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Review on Manufacturing of Cellular Polymers and Its Applications

KanagaMadhuraN, Harshini D, Sneha J, Gnanavel G, Prabhu N*
Department of Biotechnology, Vivekanandha College of Engineering for Women, Tiruchengode, Namakkal-637 205, Tamilnadu, India

Abstract: *The purpose of this article is to provide an overview of manufacturing processes used in the development of cellular polymers for a wide variety of applications. The combination of intrinsic properties of polymers and foam is considered as an attractive solution in many applications. With regard to the long-standing interest of the industry in cellular polymeric chemistry, foaming is very common from hydro salivation /condensation reactions. This well-known technology leads to homogeneous, elastic, low density and biocompatible foams. The size of the cells remains large, since the reactions are sensitive to humidity and the dangerousness of the hydrogen could be an industrial concern. Most of the researches are moving towards alternatives such as phase separation, gas foaming, sacrificial models, emulsion and syntactic charges to the manufacture of cellular materials .In addition, to explain the formation of gaseous foam the theories of diffusion, absorption, nucleation and cell growth are detailed .These methods are simple as they do not need specific foaming equipment. Pore sizes are also tuneable as function of template sizes.*

Key Words: *foam, condensation, cellular polymers, polymeric chemistry, hydro salivation, condensation, emulsion.*

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I. Introduction

Polymer, which is a class of natural or synthetic substances composed of very large molecules, called macromolecules that are multiples of simpler chemical units called monomers [Abidin et al., 2017]. Polymers make up many of the materials in living organisms, including, for example, proteins, cellulose, and nucleic acids. Moreover, they constitute the basis of such minerals as diamond, quartz, and feldspar and such man-made materials as concrete, glass, paper, plastics, and rubbers. The word polymer designates an unspecified number of monomer units [Alexander et al., 2014]. The compound is sometimes called a high polymer when the number of monomers are very large. Monomers of the same chemical composition or molecular weight and structure are not restricted by polymers. Some natural polymers are composed of one kind of monomer [Anil thappa et al., 2013]. Copolymers are the Most natural and synthetic polymers, however, are made up of two or more different types of monomers. Organic polymers potray a crucial role in living things, providing basic structural materials and participating in vital life processes. For example, the solid parts of all plants are made up of polymers. These include cellulose, lignin, and various resins [Bonfield et al., 2013]. Cellulose is a polysaccharide, which is a polymer composed of sugar molecules. Lignin consists of a complicated three-dimensional network of polymers. Wood resins are polymers of a simple hydrocarbon, isoprene. Another familiar isoprene polymer is rubber [Cho et al., 2006]. Synthetic polymers are produced in different types of reactions. Many simple hydrocarbons, such as ethylene and propylene, can be transformed into polymers by addition of one monomer after another to the growing chain. Polyethylene, are sedate of repeating ethylene monomers, is an addition polymer. It may have as many as 10,000 monomers joined in long coiled chains [Duncan et al., 2005]. Polyethylene is crystalline, translucent, and thermoplastic—i.e., it soothes when heated. It is used for coatings, packaging, molded parts, and the manufacture of bottles and containers. Polypropylene is also crystalline and thermoplastic but is harder than polyethylene. Its molecules may consist of from 50,000 to 200,000 monomers. This compound is used in the textile industry and to make molded objects. Other addition polymers include polybutadiene, polyisoprene, and polychloroprene, which are all important in the manufacture of synthetic rubbers [Deisen at al., 2007]. Some polymers, such as polystyrene, are glassy and transparent at room temperature, as well as being thermoplastic. Polystyrene can be colored any shade and is used in the manufacture of toys and other plastic objects. If one hydrogen atom in ethylene is replaced by a chlorine atom, vinyl chloride is produced. This polymerizes to polyvinyl chloride (PVC), a colorless, hard, tough, thermoplastic material that can be manufactured in a number of forms, including foams, films, and fibers [Eiji Yuba et al., 2013]. Vinyl acetate, produced by the reaction of ethylene and acetic acid, polymerizes to amorphous, soft resins used as coatings and adhesives. It copolymerizes with vinyl chloride to produce a large family of thermoplastic materials. Another important family of synthetic organic polymers is formed of linear repetitions of the urethane group. Polyurethanes are employed in making elastomeric fibers known as spandex and in the production of coating bases and soft and rigid foams. A different class of polymers is the mixed organic-inorganic compounds. The most important representatives of this polymer family are the silicones. Their backbone consists of alternating silicon and oxygen atoms with organic groups attached to each of the silicon atoms. Silicones with low molecular weight are oils and greases [Fang et al., 2012]. Higher-molecular-weight species are versatile elastic materials that remain soft and rubbery at very low temperatures. They are also relatively stable at high temperatures. Polymers or polymer foams are common in daily life. They are used as heat insulators for packaging, as acoustical absorbers and as materials exhibiting low weight and good mechanical properties .Besides these passive applications, cellular space-charge electrets polymers became quite interesting recently as an' active'' material for sensor and actuator applications [Guillaudeu et al .,2008]. These ''novel'' electrets offer a huge potential for applications in noise reduction or cancellation, non-intrusive surveillance, advanced monitoring in health care, as well as in non-destructive testing [Hu Chang et al.,2012]. There is a significant difference between these polymers and the well-established, traditional piezoelectric polymer electrets based on polar polymers, like ferroelectric polyvinylidene fluoride its copolymers, odd-numbered polyamides, etc.Foamed plastics, also called *cellular polymers* or e*xpanded plastics*, can be made from almost any type of polymer. The choice of polymer mainly depends on the performance requirements, the economics and the required material throughput [Humber plaza et al., 2009]. The majority of all produced polymeric foams are based on polyurethane (PUR), polystyrene (PS), polyvinylchloride (PVC), polyethylene (PE) and a number of elastomers such as ABS, natural rubber and silicone. The type of polymer determines whether the resulting foam will be hard and rigid or soft and flexible. In general, elastomers yield flexible foams, whereas rigid (glassy) polymers yield rigid foams. The properties of foam are also affected by its porosity (density) and cell structure. In general, foams are divided into *high-*, *medium-* and *low-density foams*, when considering their density [Isreal et al., 2012]. High density foams have a density between 0.5 g/cm³ and 1 g/cm³, medium density between 0.1 g/cm³ and 0.5 g/cm³ and low density lower than 0.1 g/cm³ [36] . Low density foams are mainly used in insulation applications whereas medium density foams find many uses in the packaging, building and construction industry [Isreal et al., 2012].

High density foams have noticeably higher strength and modulus, and thus, can often replace regular plastics in applications where lower electrical/thermal conductivity, weight per volume, dielectric constant, compression modulus as well as greater flexibility and damping is needed or required. Equally important is the cell structure of foam. The two extreme cases are all *open-cell foam* and all *closed-cell foam*. In the case of a closed-cell foam, the majority of the cells are not connected together by passageways and do not share any of their structure with other cells. This type of foam has a high plastic content and very low gas and vapor permeability [Jain et al., 2014]. It is also stronger and more rigid than open-cell foam. Open-cell foam, on the other hand, consists mainly of interconnected cells which share some of their structure with other cells. This type of foam is softer and more flexible than closed-cell foam, allows gas and vapour to move freely through the cells, and absorbs liquid when immersed in it. Both open and closed cell foams have much better thermal and acoustical insulation properties than non-porous plastics [Jain et al., 2014]. In recent years, polymeric foams continue to grow at a rapid pace throughout the world, because of their light weight, excellent strength to weight ratio, superior thermal and acoustic insulating capabilities, energy absorption ability and their good cushioning and comfort features. Polymeric foam is dispersion of a gas in a polymer matrix. It generally consists of a minimum of two phases, a solid polymer matrix and a gaseous phase (blowing agent). Other solid phases may also be present in the foams in the form of fillers [Jasen et al., 2014]. Polymeric foams may be either expanded rubbers or cellular elastomers or sponges. It may be either thermoplastics or thermosets. The physical and mechanical properties of the foam differ significantly from the solid matrix material. For example, foams can have much better heat and sound insulation properties compared to solid polymer. In addition, foams can have the ability to absorb an enormous energy, which makes them more useful in cushioning and packaging applications compared to the solid polymer. Another advantage of polymeric foams is the small amount of polymer mass is needed to obtain high volume, because of cellular structure with entrapped gas. Polymeric foams may be prepared with varying densities ranging from as low as 1.6 to as high as 960 kg/m3 [JiHoon et al., 2014]. Approximately, 70−80% of all commercially produced polymeric foams is based on polyurethane, polystyrene and polyvinyl chloride. Polymeric foams can be classified as flexible, semi−flexible, or semi−rigid, and rigid, depending upon the rigidity of the polymer backbone, which in turn depends on chemical composition as well as matrix polymer characteristics like the degree of crystalline and the degree of cross−linking. Various method of foam manufacturing can be adopted and tailor made hardness and other properties can be achieved for the foam to suit different application. Typical processing methods include continuous slab stock produced by pouring, foaming−in−place, molding, extrusion, spraying, rotational casting, frothing, precipitation, composites and lamination. The polymeric foams may be prepared in any shape and forms such as blocks, boards, slabs, sheets, tubing, molded shapes, or in composite forms as laminates, with facing materials such as solid plastics, metals, fabrics, paper, wood, etc[Joost et la.,2010].

HISTORY OF CELLULAR POLYMERS

Plastic is a word originally meant “pliable and easily shaped”. It only recently became a name for a category of materials called “polymers”. The word polymer means “of many parts”. And these are made of long chain of molecules. Polymers abound in nature. Over the last century and a half humans have learned how to make synthetic polymers, sometimes using natural substances like cellulose, but more often using the plentiful carbon atoms provided by petroleum and other fossil fuels [Jose et al.,2015]. Synthetic polymers are made up of long chains of atoms, arranged in repeating units, often much longer than those found in nature. It is the length of these chains, and the patterns in which are arrayed that make polymers strong. The first cellular polymer to be placed on the market was sponge rubber which was developed as early as 1914. It was produced by the addition of gas generating chemicals like sodium and ammonium carbonate or sodium polysulfide to natural rubber latex [Joseph et al., 2011]. The oldest rigid cellular plastic was cellular ebonite, which was produced in the early 1920. The Dunlop latex foam process originated at the end of 1928 and was based on a combination of foaming and delayed action gelling. Several other processes were subsequently developed for the production of latex foam rubber, but the only major competitive process to reach commercial importance was the Talalay process, which had its origin in about 1935. The Swedish engineers Munters and Tandberg invented the extrusion of foamed polystyrene in 1931 and simultaneously the Dow Chemical Company independently developed “Styrofoam” by extrusion process and commercial production in the U.S. started in 1943. The introduction of commercial phenolic foams occurred in 1945, while the use of phenolic “micro balloons” (hollow microspheres based upon phenolic resins and filled with an inert gas, e.g. nitrogen) for use in specialty type “syntactic” foams developed in 1953. Epoxy foams were first introduced in 1949 as light weight materials for the encapsulation of electronic components. Urea formaldehyde foams in the form of slabs used for thermal insulation whereas vinyl foam was first manufactured in Germany prior to World War II. The technology of urethane foam originated in Germany in the late 1930’s and Prof [Jyn et al.,2012]. Otto Bayer and his co−workers first developed rigid polyurethane foams based on polyester based polyol and toluene diisocyanate in the laboratories of the German I.G. Farben industry. Preparation of flexible urethane foams were first reported in the year 1952. Polyethylene foams for use as a low−loss insulation for wire and cables was introduced in 1944. Polypropylene foams, both thermoplastics and cross−linked types were introduced due to their relatively high service temperature and good abrasion resistance property. The development of silicone foams started in 1950, in order to meet the need for a light weight material that could withstand long−term exposure to temperatures in the range of 200°−375 °C. A number of other types of high−temperature resistant foams have been developed recently [Kala et al., 2012]. These include foamed fluorocarbons, cellular aromatic polyamides, and syntactic polybenzimidazole foams. In addition, many other types of flexible and rigid foams have been developed based on both natural as well as synthetic polymeric materials. These include foams based on butadiene−styrene, butadiene−acrylonitrile, neoprene, acrylonitrile butadiene styrene, acrylics, cellulose acetate, ionomers, and many others. It can be mentioned that foams can be made from almost any polymer, employing one or more processing techniques [Keren et al., 2013]

THE FIRST SYNTHETIC CELLULAR POLYMER

The first synthetic cellular polymer was invented in1869 by John Hyatt**,** who was inspired by a newyork, firm’s offer of $10,000 for anyone who could provide a substitute for ivory. The growing popularity of billiards had put a strain on the supply of natural ivory, obtained through a slaughter of wild elephants [Khakis et al., 2011]. By treating cellulose, derived from cotton fiber, with camphor, Hyatt discovered a cellular polymer that could be crafted into a variety of shape and make to imitate natural substances like tortoise shell, horn, linen and ivory. Hyatt’s andBaekeland’s success led major chemical companies to invest in the research and development of new polymers, and new plastics soon joined celluloid and Bakelite.

IMPORTANCE OF CELLULAR POLYMERS

The Second World War necessitated a great expansion of the polymer industry in the United States, as industraialmight provided as important to victory as military success. They need to preserve scarce natural resources made the production of synthetic alternatives a priority [Kaminski et al., 2013]. A time magazine noted that because of the war, “polymers have been turned to new uses and the adoptability of polymers demonstrated all over again”. During Second World War polymer production in United States increased by 300%.The surge in polymer production continued after the war ended. After experiencing the great depression and Second World War, Americans were ready to spend again and much of what they bought was made of polymer [Kaminskas et al., 2014]. According to Susan Freinkel “in product after product, market after market, polymer challenged traditional materials and won taking the place of steel in cars, paper and glass in packaging and wood in furniture”. The possibilities of polymer gave some observers an almost utopian vision of a future with abundant material wealth thanks to an inexpensive, safe and sanitary substance that could be shaped by humans to their every whim [Kaminskas and Biod et al., 2009].

STRUCTURE OF CELLULAR POLYMERS:

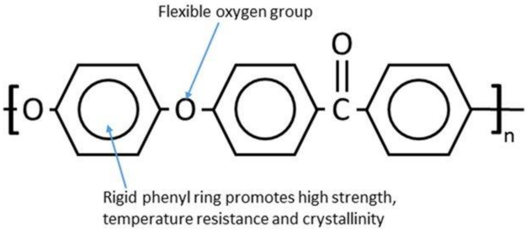


FIG 1: STRUCTURE OF CELLUALR POLYMER

BASIC PRINCIPLES IN THE FORMATION OF POLYMERIC FOAMS

In general, most of the polymeric foams are formed by a process involving nucleation and growth of gas bubbles in a polymer matrix, except in the syntactic foam where micro−beads of encapsulated gas are compounded into a polymer system or latex. According to the nucleation mechanism, the fundamental principle for the formation of polymeric foam involves three different important stages such as, bubble formation, bubble growth and bubble stability. The foam is expanded by increasing the bubble size before stabilizing the system. As the bubbles grow, the foam structure changes through number of stages [Kaminski and karallas et al., 2011]. These are the following characteristics observed during the formation of foam. Initially, small dispersed spherical bubbles are produced in a liquid polymer matrix, with a small reduction in density. The further growth of cells leads to lower foam density, which involves distortion of cells to form polyhedral structures, sometimes idealized as pentagonal dodecahedrons [Kanuri et al., 2013]. Effects of viscosity and surface tension subsequently cause materials to flow towards the uniform cell formation. Extensive rupture before the foam is stabilized may lead to foam collapse. Cooling of closed cell foam before stabilization may lead to shrinkage, because of the reduced pressure in cells. The foaming of polymeric materials can be carried out by mechanical, chemical, or physical methods [Koninis chin et al., 2013].some of the most commonly used methods are. Thermal decomposition of a chemical blowing agent, generating either nitrogen or carbon dioxide or both, by application of heat or as a result of the exothermic reaction during polymerization. Chemical blowing agents are either inorganic materials such as carbonates, bicarbonates, borohydrides, etc., or organic materials such as, hydrazides, azides, and nitroso compounds, etc.Mechanical whipping (frothing) of gases into a fluid polymer system (melt, solution, or suspension), then it hardens either by catalytic action or heat or both, thus entrapping the gas bubbles in the polymeric matrix [Kroner et al., 2012]. Volatilization of low−boiling liquids (fluorocarbons or methylene chloride) within the polymer mass as a result of the exothermic reaction or by application of heat. Chemical blowing action via in-situ reaction during polymerization. (In this in-situ reaction water reacts with isocyanate to form carbon dioxide which is responsible for polyurethane foam formation). Expansion of dissolved gas in a polymer mass upon reduction of pressure in the system. Incorporation of tiny beads or microspheres into a polymer mass. The hollow microspheres may consist of either glass or plastic beads, expandable by heat [Kobayashi et al., 2001].

II. Process Overview

Cellular polymers are achieving through injection moldingprocess (FIG 2) in industrial applications. Parker Chimeras can offer advanced engineers supportand state of manufacturing capabilities to facilitate mental replacement technology in the form of specially formulated polymers forEMI shielding, chemicalresistance, excellent thermal properties and weight/cost savings [Kojima e t al., 2010]. Advanced engineering partnership experts in injection molding technology for cellular polymers that meet design requirements. Through knowledge of FEA technology to plan out physical stress requirements. Able to facilitate simplification of parts for manufacturing flexibility and cost reduction .mold flow analysis for raw material use optimization [Karabatsos et al.,2013]. The state of art manufacturing have the capabilities of 75000 square foot purpose built polymer injection moldingfacility, advanced certifications(ISO9001 and 14001,TS16949).more than 40 injection moldingprocessare available,closed loop central material feed system for lean manufacturing of cellular polymers. Cellular manufacturing with automated assmembly and testing and value added services, ultrasonicwelding, hotstamping,testing,press fitting assembly, insert two shot and vertical moldingcapabilities, able to process 300 grades of resin[Liu et al.,2014]. It have certain markettypical applications.thera are automotive transportation (accumulation pistons, cylinder head coners, lumbersupport, ventcaps, wiper pivot housings).Telecom/IT (infrastructure, power supply housings, routers, servers).consumer appliance (homesecurity, hand tools) [Liwung et al.,2011].

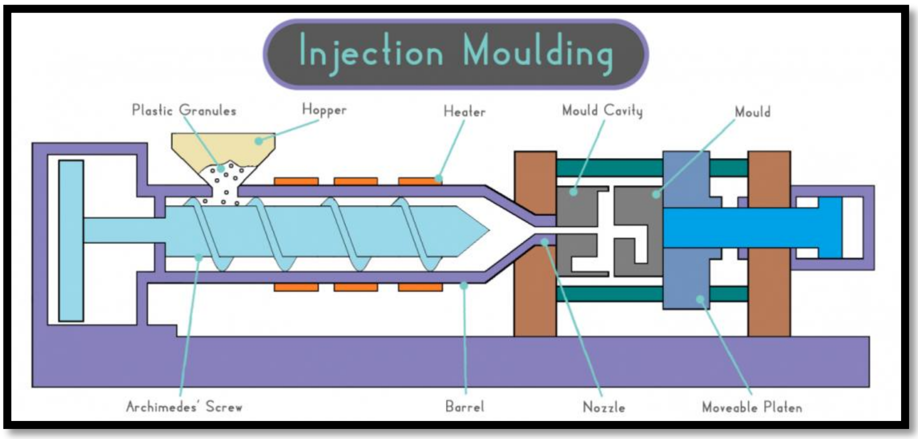


FIG 2: INJECTION MOULDING PROCESS

PRODUCTION

Mechanism for the formation of cellular structure. Chemical blowing agents are compounds that decompose under heat and liberate large amounts of inert gas, CO_2, CO, H_2O, NH_3 and H_2, etc [Malik et al.,2000]. Activators can sometimes be added to allow lower decomposition temperate and release more gas at a lower temperature. Early blowing agents were Sodium bicarbonate which liberates CO_2, other carbonates and nitrates liberate hydrogen or nitrogen. Hydrogen can be generating in large quantities, but diffuses away quicklyorganic compounds can be used for some high temperature thermoplastics there are [Marge etal.,2012]: Toluene sulfanyl hydrazine, Oxybis benzene sulfanylhydrazine, Toluenesulfanylsemicarbonate, Trihydrazinitrizine, PhenyltetrazoleCan be finally divided solid form to create cellular polymers. Nucleating agents and surfactants are used to control cellular polymers [Marshal et al., 2012].

PROPERTIES & CHARACTERISTICS

Polymers can be combined with a gas ,Forms or cells in the polymer causing the polymer to be very light, Cellular polymers are blown, expanded polymer foam,Elastometric foam matrix is an elastomeric or rubber, Flexible foam-soft plastic matrix [Michael et al.,2016] (E.g.: plastiziedPVC),Rigid foams-PS,unsaturatedpolyesters,phenolics,urethane(PU),Types of polymer matrix two classifications are thereThermoplastic cellular polymers and Thermo set cellular polymersAmount of gas added reflects the resulting density ,Light foams: density =0.01 to 0.10 g/cc (1 to 6 lb/ft3) , Dense foams : density= 0.4 to 0.6 g/cc (25 to 40 lb/ft 3) [Miller et al.,2013].

MECHANISM FOR OBTAINING CELLULAR STRUCTURE:

Aeration or frothing or mechanical agitations used to incorporate air into liquid resin system (latex, reactive urethane) [Milson et al., 2014].

PHYSICAL BLOWING AGENTS:

Add nitrogen gas into a solution or liquid melt which comes out of solution when pressure is released and form cells [Michelson et al., 2011]. Add liquids at low temperature and have low boiling point. The liquids vaporize upon the heating or by chemical reaction heat [Murugan et al.,2014].E.g. Aliphatic hydrocarbons (pentane), methylene chloride, trichloro –flourmethane or Freon 11.Another method involves permanently placing the foam in a cavity of a product, called **IN-SITU**foaming [Murazi et al.,2013]. For insulation, buoyancy, structural or combined purposes. Require good adhesion to the cavity walls and may require treatment (degreasing, Caronidischarge etc) [Muzal et al., 2012].

SPRAY ON METHOD:

Liquid or frothed resin is projected against surface (substrate) but rises on the opposite side. External insulation of tanks, vessels, roofs, truck boxes [Muzal et al., 2012].

MOLDING METHOD:

Parts are to a specific complex shape (steeping wheel covers, foam seats).Remoulding will require the use of a external spray & internal release agent .usually soap based zincseparate isused [Okada et al.,2006]. Pressure generated during moulding requires adequate control, otherwise dimensions may vary significantly and poor formation of integral skin and cells [Owens et al., 2006].

TYPES OF CELLULAR POLYMERS

Arrangement degree of interconnection can be assessed if a sample is subjected to a moderate vacuum and liquid is allowed to flow into the interconnection and causes the weight to increase cell size is important for heat and mass transfer cell density also plays an important role it characterises the coarseness or fineness of a foam of cellular polymers and distribution of gas in the cellular polymer corresponds to the structure of the foam system [Owens etal.,2006, Posocco et al.,2012] .Two types of cellular polymers are there:

Closed cell: spherical or roughly spherical voids are fully separated by matrix material (FIG 3)
Open cell: spherical or roughly voids are interconnection occurs between the cells (FIG 4)
Structural foam: foamed core is sandwiched between solid skin structured foam between integral skins, foaming can give an inhomogeneous structure.

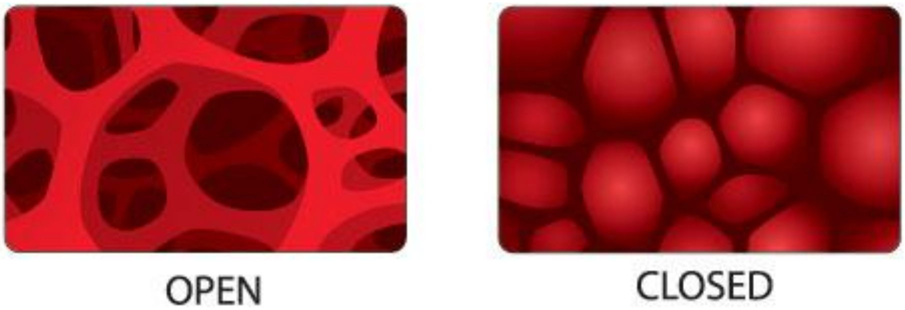


FIG 3 & 4: STRUCTURE OF OPEN AND CLOSED FOAM CELL

CLOSED CELLULAR POLYMERS

Nature of entrapped gas may have an effect on certain suitability &properties for specificapplications.Air,nitrogen,water,pentane,methylenechloride,fluorohydrocarbon vapours can be used as blowing agent [Posocco& Liu et al.,2013] .Amount of gas changes with time as the gas moves through the material & exists to the atmosphere leaving as a cellular structure polymers [Prieto et al.,2014] .

III. Methods

Based on the feature of cellular polymers produced in a variety of methods

Low pressure (union carbide) process

Foams the foam in an accumulator form which it is transferred into mould cavity under moderate pressure (35atm or 500 psi) [Prieto et al., 2014].Tooling this inexpensive surface is not very good.

High pressure (united machinery) process

High pressure (15kpsi to 20kpsi) prevents foaming and allows for better surface finish. It is a conventional injection method of the melt containing a blowing agent [Prussian et al., 2012]. Tooling is expensive, surface finish is very good. Mould cavity is enlarged to allow molten core to foam. Reaction injection moulding process can produce cellular polymers like urethane structural foam parts [Pizeeo et al., 2011].

FROTHING METHOD:

Suitable boiling point blowing agents incorporated to the resin under pressures (4 to 5 atm) (1atm= 14.69 psi) to prevent expansion (FIG 5). Pressure releases at the exit of the dispensing nozzle causes the immediate formation of a froth (foamedcream) corresponding to a pre-expansion ratio of 10X [Piazza et al., 2011].subsequent expansion is associated with the curing reaction which causes the vaporization of the blowing agent with expansion of 3X [Pomantz et al., 2015].Pressure developed in a cavity and temperature variations are lower than in the case of direct liquid feeding and much larger than by successive layer build-ups.

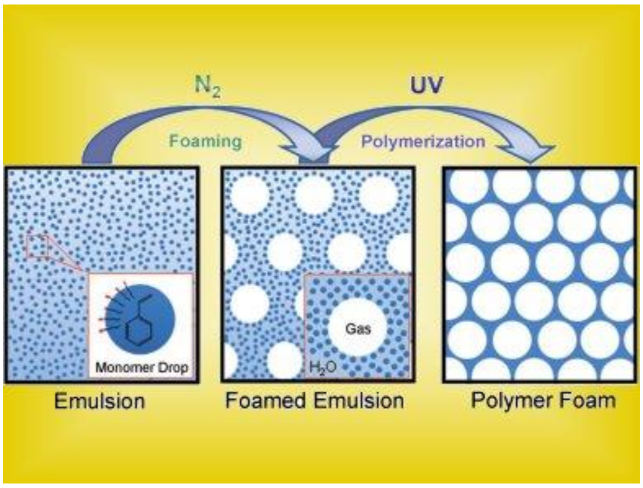


FIG 5:POLYMER FORAMTION BY FROTHING METHOD

APPLICATIONS

Cellular polymers are widely used in Shock absorption and vibration resistant applications , Automotive occupant protection , Automotivebumpering impact urethane foam and expanded polymers in a beam foam form , Acoustic insulation and dampening materials , Open cellular structures used in filtering and humidifying applications , Floatation devices generated by using closed cell cellular polymers , Closed cellular polymers used as insulation board and for packaging of frozen or perishable foods [Prussian et al.,2011],[Prieto et al.,2014]. Ex: ice cream, fish, poultry, Cellular polymers are used to produce composite floor pans, Thermal insulation properties and mechanical properties of cellular polymers are too high.

S.NO	AREAOF APPLICATION	POLYMER TYPE	USES
1.	Cushioning	Slab stock flexible polyurethane	Public transport seats, carpet underlay, furniture, bedding
2.	Cushioning	Moulded flexible PUF	PUF footwear, furniture, auto−motive seating, auto−bumper systems
3.	Insulation & construction	Polystyrene	Board stockPolyolefin’s Pipe
4.	Insulation &construction	Polyolefin’s	Pipe insulation
5.	Insulation & construction	Rigid PUF	Board stock/laminates, sandwich panels, spray/ pour−in−place, slab stock/pipe section, pipe−in−place.
6.	Insulation &construction	Phenolic	Board stock/laminates, pipe section
7.	Appliance	Rigid PUF	Refrigerators/freezers, picnic boxes/others
8.	Transport	Rigid PUF	Sandwich panels, reefer boxes
9.	Transport	Polystyrene	Sandwiched panels
10.	Packaging sheet	Polystyrene	Single service uses, food packaging, miscellaneous packaging
11.	Packaging sheet	polyolefin’s	Furniture, cushion packaging
12.	Non-insulation	Polyurethane	Miscellaneous packaging
13.	Molded	Polyolefin’s	Cushion packaging
14.	Board stock	Polyolefin’s	Cushion packaging
15.	Safety-moulded	Polyolefin’s	Auto-bumper systems,
16.	Integral skin	Poly urethane	Steering wheels,etc
17.	Sheet	Polyolefin’s	Flotation,life vests
18.	Board	Polystyrene	Flotation/buoyancy
19.	Board	Polyolefin’s	Flotation/buoyancy
20.	Molded/injected	Polyolefin’s	Flotation/buoyancy

EXAMPLES

Examples of cellular polymers are: Polystyrene, cellular silicon, chitosan, methylcellulose, polyesters

SPECIFIC EXAMPLE FOR CELLULAR POLYMERS:

Polystyrene’s or expanded polystyrene foam (EPS)

It is made from expandable polystyrene beads which are small spheres of polystyrene (diameter of 0.3-2.3mm) containing 3-7% pentane as physical blowing agent.Bulk density of beads (with air spices) is 0.7g/cc (FIG 6).

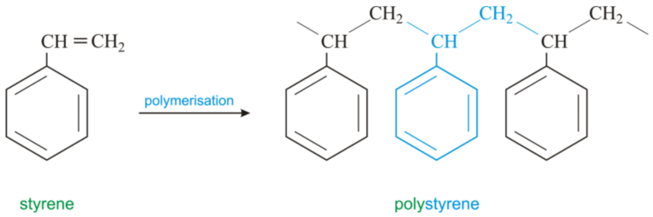


FIG 6: STRUCTURE OF POLYSTYRENE

MANUFACTURING OF POLYSTYRENE:

Beads are pre-expanded with the use of a steam chamber to a bulk density of 0.02-0.05 g/cc.Beads are cooled & reached equilibrium with air penetrating into the cells. Placed back in steam chamber & that beads are molded into final foamed shape. Forms basic cellular structure is closed cell type [Shcharbin et al., 2014]. Large blocks are molded which are cut into insulating boards or molded into custom products. Cups, insulating containers, protective elements are produced by using poly styrene (FIG 7). Extrusion process can be used with blowing agent. Meat trays & egg cartoons are made from polystyrene recently [Seizeret al., 2012]. Another example of cellular polymer is polyurethane. Stiffness can vary widely from that of a soft elastomeric to a rigid plastic [Scoopi et al., 2011]. Density can vary widely from 0.33 g/cc (rigid form) to 0.08 (flexible) .Cell structures varies from open cell structures for flexible and closed cell structures for rigid foam which traps the blowing agent.

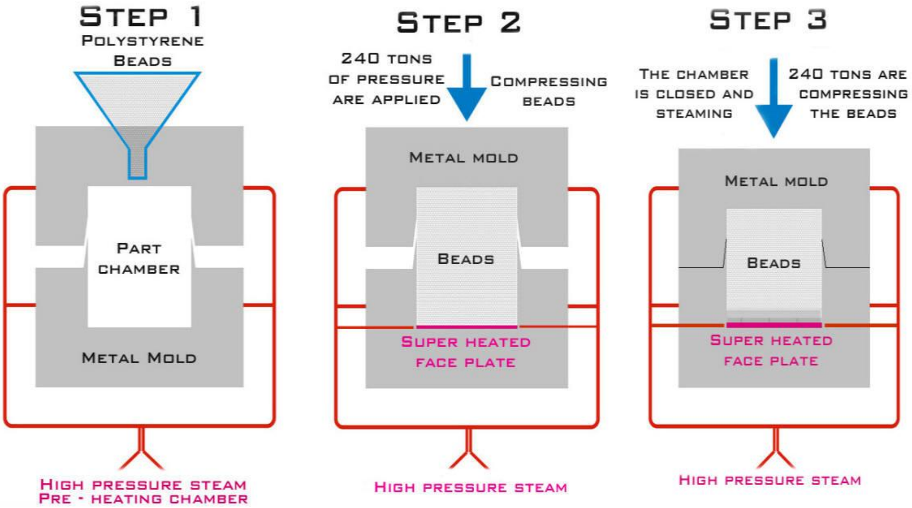
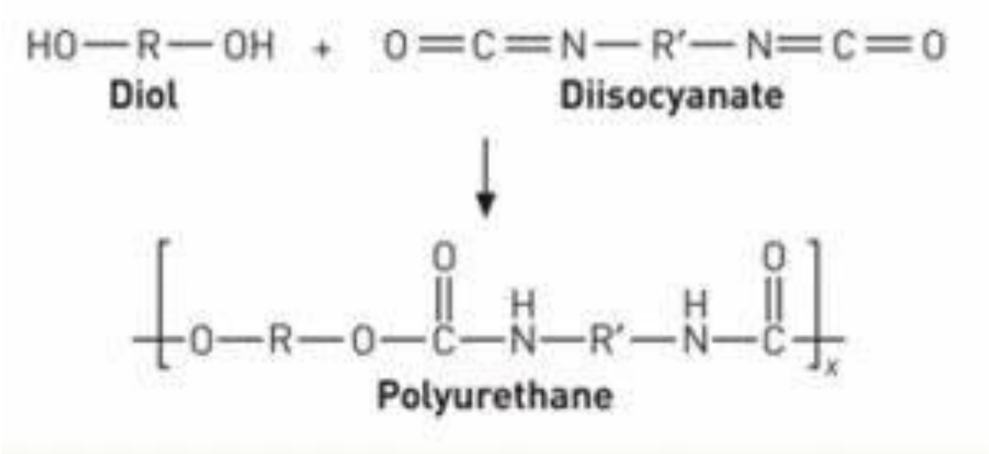


FIG 7: FORAMTION OF POLYSTYRENE FOAM

MANUFACTURING OF POLYURETHENE

Continuous formation of rigid or flexible foam of large block (log, bun, loaf).Uses a suitable mould using a mixing head on a boom that is placed on the top of a carrousel with several moulds.The resin is injected in one moldwhile others are curing(FIG 8). Typical cross section is 2m×1m and a typical linear speed of production is 4m/min.Subsequent products are cut from foam stock using hot wires.



$$HO-R-OH + O=C=N-R'-N=C=O$$

FIG 8: STRUCTURE OF POLYURETHENE FOAM

Polyurethane (PU) Foams

Polyurethane foams are the largest class of polymeric foams accounting for more than 50% of the worldwide usage of plastic foam. The properties of urethane foam can be tailored over a wide range for a large number of applications. They can be thermosetting or thermoplastic, rigid and hard or flexible and soft. They are formed from the reaction of an organic diisocyanate with a polymer which leads to urethane linkages in the backbone (-NH-C (=O)-O-) [Soldranzo et al., 2013]. The polyol compound is typically a polyester or polyether, but can be any other resin having hydroxyl groups. This compound is typically the flexible portion of the urethane polymer and, thus, determines how rigid or flexible the foam will be. To produce foamed urethanes a small amount of water and an excess of isocyanate is added to the polyol. The water reacts with some of the isocyanate groups to form amines and carbon dioxide gas which forms the cellular structure of the foam [Taco et al., 2012]. As the polymer hardens, the bubbles of carbon dioxide are trapped in the urethane. These bubbles give the polyurethane its cellular texture. Generally, during the early part of the polymerization process, the mixture is vigorously stirred to produce smaller bubbles. Depending on the process conditions and the amount of water added, the density of these materials can range from as low as 0.015g/ml or lower to as high as 0.95 g/ml [Thomas et al., 2015]. Polyurethanes can also be foamed using low-boiling, inert liquids such as fluorocarbons which are mixed with the polyolportion. During the polymerization process, the released heat causes the liquid to volatilize and to act as a blowing agent [Tatasurogodo et al., 2014]. Polyurethanes can be converted into a wide range of materials including soft and flexible foams as well as tough and rigid foams

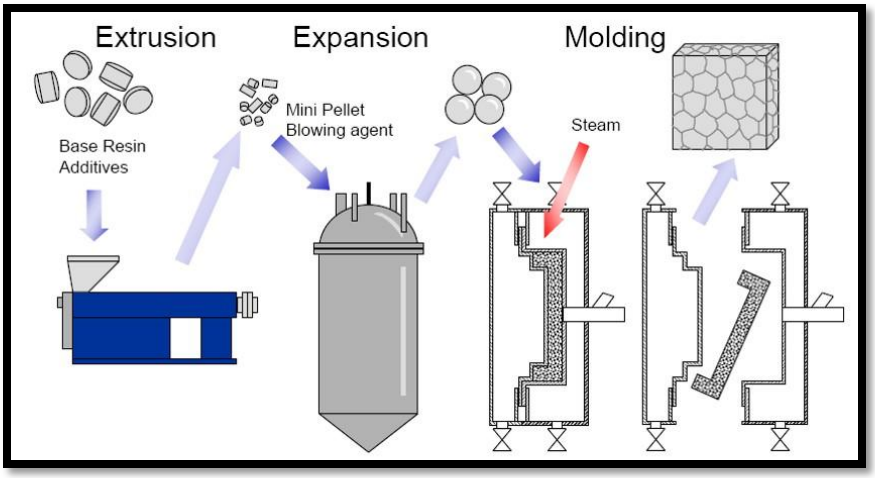


FIG 9: FORMATION PROCESS OF POLYSTYRENE FOAMS.

Flexible foams have typically a low density and semi-rigid foams have a medium density. Due to the versatile chemical characteristics and low price, polyurethane foams find a multitude of applications. Major applications for open-cell urethane foam include carpet backing as well as cushioning products for furniture and bedding. Rigid urethane foams are used in many light-weight (structural) parts including automobile bumpers, dashboards, and furniture (FIG 9). The demand of foamed urethane is expected to continuously grow based on the ever increasing demand for foamed plastics [Tatasurogodo et al., 2013].

Expanded Polystyrene (EPS) Foam

Polystyrene foam, also known as Styrofoam (Dow Chemical), is the second most important plastic foam. It amounts to about 28% of the worldwide plastic foam consumption. Foamed styrene is typically made from expandable polystyrene (EPS) which is produced in the form of free-flowing pellets or beads impregnated with a low-boiling-point aliphatic hydrocarbon blowing agent such as pentane or hexane. The EPS beads have a closed-cell structure with low thermal conductivity and moisture absorption which can be stored for several months at room temperature in closed containers. Foamed styrene products are typically produced by a two-step process [Tracey et al., 2018]. In the first step, the expandable beads are preexpanded or preformed by heat and then stored in a storage tank for several hours to allow them to equilibrate. In a second step, the beads are injected into a mold and further expanded to the final dimensions and, as the temperature exceeds the glass transition temperature, fused to the ultimate shape. The typical heat source is steam which is injected through perforations or tubes in the mould [Tian et al., 2013]. Polystyrene foam is used mainly as a thermal insulation material in the building & construction and packaging industries. Important products include insulation boards, drinking cups, egg cartons, and various other food containers. One of the major limitations of polystyrene foam is its rather low maximum service temperature of about 80°C (175°F).Both polystyrene and polyurethane are polymers, synthetic substances made from long chains of molecules. These molecules consist mostly of carbon and hydrogen atoms [Tiekrick et al., 2018]. Industry produces these ubiquitous plastic building materials to make all sorts of common items. The computers we use are typically encased in polystyrene, which is an older polymer. However, polyurethane is increasingly coming to replace polystyrene in certain situations, particularly those which require more flexibility. Though they are sometime confused, there are differences between the two in terms of their composition, the ability of finished products to resist chemicals and conduct heat and their tolerance for thickness [Trientz et al., 2016].

DIFFERENT BETWEEN POLYSTYRENE AND POLYURETHENE

CELLULAR POLYMER CHARACTERISTICS	POLYSTYRENE	POLYURETHENE
COMPOSITION	Polystyrene is a polymer containing molecules composed of carbon and hydrogen atoms, typically eight of each. The molecular formula of polyurethane, on the other hand, describes a much more complex polymer made from molecules composed of nitrogen and oxygen as well as carbon and hydrogen.	Unlike polystyrene, which forms a hard plastic, polyurethane's polymers can be arranged differently to create substances with varying degrees of flexibility.
R-VALUE	The R-value of a building material measures its thermal resistance. , Polyurethane demonstrates about twice the resistance to heat that polystyrene manages and is an excellent material for electrical insulation.	Polyurethane continues to maintain flexibility in very cold conditions, though gradual stiffening begins at -17.8 degrees Celsius. However, this resistance varies according to the density and thickness of each
FIRE RESISTANCE	Polystyrene will melt at temperatures in the 200- to 300-degree range. Polyurethane makes a superior fire-retardant material.	Polyurethane does not melt, unlike polystyrene. In fact, polyurethane will remain mostly undamaged by heat until temperatures reach 700 degrees, at which point the material begins to char
CHEMICAL WEATHERING RESISTANCE AND ABRASION	While polystyrene will suffer when subjected to solvents such as gasoline and certain insect sprays, polyurethane is resistant to all chemicals. This polymer also outperforms polystyrene in resisting atmospheric damage due to oxidation and sunlight	Polyurethane withstands all physical attacks and stresses better than polystyrene.
LOAD BEARING	Polystyrene does not have the flexibility for these tasks	polyurethane resembles rubber as well as plastic, it can be effectively used to make load-bearing wheels, mechanical joints, couplings and machine mounts
NOISE ABATEMENT	Polystyrene make more noise	Polyurethane is useful in achieving mechanical sound reduction. Gears made from this polymer make much less noise.

VINYL (Plastisol, PVC) FOAMS

Vinyl foams are the third largest class of polymeric foams accounting for about 6% of the worldwide usage of plastic foam. They can be flexible or rigid depending on the type and amount of plasticizer added. They are often the preferred material for applications where low-flammability at a low cost is required. PVC is typically foamed with organic nitrogen compounds such as diazoaminobenzene (DAB) or azobisbutyronitrile (AIBN). The gas evolution occurs typically over a narrow temperature range depending on the type of blowing agent. Often metal organic activators are added to lower the decomposition temperature and to increase the gas evolution [Vandewetering et al., 2014]. In a first step, the powdered blowing agent is dispersed in the plasticizer which is then added to the PVC. The plastisol blend is then injected into a heated mold or extruded through a heated die. The heat causes the plasticizer to dissolve in the PVC resin which dramatically increases the viscosity of the plastisol by salvation of the PVC. To prevent collapse of the gas filled cells at too low temperatures or the formation of large pores and cracks at too high temperatures, the decomposition temperature of the blowing agent should be very close to the gelatin temperature of the plastisol [Valsen et al., 2012]. If the decomposition of the blowing agent occurs in a closed mold, the internal pressure increases to very high levels which causes the gas to dissolve in the resin system which produces closed-cell plastisol with microscopically small bubbles. The product is then cooled and solidified in the mold before ejected. Open-cell vinyl foam with high porosity can be produced by either mechanically dispersing air in the plastisol near the gelation temperature or by a chemical blowing process with subsequent unrestricted expansion of the vinyl [Vierling et al., 2001]. The foamed plastisol is cast onto a belt or onto a fabric or sheet, knifed to the chosen thickness, and then solidified. Important applications of open-cell vinyl foams include upholstery, garment insulation, flooring underlays, carpet backing, and wall coverings. Rigid close-cell vinyl is often used in composite application where the low-density PVC foam is part of a multi-layer (sandwich) structure. Other applications include life jackets, buoys, and floats [Vierson et al., 2011].

POLYOLS

The most important characteristics of the polyol are its hydroxyl number, equivalent weight, functionality and rigidity or flexibility of chain units. The source of hydroxyl groups for almost all commercial uses of urethane foams are polyether and polyester based polyols. Both types of polyols are branched and have low molecular weight with relatively high viscosities. Sometimes the polyols based on naturally occurring oils bearing hydroxyl group, such as caster oils and its derivatives are also used [Valrech et al.,2014]. Worldwide about 90% of the polyols used for the preparation of PUF are based on polyether's, because of their low cost, easy process ability (lower viscosity), very low levels of contaminants, uniform narrow molecular weight distribution and compatibility with most formulation additives. Polyester polyols have higher cost and are difficult to process because of higher viscosity. So they are used in very specific applications such as better thermal stability and flammability properties [Valtman et al., 2013]. The polyester polyols are generally the condensation products of dicarboxylic acids such as adipic acid or ophthalmic anhydride and saturated polyfunctional alcohols such as 1, 2, 6−hexane triol, trimethylolpropane and diethylene glycol [Valtman et al., 2013].

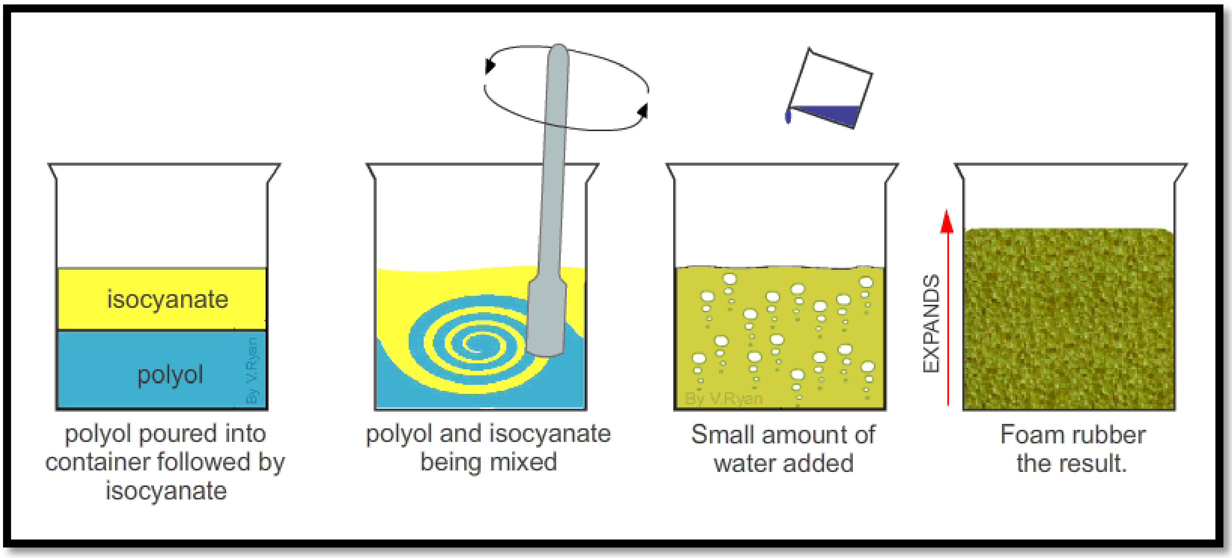


FIG 10: FORAMTION OF POLYOL INTO FOAM

The polyether polyols are produced by reacting alkaline oxides (ethylene/propylene) with polyfunctional alcohols such as glycerine, trimethylolpropane, pentaerythritol, sorbitol, α− methylglucoside, sucrose and polyamines (ethylenediamine, diethylenetriamine and piperazine) or oxyphosphorus acids. The choice of polyfunctional alcohols depend on their average functionality or degree of branching. It has also a profound influence on its final viscosity. Most rigid foams are prepared from formulated blends or copolymer polyols. The blends consist of one or several polyols, surfactant and flame retardants [Wang et al., 2012].

Sometimes they also contain catalysts and blowing agents. The formulation may also contain cross−linking agents such as trimethylolpropane, glycerine which improve curing and strength of the foam. Recently, there is an increasing interest to use raw materials based on renewable resources, like vegetable oil, which are biodegradable as well as good alternative to petroleum products [Wang &chang et al., 2013]. Some of the works have been carried out to identify the polyols from natural sources and recycled polyethylene terephthalate (PET) waste used as alternative source to prepare the rigid PUF (FIG 10). The rigid PUFs made from starch based polyols have properties comparable with the properties of PUF based on conventional polyol. The natural oils such as jet cooked starch oil, defatted soy flours, soybean oil, palm oil, linseed and rapeseed oil, sunflower and flaxseed oil, and biomass materials (soy protein isolate, soy fibre, corn starch) and also resin and modified rosin, lactitol,reduced sweet whey permeate have been used as natural resources for polyols [Wijikanalan et al.,2011]. These oily materials do not impart sufficient rigidity to make a stable PUF when they are used alone. This is due to their high equivalent weights and more flexible aliphatic structures. But when they are used in combination with conventional polyols the properties of PUF formed are found to be better. For example, The PUF from sodium lignosulfonate mixed with diethylene, triethylene and polyethylene glycols were prepared and thermal properties were reported [Wijikanalan et al., 2011]. The PUF from recycled PET waste are found to be better in flame retardant properties compared to PUF made from conventional polyols.

ISOCYANATES

The aromatic isocyanates these used for preparation of rigid PUF are generally toluene diisocyanate (TDI) and polymeric methane biphenyl diisocyanate (PMDI) [Wang etal., 2011]. TDI plays a minor role in rigid PUF production; because of unfavorablephysico− mechanical properties of TDI based rigid PUF.

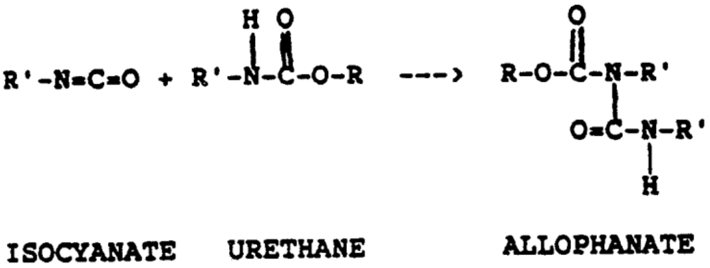


FIG 11: FORMATION OF ALLOPHANTE FROM ISOCYANTE

TDI is also very difficult to handle because of its higher vapour pressure. PMDI is currently the predominant isocyanate component for rigid PUFs. It has significantly lower cost than crude TDI and also has lower vapour pressure. Therefore this minimizes the toxicity problems usually encountered with general isocyanates (FIG 11).PMDI is prepared by the phosgenation of aniline formaldehyde condensed products [Wiwattanapatapee et al., 2015]. The different types of PMDI are available for various applications, for example, when priority is placed on flow ability; the expanding reaction mixture has to fill narrow gaps, and low viscosity PMDI with low functionality are preferred [Yang et al., 2013]. The viscosity range of PMDI may vary from 50 to 2000 mPa·s at 25 °C, the functionality varies from 2.5 to 3.2 and the NCO content varies between 25% and 29%. Sometimes the mixture of TDI and PMDI is used as isocyanate component to prepare rigid PUF [Zhang et al., 2012].

ADVANTAGES OF CELLULAR POLYMERS

Can form any shape, easy to produce, cost effective, high tensile strength, they don't corrode, cheaper than alternative materials, good insulator of heat (home insulation), good insulator of electricity (wire covers), wind power is impossible without cellular polymers(Special plastics are used in the wind turbine covers and huge blades to tap into this environmentally friendly energy source) [Zhang et al.,2013].The amount of fuel a delivery truck needs could be considerably reduced, low density, swell with water, low thermal conductivity, they require room temperature, they sense to UV light[Zhon et al.,2012].

DISADVANTAGES OF CELLULAR POLYMERS

Use up a nonrenewable/finite resource,flammable,toxicity, take a long time to decompose, take up space in landfill cause pollution in oceans, produce poisonous gases on combustion, finishing look isn't good, Thermoplastics flow when heated and solidify when cooled. Thermosets decompose when heated and often decompose due to the cross links between long chains, making them unstable [Zhan et al., 2013]. Elastomers are rubbery at room temperature and must be heated to a high temperature to react. Polymers such as plastic can be easily formed to make almost any imaginable shape and they are normally durable. However, many polymers cannot take exposure to extreme temperatures and don't always hold their shape in water.

IV. Conclusion

Supplementation enhanced the production of both the cellular polymers besides producing a maximum of 7.45g/L of biomass. The increased production of polymers using low cost nutritional supplement can reduce the production cost of these polymers. Production of value added biopolymers especially the copolymer of polystyrene can reduce the use of petroleum derived no biodegradable polymers and thereby reducing the environmental pollution. The chitosin produced also has a potential for industrial applications.

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