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POLYMER FOAMS

3.063 Polymer Physics

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Introduction

It is hard to go a day without coming across some sort of polymer foam. Polymer foams are found virtually everywhere in our modern world and are used in a wide variety of applications such as disposable packaging of fast-food, the cushioning of your furniture and insulation material.

Polymer foams are made up of a solid and gas phase mixed together to form a foam. This generally happens by combining the two phases too fast for the system to respond in a smooth fashion. The resulting foam has a polymer matrix with either air bubbles or air tunnels incorporated in it, which is known as either closed-cell or open-cell structure. Closed-cell foams are generally more rigid, while open-cell foams are usually flexible.

The gas that is used in the foam is termed a blowing agent, and can be either chemical or physical. Chemical blowing agents are chemicals that take part in a reaction or decompose, giving off chemicals in the process. Physical blowing agents are gases that do not react chemically in the foaming process and are therefore inert to the polymer forming the matrix.

Polymer foams are produced in a number of different ways. Examples are through slab-stock by pouring, extrusion and different forms of molding.

Polymer foams can be divided into either thermoplastics or thermosets, which are further divided into rigid or flexible foams. The thermoplastics can usually be broken down and recycled, while thermosets are harder to recycle because they are usually heavily crosslinked.

Issues facing the polymer foam industry is that of waste disposal, recyclability, flammability and the effect of blowing agents on the environment. The restrictions on the use of CFC's (chloro-fluoro-carbons) has become very important in making polymer foams more environmentally friendly. Advances in biodegradable foam materials are also helping to improve the recyclability and waste disposal.

The reason polymer foams are so widely used is that they have a lot of advantageous properties. The density is low, and so the weight reduction compared to other options is significant. Some polymer foams have very low heat transfer, making them optimal insulators. Many are flexible and soft, meaning they provide more comfort when used for furniture and bedding.

Through this paper I will examine these topics, and specifically focus on polyurethane foam as one of the most common polymer foams used in everyday life and applications.

Brief history

Polymer foams were first made in the 1930's and -40's, with foamed polystyrene being the first polymer foam in 1931. Polyurethane was invented by Dr. Otto Bayer at the start of the second World War. It was first used as a replacement for rubber and also used as a coating to protect other common materials at the time such as metals and wood.

A few years after the war, the flexible polyurethane foam was invented and it was first then that it started being used for cushioning in furniture and automotive industry.

The two decades following made polymer foams more widely used as new technologies developed, introducing methods such as injection molding, twin screw for foam and several extrusion techniques.

The use of blowing agents that contributed to the ozone layer depletion raised concerns in later years and has led to a focus on finding blowing agents that will not have a negative environmental impact.

Types of polymer foam

Polyurethane

Polyurethanes are any type of polymer containing a urethane linkage. The urethane linkage is $-NH-CO-O-$. The way to form polyurethanes is done by reacting isocyanates with compounds that have an active hydrogen, such as diols, that contain hydroxyl-groups, in the presence of a catalyst. Since there are many compounds containing active hydrogens and many different

diisocyanates, the number of polyurethanes that can be synthesized is also large. The specific properties of the polyurethane can be tailored to a specific need by combining the appropriate compounds.

Polyurethanes can exist as both rigid and flexible foams, and as a coating or adhesive material. Since polyurethanes come in so many forms and can have a wide variety of properties, it is also used in many different applications. Rigid polyurethanes are used as insulation and flotation, while flexible ones are used for cushioning and packaging. In addition, they are used as adhesives in construction and transportation. Rhinoskin is an example of a polyurethane used for coating and protection. It is sprayed onto a surface and then sets to protect the underlying layer.

Polyurethanes are mostly thermosets, which means they are hard to melt and reprocess and can therefore have the disadvantage of being non-recyclable.

Biodegradable foams

Biodegradable polymer foams are investigated not only because of the increasing waste and environmental problems for traditional polymer foams, but also because of the increasing price of petroleum products that are used in manufacturing the polymer foams.

Biodegradable foams are water soluble and sensitive to humidity, while traditional petroleum-based foams are more inert to water. Biodegradable foams are also limited in making foams that have microcellular structure, which means they will be hard to make into thin sheets.

However, they are important in reducing the amount of CO₂ emission. There is also a wide range of different candidates of biomaterials that can be used for biodegradable foams, including ethylene vinyl alcohol, polyvinyl alcohol, polycaprolactone, polylactic acid and starch.

Starch

Starch foam was made already in 1989 as biodegradable packaging, and is an alternative material to the traditional polystyrene foams. Starch is a polysaccharide made up of glucose units linked by glycoside linkages, and its length is generally between 500-2000 repeat units.

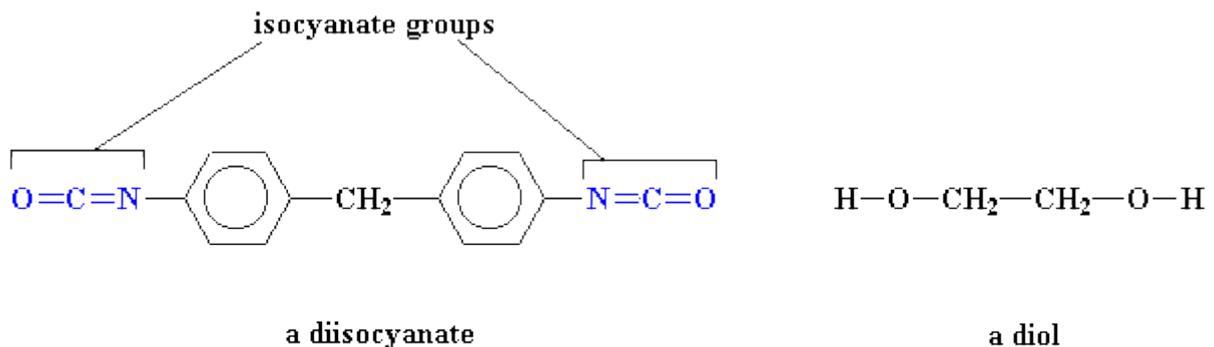
Starch is made up of amylose and amylopectin. Amylose is more linear and gives the foam flexibility and keeps the density low, while amylopectin is highly branched and makes the product more foamable. Starch can be extracted from for example corn or potatoes.

Starch foams are produced by extrusion where the starch is melted and mixed with a blowing agent. The blowing agent for starch is often water or methanol, which is turned into steam when the system is heated and forms air bubbles within the starch matrix. The extrusion process is a continuous, low-cost method that is easy to use. It is still hard to make the foam smooth and have a high number of closed cells. The use of thermoplastic polymer additives can help even out the surfaces, but can also decrease the degradability of the foam by incorporating slowly degrading or non-degradable polymers.

Synthesis

Polyurethane

As mentioned earlier polyurethanes are made by the addition reaction of polyisocyanates and polyols. When there are two functional groups it's termed a diisocyanate and diol as seen below.



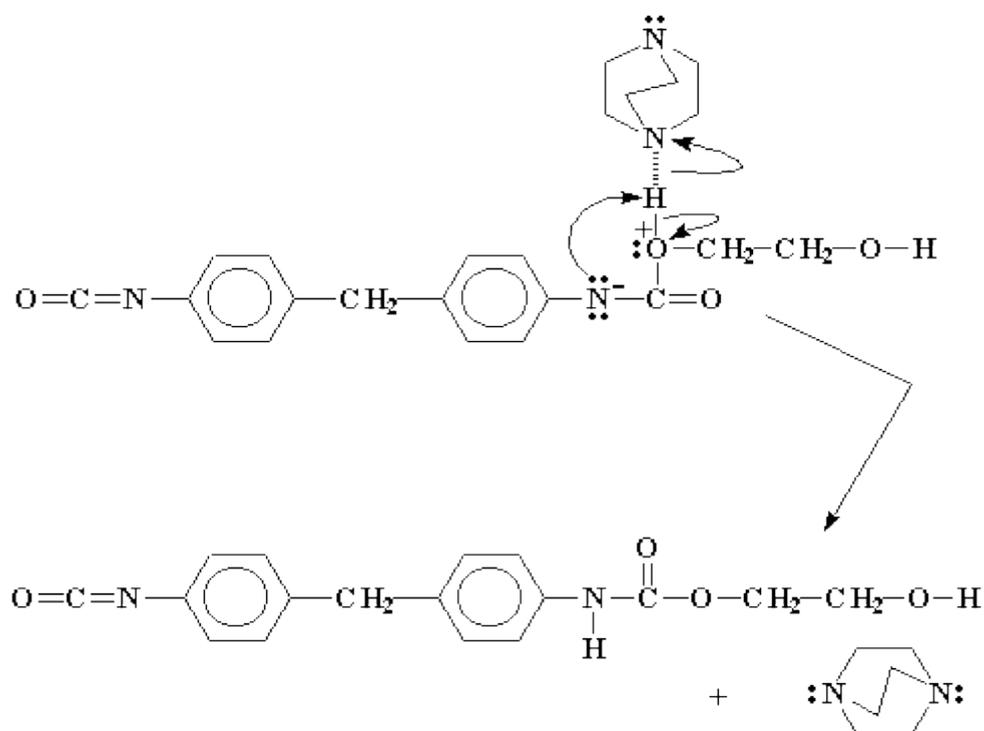
<http://www.pslc.ws/mactest/uresyn.htm>

Figure 1: Reactants used for polyurethane

Along with a nucleophile like diazobicyclo[2.2.2]octane (DABCO), the mixing of these two monomers will form a dimer, which again will continue to react with other monomers,

dimers and oligomers and form long polyurethane chains.

The positive charge due to oxygen's electronegativity on the hydrogen at the end of the diol attracts the nucleophile, which wants to bind to a nucleus (nucleophile=nucleus loving). The oxygen then becomes more negative and reacts with a carbon on an isocyanate group. This leaves the nitrogen on the isocyanate group to be negative, which is highly unfavorable. The nitrogen will give off its negative charge to the hydrogen atom on the alcohol group, finally forming a urethane bond between the two monomer units, resulting in a urethane dimer. The dimer will have one end group that is isocyanate, while the other is an alcohol group. Each end can now react with other monomers and oligomers until polyurethane is formed. This is called a step-growth reaction. Step-growth reactions are characterized by longer chains being able to react and add to a growing chain just like monomers can, unlike chain-growth polymerization where only monomers can add to the growing chain. It is also an addition reaction since no small compounds are given off during the reaction.



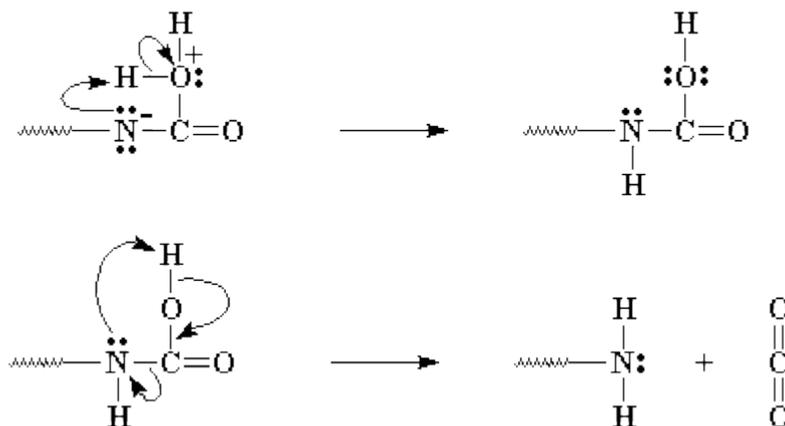
<http://www.pslc.ws/mactest/uresyn.htm>

Figure 2: the DABCO attaches to the hydrogen of the alcohol group. The negative oxygen then reacts with the carbon on the isocyanate group, leading to a negative nitrogen. The nitrogen gives off its charge to the

hydrogen and the two monomers become bound together to a dimer by a urethane linkage.

If instead of a diol, a macrodiol is used in the reaction, the polyurethane gets alternating soft and rigid segments, where the macrodiol makes up the soft segments in between the rigid blocks from the diisocyanate monomers.

The difference between making polyurethane and polyurethane foam is that a gas has to be incorporated in the final product. To achieve this the isocyanate group is reacted with water forming an amine and CO₂ gas. Because the isocyanate group turns into an amine, the reaction with other diisocyanates will result in some urea-linkages in the polyurethane foam, but this doesn't affect the properties of the polymer foam much, and is necessary to get the gas to be produced and expand the polymer into a foam.



<http://www.pslc.ws/mactest/foamsyn.htm>

Figure 3. The reaction of water with isocyanate group forms an amine group and expels carbon dioxide gas.

Blowing agents

As seen in the last paragraph, water was used as a blowing agent to produce CO₂.

Because the water needed to be part of a reaction, it's a chemical blowing agent. Physical blowing agents don't take part in a chemical reaction, but are volatile liquids that evaporate and make the foam expand. First generation physical blowing agents are mostly outdated because of their negative

environmental impact on the ozone layer. This is especially the case for chlorofluorocarbons.

CFC's and HCFC's

CFC's are ideal blowing agents besides the tremendous environmental concerns associated with them. They are not flammable, have fitting boiling points and are non-toxic. They also have good thermal insulation properties. This is why it has been hard to find a replacement for these blowing agent that has equivalent properties

Hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC) are blowing agents with a lot smaller impact on the ozone layer and with similar properties. HCFC's are being phased out since they still have ozone depletion problems. Although HFC's have no impact on the ozone depletion, it has high global warming potential. However, they have a lower shelf life and can sometimes be flammable, which creates concern because this decreases the safety of polyurethane foams.

CO₂

Liquid CO₂ is used as a blowing agent because it does not have the same environmental issues as CFC's and HCFC's. It has a low global warming potential and is inexpensive. It is also easier to obtain low density foams using CO₂.

Manufacturing methods

Slabstock

Slabstock processing has its name from the way that the foam is cut into large slabs after being processed, instead of formed into specific geometric shapes. The materials are spread onto a conveyor through a mixing head, and the foam forms on the conveyor constrained by walls so the foam forms a large slab of material. The foam is then cut into suitable size slabs.

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Please see Harrington, R. and Hock, K. *Flexible Polyurethane Foams*, 2nd ed. Midland, MI: Dow Chemical Company, 1998.

http://scholar.lib.vt.edu/theses/available/etd-12032002-170009/unrestricted/02_Chapter_1.pdf

Figure 4: The foam is mixed and poured onto a conveyor and forms one large continuous piece that is cut into slabs.

Molding

Molding processes can be divided into either cold-molded or hot-molded processes, differing by their molding temperatures. The process injects foam into separate formed molds and shapes the foams into individual pieces with the same shapes. This process is more complicated than slabstock and more costly.

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Please see Harrington, R. and Hock, K. *Flexible Polyurethane Foams*, 2nd ed. Midland, MI: Dow Chemical Company, 1998.

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Figure 5: Individual molds on a turntable. The mixing head inserts an equal and discrete amounts of material into each mold. The molds are made to form the foam into specific geometries.

Properties of polymer foams

Structure

As mentioned earlier foams can be divided into open-cell and closed-cell structures.

However, the term cell in this context is somewhat different than what it is usually considered as. In all foams the cell or pore structure is not a specific uniform unit, there is instead a wide range of different sized cells and pores and a certain amount that are closed-cell and open-cell although one will be the dominating structure.

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Please see <http://ciks.cbt.nist.gov/%7Egarbocz/closedcell/img54.gif>

Figure 6: A model of a closed-cell structure where all the pores are constrained by polymer matrix walls.

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Please see <http://irc.web-t.cisti.nrc.ca/cbd/figures/166f03.gif>

Figure 7: Open cell structure of polyurethane foam at 20x magnification. The pores are not enclosed but form a continuous network.

Since the size and shape of the cells or pores are very disperse the best approach to describe foam structures is through statistical models, since there is never a regular packing of spherical cells in a foam. The models used range from cells being modeled as spheres, polygons and dodecahedrons. In addition the cells are usually elongated in a certain direction as the polymer is foamed, making it harder to model the foam as any ideal model. It is not only the polymer itself that contributes to the properties of the foam, but the gas-filled space between them. In comparison to other non-polymeric foams where the voids or gas-filled spaces do not interact with the surrounding matrix, in polymer foams the intercellular gas interacts with the matrix and affects its properties and behaviors and can change them over time.

The parameter G is the relative geometrical volume and φ_g is the volume fraction of cells/pores which the gas occupies. The total volume is the sum of the volume fraction of the gas, polymer and moisture, since the foam always sucks up some moisture from the environment.

G is the quotient of the total number of voids over the net volume.

$$G = V_g / V_o$$

The gas-filling factor is a similar parameter that is often more convenient. It is the quotient of the total number of voids over the solid phase volume.

$$G = V_g / V_s$$

The volume fraction of cells/pores is

$$\varphi_g = (\rho_p - \rho) / \rho_p$$

which is the difference between the density of the unexpanded polymer and the apparent density of the foamed polymer over the unexpanded polymer density. This formula neglects the weight of the gas in the pores.

This can also be written in terms of the mass and density of the gas:

$$\phi_g = (m_g) / (V_o \rho_g)$$

The amount of pores in the foam structure affects many of its properties. When there are more and smaller pores the foam is a much better insulator, because the gas basically cannot transfer heat and the heat convection has to find its way around all the pores. The more pores there are the more tortuous the path, and there is less chance of the heat transfer happening effectively. In this case, the gas phase is more dominant in determining the foam properties than the actual polymer.

The mechanical response of the foam is also dictated by the structure. In an open-cell structure the gas phase is not held together and the foam can compress much more. The foam will reform by sucking up air again, but will not be able to mimic its original shape exactly and the strength and energy absorption of the system will be weaker.

The size of the cell also affects the properties of the foam. Foams with smaller cells are better at energy absorption. At smaller cell sizes the amount of open-cell structure also decreases.

Mechanical

Since gas has the least mechanical strength, the more gas there is the less strong the foam will be, which means the lower density foams exhibit the smallest Young's modulus. Even if the cells of the foam have varying shape, there is usually some anisotropy to the foam because of the direction it is being formed at. The strength is better along the direction of foaming. If the ratio of height to width of a cell is increased by a certain amount, the compressive strength and the tensile strength of the foam also increases by the same amount. So the geometry of the cells could have more to say for the strength than density, chemistry and the amount of open-cells in the structure.

Open-cell structures have the disadvantage of lower mechanical properties, but is much better at sound absorption. Because the open-cell structure affects the modulus of the foam, this must be taken into account when calculating the modulus.

The modulus is:

$$M_f/M_p = (1-x)\phi^2 (\rho_f/\rho_p) + x(1-\phi)(\rho_f/\rho_p)$$

where M_f is the modulus of the foam and M_p is the modulus of the polymer. Φ is the volume fraction and ρ is the density, with the subscripts f and p for foam and polymer. X is the closed-cell fraction.

Impact absorption is a key advantage of polymer foams over the unfoamed polymer. The cells deform to absorb the energy impact and then reform when the load is removed. The polymer foam has to be able to resist multiple loadings, and resisting change to the structure so the loading can be repeated many times. If the foam is exposed to loads that are too large the cell walls will rupture and the amount of open-cell structure will increase and weaken the mechanical properties of the foam.

Thermal conductivity

The total thermal conductivity is the sum of the conductivities of both the gas and solid phase plus the thermal conductivity due to convection and radiation. The thermal conductivity is very low for polymer foams because the amount of solid in the foam is very small (on the order of 3%-10% of the total volume). The fraction of solid used is not always minimized though, because of a decrease in mechanical strength of the foam or because it is harder to produce low density foams for some raw materials.

The gas phase contributes the most to heat transfer. The thermal conductivity of a gas decreases with an increase in molecular weight, so a heavy gas is more desirable as a blowing agent, although this is not always possible either because of cost or convenience. After usage and time the gas phase in the foam is replaced by air which has just a slightly higher thermal conductivity than some heavier blowing agents like CFC's and CO₂. The larger molecular weight compounds also diffuse much slower through the polymer matrix, and the replacement of air into the foam goes much slower, keeping the thermal conductivity as low as possible.

Radiative heat transfer happens through cell walls, so a foam with many small cells will transfer less heat than a foam with a small amount of large cells. The cell size has a larger impact

than just changing the density.

Convective heat transfer only takes place in foams with very large cell sizes and is for the most part negligible.

The thermal conductivity has a minimum at a certain density. At low densities the radiative component is more dominant since the cell size is larger, and so is the convective component. At high densities the number of cell walls and the thickness of them is higher so the radiative component is less important, but the heat transfer through the solid phase becomes more dominant.

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Please see <http://www.scielo.br/img/revistas/jbsmse/v28n1/28260f1.gif>

Figure 8: The lowest curve shows how low thermal conductivity foam has compared to other insulating materials and that it has a minimum at a certain density value.

Flammability

The volatile liquids that are often used as blowing agents in foams and lead to easily combustible foams. The flexible polyurethane foams are low density and have a lot of open-cell structure, which means it is permeable to air. This means that it will easily burn when exposed to a

flame. This is a concern that the industry has to deal with in increasing the safety of their products.

One of the solutions is to use flame retardants in the foam. Chlorinated phosphate esters, chlorinated paraffins, melamine powders and graphite are common as flame retardants.

Applications

Polyurethane foam

Rigid

Rigid polyurethane foams are mostly used in thermal insulation applications such as refrigerators, freezers, insulated buildings, insulated trucks carrying produce, water heaters, thermoses etc. Hence, rigid polyurethanes contribute a lot to energy saving appliances.

Polyurethane foams with a high closed-cell structure are moisture resistant and can be used as buoyancy in boats. The advantage is that the foam will not deflate upon a puncture, but retains its buoyancy even after many load-unload cycles.

Flexible

Most of the flexible polyurethane foam produced is made for cushioning. This includes furniture, packaging and transportation. Furnishings use polyurethane foam for carpet underlay, bedding, home furniture. The transportation industry uses it in seating cushions for the airlines, trains and bicycles and cars. It is also used in a wide range of other applications for cars such as sound insulation and vibration dampening. Other applications include clothing, toys, electronics and other applications for protection or cushioning issues.

Polystyrene foam

Polystyrene foam's most known application is the white polystyrene cups which are ideal for hot beverages because of the foam's good thermal insulation properties. Polystyrene foam is also used for packaging purposes, mostly food containers and disposable dishes and egg cartons.

High-impact polystyrene can also be used in structural appliances instead of rigid

materials like wood and metal.

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Figure 9: Examples of polystyrene applications

Conclusion

The structure is divided into open-cell or closed-cell foams, but most have a small amount of the other as well. Production of the foams can happen in many different ways, slabstock and molding were two that were mentioned here. Since polymer foams are used widely all over the globe the technology to produce foams is continuously being improved.

Although many blowing agents are good in that it produces a satisfying product, the environmental impacts can be large, so blowing agents such as CFC's and HCFC's are not in use anymore. CO₂ and other less environmentally dangerous substances are being used instead.

Polymer foams have great thermal insulation properties and can also be tuned to have different mechanical strength and moisture absorption.

Polymer foams are widely used in all kinds of different applications because they can be manufactured from many different types of polymers and there are plenty of different blowing agents available to customize the foam to specific requirements. Polymer foams can be made to be rigid or flexible by changing the chemistry, density, structure and raw materials used.

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