



POLYMER DEGRADATION AND TYPES

Sachin S. Shende

Department of chemistry, Netaji Subhashchandra Science College, Mulchera, Gadchiroli, India

Communicated :10.12.2022

Revision: 20.01.2023 & 24.01.2023

Published: 30.01.2023

Accepted: 26.01.2023

ABSTRACT:

Readers can find basic knowledge of polymer degradation, its causes, processes, and consequences in a broader context, as indicated by the list of chapter headings. Depolymerisation; initiation of cleavage (degradation) of macromolecules. thermal degradation; photochemical degradation; mechanochemical degradation; oxidative degradation; polymer sintering; Degradation during polymer recycling. Protection of polymers from degradation. Demotion is the act of making something or someone less respectable. In polymer science, degradation generally refers to the complex process by which polymeric materials lose their original properties when exposed to the environment and workload. Degradation is usually an undesirable process. However, in some cases, controlled polymer degradation is useful. Polymer degradation is a complex process in which polymers lose their original functional properties due to irreversible structural changes.

Keywords: - Polymer degradation, Depolymerisation, macromolecules, photochemical degradation.

INTRODUCTION :

Demotion is the act of making something or someone less respectable. In polymer science, degradation generally refers to the complex process by which polymeric materials lose their original properties when exposed to the environment and workload. Degradation is usually an undesirable process. However, in some cases, controlled polymer degradation is useful. For example, it can be used to improve the processability of polymers or to recycle or biodegrade waste polymers. In most cases, macromolecular cleavage is an integral part of polymer degradation. In a narrower sense, therefore, the process of splitting macromolecules into fragments of different structures and sizes is often referred to as polymer degradation. However, when a monomer is the final product, cleavage is the opposite of polymerization and hence depolymerisation [1,2].

Depolymerisation Like any other chemical reaction, depolymerisation occurs only when

the free energy of the system is reduced. If the polymer is formed by product-free polymerization, with polymerization entropies $\Delta S_p < 0 > 0$ and $\Delta H_p > 0$, and depolymerisation occurs below the so-called bottom temperature, then $T_f \cong \Delta H_p / \Delta S_p$ is preferred [3]. When a polymer is formed by polycondensation, such as esterification or polyamidation, the by-products participate in the polymer-monomer balance and, if present (added), facilitate depolymerisation. But even in these cases, temperature is very important. An ideal chain depolymerisation occurs in a living polymerization system where each macromolecule has end groups with active sites (radicals, ions). Since the Gibbs energy of activation is small both in propagating and depropagating, such a system can be implemented by gradually releasing monomer molecules from the active ends of the living chains until a new equilibrium between polymer and monomer molecules is reached. Responds to temperature rise. This is known as end-of-

chain splitting mode and is often called unwrapping. Subsequent return of temperature leads to reintegration of monomer molecules into macromolecules. A nearly ideal stepwise depolymerisation occurs during the hydrolysis of water-soluble polyesters in dilute aqueous solutions (the reverse of polyesterification). In this case, each ester bond can be cleaved with equal probability in the following time intervals: This corresponds to the random mode of disconnection.

Initiated cleavage (degradation) of macromolecules

Polymers without active sites are now stable at temperatures well above T_c due to the high free energy of activation of the centre. It is thermodynamically unstable but kinetically stable. However, the polymer begins to degrade as active centres are formed after initiation. The major active decomposition centres are radicals generated within polymers by thermal, photochemical, mechanochemical, or oxidative processes. Mode of initiation is used as an adjective to indicate the mode of polymer degradation.

Thermal degradation

An increase in temperature amplifies intramolecular vibrations and accelerates structural changes in macromolecules. Intrachain chemical bonds sufficiently stressed by these movements dissociate homolytically, resulting in radical terminal fragments. These radicals enable fragment depolymerisation (unpacking) at $T > T_c$ and other environment-dependent reactions (usually oxidation) when exposed to air.

Photochemical degradation

In a typical photolysis, depending on the photon energy, radiation electronically excites some groups in the polymer, making them reactive (light, UV) or dissociating some of the bonds into radicals (UV, RTG) or emit electrons from the polymer. (RTG, gamma rays), producing

radical ions [4,5]. Depending on the polymer structure and environmental conditions, the photogenerated species enter into depolymerisation (at $T > T_c$) and/or various subsequent reactions, resulting in cleavage, cross-linking, or modification of polymer molecules or all. Occurring in air, photochemical initiation is followed by oxidation of the polymer, and the overall complex process is termed photooxidative degradation [2]. Thermal and chemical degradation accelerated by microwave or infrared radiation are considered radiation rather than photochemical degradation.

Mechanochemical degradation

Cutting the rubber band actually breaks many of the chemical bonds in the original network polymer. Linear macromolecules can also be mechanically degraded into two radical fragments when sufficient mechanical work is imparted by intermolecular interactions under flow shear stress [6]. Such cleavage is not visible for small molecules that cannot transfer the energy required for destruction in this manner. Efficient energy transfer by flow shear is only possible for long molecules[2]. Therefore, the mid-strand scission mode is typical of this decomposition. For example, shear degradation is desirable in the production of rubber compounds by calendaring (before vulcanization). In fact, some rubbers contain many macromolecules with relative molecular weights (MW) greater than 1 million, the cleavage of which significantly reduces the viscosity of the vulcanized mixture, allowing the mixture to homogenize faster and more efficiently. It will get better. Flow-induced degradation, on the other hand, is present in SEC (Size Exclusion Chromatography) columns, but is undesirable. In this case, scission of long linear macromolecules, typically >2 million MW, skews the measured His MW distribution of the polymer. Mid-chain scission is also induced by

ultrasound, imposing periodic conformational changes on macromolecules, leading to macromolecular degradation [7].

Degradation in polymer recycling

The preferred route for polymer recycling is to use cleaned and properly pretreated polymer to manufacture new products. This can be easily done when the degradation of the waste polymer is so small that it is not critical to the properties of the new product. For example, PET bottles are cut, washed and processed into PET fibres for car mats and fabrics, and upholstery padding for armchairs and seats. Recycled high-density polyethylene (HDPE) is now used to make outdoor furniture, buckets and other products. However, similar procedures are not often seen. The depolymerisation of waste polymer into monomers is then used to synthesize new polymers. This is another important recycling opportunity for polymers produced primarily by polycondensation such as depolymerised polyesters, polycarbonates and polyamides. by hydrolysis or solvolysis [8]. These processes require high temperature or microwave assistance and efficient separation and purification of the resulting products. It makes them expensive.

Biodegradation

Polyesters made from natural monomers such as the well-known poly(lactic acid) and poly(lactide) undergo hydrolysis and biodegradation into harmless natural products, but in normal natural environments up to dozens of years. Therefore, they are rarely recycled and composted as waste, and there is increasing interest in chemical depolymerisation into useful products [9]. There are a number of 'desired' biodegradation processes for natural and specialty polymers that are widely used in the food industry and medical practice. An example in the food industry is the enzymatic cleavage of amylose

(the linear polymeric component of cereal starch) in malting to the maltose disaccharide, from which beer is made. The best-known examples in medicine are the absorbable surgical sutures and threads used in surgery. These are made from biodegradable polyesters such as glycolic acid and its cyclodimer glycolide, lactic acid or its cyclodimer lactide, and random and block copolymers of ϵ -caprolactone and 1,3-dioxan-2-one ("trimethylene carbonate"). It is The rate of suture strength loss and complete degradation in the body is modulated by material composition [10]. Thermal degradation, Pyrolysis of waste polymers to diesel, kerosene, gasoline fuel and syngas is not polymer recycling, but is another polymer waste treatment method used industrially. These processes consume hydrogen needed for hydrogenation of unsaturated intermediates formed during thermal cleavage of polymer chains [11].

CONCLUSION :

Polymer degradation is a complex process in which polymers lose their original functional properties due to irreversible structural changes. All kinds of polymer reactions are involved in corrosion. (i) chemical transformations of functional groups, (ii) cleavage of polymer molecules by oxidation, hydrolysis, photochemical and other chemical reactions, mechanochemical processes and depolymerisation, and (iii) crosslinked polymer molecules and their fragments. Crosslinking makes the aged polymer brittle, while the cleavage process becomes waxy or sticky due to the unsaturated chromophores formed yellowish or brownish.

REFERENCES:

- Horie, K., Baron, M., Fox, R.B., He, J., Hess, M., Kahovec, J., Kitayama, T. (2004): Definitions of terms relating to reactions of polymers and to functional polymeric

- materials. *Pure Appl.Chem.* 76 (4):Pp. 889-906.
- Jellinek, H.H.G., Chaudhuri, A. & Takada, K. (1978): Inhibition of hydrocyanic acid evolution from polyurethanes during oxidayive degradation. *Polymer Journal*, 10(3) :Pp. 253-268.
- Penczek, S. & Moad, G. (2008): Glossary of terms related to kinetics, Thermodynamics, and mechanisms of polymerization. *Pure Appl. Chem.*, 80(10) :Pp. 2163-2193.
- Dan, E. & Guillet, J.E. (1973): Photochemistry of ketone polymers. Ten. Chain scission reaction in solid state. *Macromolecules*, 6(2) :Pp. 235.
- Rabek, J.F. & Ranby, B. (1975): Role of singlet oxygen in Photo-oxidative degradation and photostabilization of polymers. *Polymer Engineering and science*, 15(1) :Pp. 11-13.
- Ballauff, M. & Wolf, B.A. (1984): Degradation of Chain Molecules. 2. Thermodynamically induced shear degradation of molten polystyrene. *Polymers*, 17(2) :Pp. 209-216.
- Bath, H. G., & Carlin, F.J., Jr. (1984): Overview of polymer shear degradation in size exclusion chromatography. *Journal of Liquid Chromatography*, 7(9) :Pp. 1717-1738.
- Webb, K., Arnott, J., Crawford, J. & Ivanova P. (2013): Plastic degradation and its environmental implications with special reference to polyethylene terephthalate. *Polymers*, 5:Pp. 1-18.
- Mckeown, P., Kamran, M., Davidson, M., Jones, M., Roman-Ramirez, L. & Wood, J. (2020): Organocatalysis for versatile polymer degradation. *Green chemistry*. 22:Pp. 3721-3726.
- Middleton, J. & Tipton, A. (2000): Synthetic biodegradable polymers as orthopaedic devices. *Biomaterials*. 21:Pp. 2335-2346.
- Ramin, L., Assadi, H. & Sahajwalla, V. (2014): High-density polyethylene degradation into low molecular weight gases at 1823K: An atomistic simulation. *Journal of Analytical and Applied Pyrolysis*. 110 :Pp. 318-321.