

Degradation of Polymers

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ABSTRACT:

Polymer is a long chain molecule that is composed of a large number of repeating units of identical structure. Polymeric materials are used in nearly all areas of daily life and their production and fabrication are major worldwide industries. Polymers susceptible to attack by a wide variety naturally occurring and manmade agents during the period of application. Sometimes this degradation may limit the life time of the polymer and in some cases it may be desirable goal. A few factors of polymer degradation are discussed in this paper.

KEYWORDS:

polymer degradation, polystyrene, polyethelene, thermoplastics, addition polymers, condensation polymers, nylon-6,6, adipic acid, hexamethylene, thermal degradation, mechano degradation, oxidative and UV degradation, hydrolysis, radiolysis.

Polymers are large molecules with anumber of identical units covalently bonded together. Certain polymers , such as proteins, cellulose, and silk are found in nature , while many others , including polystyrene, polyethylene and nylon are produced only by synthetic routes. The application of polymers in daily life has increased manifold in recent times. Polymers are classified into two groups based upon their processing characteristics or type of polymerization mechanism. Those polymers that can be heat softened in order to process into a desired form are called Thermoplastics. Polystyrene, polyolefins, poly(Vinyl-chloride) are some example of thermoplastics. In addition to classifying polymers on the basis of their processing characteristics , polymers may also be classified according to the mechanism of polymerization as either addition or condensation polymer. Polystyrene, which is polymerized by a sequential addition of styrene monomer is an example of addition polymer. Most important addition polymers are polymerized from methylenebased monomers. Polymers obtained by random reaction of two molecules is a condensation polymer. Typically, condensation polymerization is the synthesis of nylon-6,6 by condensation of adipic acid and hexamethylene diamine is accompanied by the liberation of two molecules of water for each repeating unit.

Degradation is a process by which depreciation in

Both physical and chemical properties occur when these materials are exposed to different types radiations including mechanical degradation. Some of the factor affecting the degradation of polymers are discussed as follows.

- a. Thermal degradation: Polymers can degrade by exposure to high temperatures Vinyl polymers are particularly susceptible to thermal degradation, which occur either by chain scission involving the breakage of the backbone bonds to yield free radical segments, or by non chain scission, involving the elimination of a small molecule from a substituent group and subsequent double bond formation. Whether or not a polymer will thermally depolymerize to yield monomer is partly relate to its ceiling temperature. Ceiling temperatures of some common vinyl polymers is shown in the table below.

Polymer	Structure	T_c (°C)
Poly(α -methylstyrene)		61
Poly(methyl methacrylate)		220
Polypropylene		300
Polystyrene		310
Polyethylene		400
Polytetrafluoroethylene		580

- b. Mechano-degradation: Polymer degradation can also occur result from the application of stress such as high shear deformation of polymer solutions and melts. Stress induced

degradation may result from grinding, milling, or crushing, machining, stretching, fatigue tearing or wear. Mechanodegradation is severe for high molecular weight polymers that exist in a highly entangled state. The result of stress induced degradation is the generation of macro radicals originating from random chain rupture.

- c. Oxidative or UV degradation: With exception of fluoropolymers, most polymers are susceptible to oxidation or during exposure to ultraviolet light. Oxidation usually leads to increasing brittleness and deterioration in strength. The mechanism of oxidative degradation is free radical and is initiated by the thermal or photolytic cleavage of bonds. The free radicals then react with oxygen to yield peroxides and hydro peroxides.
- d. Hydrolysis: Many polymers are susceptible to degradation due to effect of water, particularly under acidic conditions. These include some naturally occurring polymers, such as proteins, as well as some synthetic polymers, principally condensation polymers such as polyesters and polyamides. The hydrolysis of a polymer results in the formation of chain segments terminated by hydroxyl and carboxylic groups.
- e. Radiolysis: Many polymers are susceptible to degradation and cross linking upon exposure to high energy ionizing radiation such as γ -radiation, electron beams, and X-rays. The primary event in radiation damage is the ejection of a high energy electron. This primary electron can then ionize additional molecules with the release of additional electrons in a chain reaction.
- f. Biological degradation: Most polymers, including polyamides, polyfluorocarbons, polyethylene, polypropylene and polycarbonate, are highly resistant to microbial attack. Naturally occurring polymers are more biodegradable than synthetic polymers. Biodegradation of these polymers proceeds by attack of ester groups by nonspecific esterases produced by ground microflora combined with hydrolytic attack. Products of the degradation can be quickly metabolized by micro organisms.

CONCLUSION:

Polymers can degrade by exposure to high temperature (Thermal degradation), Shear action (Mechanodegradation), Oxygen and ozone, Electromagnetic (r, UV) and ultrasonic radiation, Moisture (Hydrolysis) and chemical agents. Multiple exposure such as a combination of moisture and heat or oxygen and light (Photooxidation), can result in accelerated deterioration. Some of these environmental agents and examples of polymers that are particularly susceptible to their action are listed in the table below.

Effects of Environmental Agents on Polymers		
Agent	Susceptible Polymers	Examples
Biodegradation	Short-chain polymers, nitrogen-containing polymers, polyesters	Polyurethanes Polyether-polyurethane
Ionizing radiation	Aliphatic polymers having quaternary carbon atoms	Poly(methyl methacrylate) Polyisobutylene Polypropylene
Moisture	Heterochain polymers	Polyesters Polyamides Polyurethanes
Organic liquids and vapors	Amorphous polymers	Polystyrene, Poly(methyl methacrylate)
Ozone	Unsaturated elastomers	Polyisoprene Polybutadiene
Sunlight	Photosensitive polymers	Polyacetals Polycarbonate

UV radiation and ozone can seriously degrade the unsaturated elastomers use in rubber tyres. This degradation will limit the life time of the tyre and could cause catastrophic failure. In practice, UV and ozone resistance is provided by adding various fillers and stabilizes to the formulations. In some cases, degradation may be advantageous. For example , to design plastic bottles and packaging films so that a rapidly degrade in to environmentally safe by products (e.g , carbondioxide , water and biomass) that will occupy less volume in a land fill. Therefore it is necessary to ensure that degradation does not occur during the normal shelf life of the plastic and that cost and mechanical and other properties are not overly compromised to achieve biodegradability.

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