material. Polyurethane recycling, unlike other plastics, usually happens elsewhere—on job sites, in industrial settings, during building demolition and takes many forms, from relatively simple reuse to breaking down

Chemical Recycling involves glycolysis to regenerate the polyol, hydrolysis, resulting in polyols and various intermediate chemicals, pyrolysis to create gas and oils and hydrogenation to produce gas and oil from used polyurethanes through a combination of heat and pressure and hydrogen.

In spite of many options, economically viable PU recycling still remains a challenge. The low density of PE foams poses a challenge for collection and transportation.

Furthermore, the industry is poorly organized to handle end of life issues related to used mattresses and refrigerators.

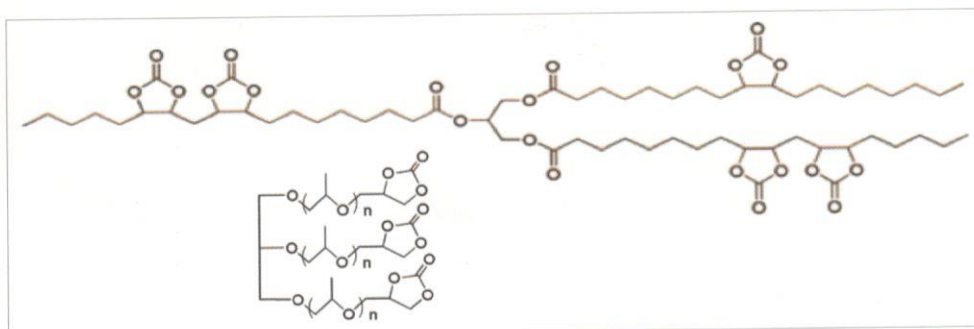


Figure 7 : Multifunctional cyclic carbonates for NIPU

In addition, NIPU displays increased chemical resistance and lower permeability as well as improved water absorption and thermal stability. Moreover, NIPU is not sensitive to moisture in the surrounding environment. These properties endow NIPU with numerous potential applications, such as chemical-resistant coating, sealant foam, etc. The rate of the reaction between amine and carbonates is quite slow compared with the direct $-NCO + -OH$ reaction; this is an area which requires improvement. Also, NIPU does not exhibit adequate elasticity to permit elastomer applications.

Waste recovery, recycling and reuse of PU assumes significance in the wake of increasing realization of the goals of a circular economy

the material into its chemical constituents. The major recycling processes currently employed for PU are use of reclaimed PU to create rebond cushioning for carpet underlay, mattress recycling and recovery of polyols from waste PU. Polyurethane is recycled in two primary ways: mechanical recycling, in which the material is reused in its polymer form, and chemical recycling that takes the material back to its various chemical constituents. Mechanical recycling involves rebonded flexible foam, regrind or powdering which is then mixed with virgin materials to create new polyurethane foam or reaction injection molded (RIM) parts, adhesive pressing/particle bonding and compression moulding of process grinds.

Conclusions

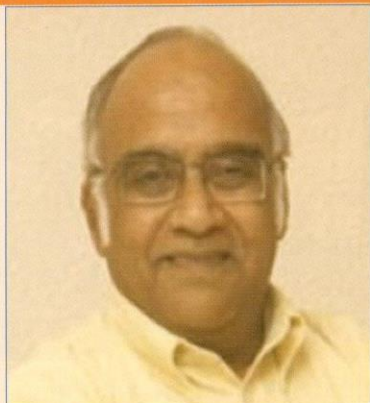
Urethane/urea bonds have proven their versatility. A unique feature of this chemistry is the high reactivity of the NCO group, even at room temperature. This allows rapid curing of cast-molded materials or coatings, as well as enables the preparation of prepare solid foam (chemical reaction rate is competitive with gas release rate, thus, facilitating trapping of the gas in the network). Additionally, the reversibility of covalent links based on isocyanate chemistry provides an opportunity to combine processability, reparability, recyclability and high elasticity or rigidity. An approach to addressing the toxicity issues associated with the reactive isocyanate group is by using the carbonate-amine reaction (NIPUs). Recycling and re-use remain one of the most important concerns of

the PU industry. Although, the urethane bonds are, in principle, hydrolytically or pyrolytically degradable, efficient and rapid reversion to the constituent polyol is not easy [11]. With growing consumption, end of life issues will become increasingly important and the concept of "extended producer's responsibility" with regard to PU products could become important in the years to come.

References

1. O. Bayer, German Patent 728.981 (1937) to I.G. Farben.
2. O. Bayer, *Angew. Chem. Inter.Ed.*, 59, 257, 1947.
3. *Handbook of Polyurethanes*, M. Szycher (ed), 2nd Edition, CRC Press, 2012.
4. Z.S. Petrovic, *Polymer reviews*, 48, 109, 2008.
5. M.J. Donnelly, J.L. Stanford and R. H. Still, *Carbohydrate Polymers*, 14, 221, 1991; US Patent 7151121 B2, December 19, 2006 to Danisco A/S; Q. Zhang, G. Zhang, J. Xu, C. Gao and Y. Wu, *Rev. Adv. Mater. Sci.*, 40, 146, 2015.
6. www.polymerspintcolourjournal.com/news/view/polyol-production-with-carbon-dioxide; www.novomer.com/?action=press_release&article_id=64; www.novomer.com/?actions=CO2; www.econictechnologies.com/technologies/products/polyols; www.4spe.org/Resources/resource.aspx?ItemNumber=10075.
7. S. Sujith S., K.M. Jae, E.S. Joung, Y.L. Bun, *Angew. Chem. Int. Ed.*, 47, 7306, 2008; D. J. Darensbourg, *Chem. Rev.*, 107, 2388, 2007; (b) G. W. Coates, D. R. Moore, *Angew. Chem. Int. Ed.*, 43, 6618, 2004; J. Langanke, A. Wolf, J. Hofmann, K. Böhm, M. A. Subhani, T. E. Müller, W. Leitner and C. Gürtler, *Green Chemistry*, 16, 1865, 2014.
8. D. Zhang, H. Zhang, N. Hadjichristidis, Y. Gnanou, and X. Feng, *Macromolecules*, 49, 2484, 2016.
9. J. Guan, Y. Song, Y. Lin, X. Yin, M. Zuo, Y. Zhao, X. Tao, and Q. Zheng, *Ind. Eng. Chem. Res.*, 50, 6517, 2011; E. Delebecq, J-P Pascault, B. Boutevin and F. Ganachaud, *Chem. Rev.*, 113, 80-118, 2013; O. Figovsky, L. Shapovalov, A. Leykin, O. Birukova and R. Potashnikova, *PU Magazine*, 10, 2, 2013.
10. *Towards the circular economy*, Ellen MacArthur Foundation, 2010; *the new plastics economy: Rethinking the future of plastics*, World Economic Forum, January 2016.
11. D. K. Schneiderman, M. E. Vanderlaan, A. M. Mannion, T. R. Panthani, D. C. Batiste, J. Z. Wang F. S. Bates, C W. Macosko and M. A. Hillmyer, *ACS Macro Lett*, 5, 515, 2016.

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Dr. Swaminathan Sivaram is an INSA Senior Scientist and Professor at the Indian Institute of Science Education and Research, Pune, India. Prior to this he was a CSIR Bhatnagar Fellow (2010-15) and J.C. Bose National Fellow of the Department of Science and Technology (2007-15) at CSIR-NCL. He served as the 8th Director of National Chemical laboratory from 2002-10. An alumnus of IIT-Kanpur, he received his PhD in Chemistry from Purdue University, USA. He was a Research Associate at the Institute of Polymer Science, University of Akron, USA before returning to India to pursue his professional career.

He is widely recognized for his contributions to polymer science, technology development, institution building and management of innovation in publicly funded organizations. The President of India honored Dr. Sivaram with the coveted civilian award, Padma Shri, in 2006.

He has mentored the PhD thesis of 36 students and over 15 postdoctoral fellows. He has to his credit over 210 publications in peer reviewed scientific journals and is cited as an inventor in over 92 patent applications and 50 granted US patents.

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