Degradation and Life Prediction of Polyethylene

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Contributor: Yang Wang, Guowei Feng, Nan Lin, Huiqing Lan, Qiang Li, Dichang Yao, Jing Tang

Polyethylene is one of the most significant and useful polymers that has been extensively studied for use as a plastic material. The benefits of using polyethylene as a commercial plastic material include its excellent mechanical properties, good flexibility, good chemical resistance, lightweight properties, good thermal stability, and high-cost performance. The piping sector has been impacted by the trend of replacing steel with plastic during the past, resulting in the steady replacement of metal-based pipes with plastic pipes. Polyethylene pipes are the most commonly utilized among them. Consider the case of high-density polyethylene pipes. Its market worth was USD 15.975 billion in 2018, and 9.283 million tons were consumed each year. The service life of polyethylene pipes will not be less than 50 years, and it will continue to grow at a rate of at least 5% annually in the upcoming years.

Keywords: polyethylene ; degradation ; kinetic models ; thermal analysis ; lifetime prediction

1. Aging Degradation of Polyethylene

1.1. The Process of Degradation

Catalytic peroxide decomposition, direct interactions of metal compounds with organic substrates, oxidation, and energy transfer during photolysis are the primary mechanisms of the chemical degradation of polymers [1]. While the chemical structure of a polymer frequently does not change much, polymer degradation involves a reduction in the polymer's molecular weight [2]. A macromolecular complex called a polymer is made up of big molecules with repeating structural elements. Polymers are typically combinations of substances with various chain lengths or substances with various molecular weights. The properties of polymers are strongly affected by their molecular weight, and this is also one of the processes through which macromolecular substances are created [3].

The primary source of the polymer degradation process is the continuous interaction between oxygen and the polymer's macromolecules, as well as free radicals created as a consequence of environmental factors such as temperature, humidity, light, mechanical stress, and radiation [4]. In addition, it appears to suggest a decrease in molecular weight, potential branching, and, in a few cases, the formation of cross-linked structures [5]. The unstable oxidized substances formed by degradation gradually converge towards the formation of stable macromolecules with oxidation groups and cause significant changes in the molecular structure, such as molecular weight, polydispersity, branching, etc. While other polymers often migrate in the direction of lower molecular weights, the development of cross-linked structures as mentioned above occurs primarily in the degradation of polyethylene.

For polyethylene materials, aging is bound to occur with extended use. Both aging and degradation can have a significant impact on the performance of polyethylene. Exposure to numerous environmental variables, such as heat, UV radiation, ozone, chemical attack, mechanical stress, and microbes, can cause polyethylene to degrade, eventually resulting in embrittlement, cracking, discoloration, etc. [6][7]. Understanding the primary stages of polyethylene breakdown is crucial for this reason.

1.2. Types of Degradation

Premature failure of polyethylene materials is caused by irreversible chemical reactions or physical alterations. Abiotic and biodegradation are the two categories into which polyethylene degrades. Biodegradation is the term used to describe the degradation caused by the action of microorganisms that alter and consume polyethylene and change its properties. Abiotic degradation is defined as deterioration caused by external environmental variables, such as temperature and UV irradiation. Even though each of these two degradation mechanisms can be used to classify the deterioration of polyethylene, the two types work together in nature [8].

1.2.1. Biodegradation

The process of biodegradation happens when microbial populations, other decomposing organisms, or abiotic forces work together to break down biodegradable materials into minute parts [9]. Three primary processes make up the biodegradation of polyethylene: (1) biodegradation, which occurs when microorganisms grow on the polyethylene's surface or within it, altering its mechanical, physical, and chemical qualities; (2) biodegradation, which is the process of having microorganisms break down a polymer into oligomers and monomers; (3) assimilation, which is the process by which microbes acquire the requisite carbon, energy, and nutrients from the breakdown of polymers and transform the carbon in the material into carbon dioxide, water, and biologically necessary chemicals [10]. The chemical composition, molecular weight, and crystallinity of the polymer, as well as other physical, chemical, and biological aspects, all affect how effectively a substance degrades [11].

Biological factors that may cause the biodegradation of polyethylene include bacteria, fungi, and microorganisms. Over the past few decades, numerous bacterial strains have been found to interact with polyethylene, and research studies have shown that there are already several genera of bacteria and a small number of genera of fungus that are able to degrade polyethylene.

1.2.2. Non-Biodegradable

The abiotic degradation of polyethylene is influenced by environmental and molecular factors. The breakdown of polyethylene is promoted and accelerated by environmental elements such as sunlight's UV radiation, oxygen, heat, water, certain animals, and contaminants. The combined action of these factors may have a synergistic effect on the degradation rate of polyethylene [12]. Photoreactions and thermal oxidation reactions, which result in the creation of new products during chain breakage, hydrogen atom detachment, or cage effects, are the main environmental drivers of polymer degradation [13].

The interaction between oxygen and UV light causes polyethylene to begin to photodegrade. While photodegradation is the process by which molecules produce free radicals, photooxidation is the process by which polymers are destroyed by absorbing photons of visible, ultraviolet, or infrared light in the presence of oxygen [14]. Random chain breakage and photooxidation are the primary outcomes of photodegradation, and these processes in turn cause secondary crystallization and the creation of several degradation products, including carboxylic acids, ketones, and aldehydes, which are collectively known as carbonyl compounds [15][16]. The Norrish reaction can result in the synthesis of vinyl groups (such as unsaturated bonds and conjugated systems), and it is crucial to realize that hydroperoxides are byproducts of the free radical formation process [17]. In addition to the breakdown of hydrogen peroxide, Norrish types I and II processes involving ketone groups can also start the photooxidation of polyethylene [18],

The process by which heat or high temperatures are applied to a material, product, or component and where the outcome is a loss of physical, chemical, or electrical qualities is referred to as "thermal degradation" [19]. Free radical chains that are engaged in thermal and photodegradation have fundamentally identical processes. Typically, the degree to which the reaction with oxygen takes place has a significant impact on the mechanism and rate of degradation. The molecular amplification reactions are mostly chain-breaking reactions when oxygen is present [20]. Depending on the physical and chemical makeup of the polymer, for which many thermal degradation mechanisms exist, thermal degradation may cause molecular deterioration. The most frequent is the polymer's intermolecular links being broken or unchained, releasing oligomers and monomer units. Some polymer backbone and side chain reactions will also contribute to the polymer's final decomposition [21].

One of the crucial components of abiotic degradation's parameters is chemical degradation. The characteristics of polyethylene macromolecules may change as a result of reactions with atmospheric contaminants and some agrochemicals. Many materials must come into contact with air when used in daily life, making reactions with oxygen in the air simple. Free radicals are created when the covalent bonds in polyethylene react with the oxygen molecules in the air. The covalent bonds of polyethylene are subject to oxidative degradation, which is dependent on the chain structure of polyethylene and works in conjunction with photodegradation to form free radicals. Peroxyl radicals from oxidative degradation can also act on polyethylene and cause cross-linking or chain breakage, just like the byproducts of the Norrish reaction stated above. Another process that might lead to the chemical breakdown of polymers is hydrolysis reaction [22][23][24]. It is significant to note that because polyethylene molecules are entirely composed of alkyl groups and lack any radical energy groups that could interact with water molecules, they cannot be hydrolyzed.

As the name suggests, catalytic degradation refers to the use of catalysts to break down polyethylene. Typically, catalytic degradation is employed in scientific research or to degrade polyethylene materials. The use of an appropriate catalyst and optimal processing conditions might result in the development of the intended, more precise product, and, in some situations, prevent the formation of inferior products, giving catalytic degradation some advantages over the other degrading methods previously discussed [25]. The ability to shorten experiment durations and lower reaction temperatures during studies is a more significant benefit of catalytic degradation.

Polyethylene experiences mechanical degradation most frequently as a result of the influence of various stresses on the material. These forces can occur for a variety of reasons. For example, buried polyethylene pipes may experience operational issues during installation, and wild animals may unintentionally harm them as a result of the pressure that the soil and carried material exert on them [10]. This also applies to polyethylene products used outside, such as mulch film and protective jackets used on some cables, which may experience multiple mechanical degradations under unforeseen outdoor conditions [26][27][28]. In general, damage to polyethylene materials caused by macroscale factors, including soil or water pressure, may not be immediately noticeable but may start to have an impact at the microscopic molecule level. Even though mechanical causes are not the primary cause of degradation, once a material has been mechanically traumatized, it may be more susceptible to the effects of biodegradation [21]. Under field circumstances, mechanical forces and other abiotic parameters (such as humidity, radiation, and contaminating substances) interact with polyethylene material.

1.3. General Mechanism of Degradation

Various types of polymers have different degradation mechanisms. The deterioration of polymeric materials may involve multiple degradation pathways at once [29]. Bond fractures in the polymer's backbone are the main method by which they degrade, and these breaks can occur anywhere in the chain or at the ends of the chain due to random generation. A frequently used mechanism in the breakdown of polymers is the chain-break decomposition mechanism. A multi-step free radical chain reaction with the general properties of such reaction mechanisms as initiation, proliferation, branching, and termination is involved in the chain-breaking breakdown process [30].

Free radicals are produced in both induced reactions—when a chain break happens at a random location in the main chain—and the terminal chain breaks reactions, where such a tiny unit or group is broken at the end of the main chain [21]. The following is the reaction sequence:

$$\mathrm{R-H} \xrightarrow{heat,light} R\cdot + H\cdot \quad (1)$$

The proliferative process begins with a free radical reaction with oxygen molecules, then produces a peroxide radical, a hydroperoxide group with hydrogen atoms, and finally, a peroxide radical with oxygen molecules [31]. The resulting groups are extremely unstable and readily decompose into renewable free radicals. The following is the reaction sequence:

$$\mathrm{R}\cdot + O_2 \rightarrow ROO\cdot \quad (2)$$

$$\mathrm{ROO}\cdot + RH \rightarrow R\cdot + ROOH \quad (3)$$

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \cdot OH \quad (4)$$

$$\mathrm{RO}\cdot + RH \rightarrow R\cdot + ROH \quad (5)$$

$$\mathrm{OH} + \mathrm{RH} \rightarrow \mathrm{R}\cdot + H_2O \quad (6)$$

Taking over a hydrogen atom or another atom on a carbon atom next to a radical from another chain is known as a "termination reaction". The following is the reaction sequence:

$$\mathrm{R}\cdot + R\cdot \rightarrow R - R \quad (7)$$

$$2\mathrm{ROO}\cdot \rightarrow ROOR + O_2 \quad (8)$$

$$\mathrm{R}\cdot + ROO\cdot \rightarrow ROOR \quad (9)$$

$$\mathrm{R}\cdot + RO\cdot \rightarrow ROR \tag{10}$$

$$\mathrm{HO}\cdot + ROO\cdot \rightarrow ROH + O_2 \tag{11}$$

Both biotic and abiotic circumstances, such as photooxygenation, can cause the aforementioned degradation pathways to occur in polymeric materials. From a macro perspective, the biodegradation process can be broken down into three stages. In the first stage, a particular enzyme secreted by microorganisms can lead to the depolymerization of polyethylene molecular chains. In the second stage, the microorganisms absorb the products of the first stage and transform them into the energy they need. In the third stage, the microorganisms use these products to finish their own cellular metabolism and convert them into other compounds [20].

In conclusion, the degradation of polymers under actual conditions is frequently a combination of various degradation mechanisms because the mechanism of degradation of polymers is quite complex and no one mechanism can fully describe the situation.

2. General Service Life of Polyethylene

Due to their strength, durability, and low cost when compared to other materials, polyethylene-based products are frequently seen in daily life. This low cost significantly lowers manufacturing costs and promotes the sustainable growth of the global economy.

Polyethylene materials are commonly used for the packaging of food products. The materials used to create food packaging are produced in a way that does not detract from the food’s flavor, appearance, or nutritional value. In order to ensure that the shelf life of the packaging material is longer than the shelf life of the food itself, it is crucial to safeguard the food’s quality. This is because the substances in the packaging material may spread into the food and harm it.

High-density polyethylene, which is frequently used for cable sheathing and has an initial design life of roughly 50 years, typically does not last as long as predicted outdoors due to numerous uncontrollable circumstances. Due to prolonged exposure to UV light, the cable sheath typically cracks after fewer than 10 years of operation in terms of ultraviolet light alone [32].

Natural gas and drinking water are both transported via polyethylene pipes because of their flexibility, light weight, ease of connecting between pipes, and comparatively low installation costs [33]. The polyethylene material will deteriorate and age with continued use, which will affect the pipe’s functionality. Premature pipe damage can result in major safety issues, such as gas leaks, which can seriously endanger people’s lives and property.

Notable medical uses for polyethylene include complete hip replacements. One of the best therapies for advanced femoral head necrosis is total hip replacement, which typically has a lifespan of at least ten years [34]. Traditional polyethylene has been replaced with highly cross-linked polyethylene since it is extremely prone to wear and tear during use [35].

Materials made of polyethylene are frequently employed in horticulture and agriculture. Films are the primary form of application in agriculture [27], and they are typically used as mulch to cover crops [36]. By more effectively blocking all types of weather that are not favorable for crop growth, such as violent storms, polyethylene mulch can reduce the growth of weeds, retain the moisture and nutrients needed by crops [28], and provide a desirable growing environment for crops. In order to prevent soil contamination, polyethylene mulch is recycled after use and normally lasts a few months to a year outdoors [37]. If polyethylene film breaks down while in use, the ensuing degradation chemicals may be environmentally hazardous. They may also seep into rivers and contaminate the water [38]. To prevent unwanted environmental pollution, it is crucial to recycle polyethylene film within a set time range.

3. Accelerated Ageing of Polyethylene

Understanding the degradation process is crucial for polyethylene applications. To gauge the degree of performance degradation of the product, or, in other words, to further gauge the robustness of polyethylene products in long-term use situations, it is important to first comprehend how long the process of degradation takes to become obvious [20]. As a result, when carrying out pertinent experimental tests, the material’s aging must be sped up [39]. Accelerated aging techniques are useful for estimating the remaining useful life of polymeric materials like polyethylene, and they can be contrasted to choose the most appropriate technique [40][41][42][43][44][45].

According to a widely used standard protocol for accelerated aging tests, polyethylene materials are put through cyclic tests in one or more substances for a specified amount of time or a specified number of cycles. To alter the effect of the same substance, the content of the substance utilized as a variable in this test procedure should be significantly different from the level of the substance itself during usage [46][47][48]. Depending on the needs of the experiment, these studies are typically carried out in suitable climate chambers where polyethylene samples may be exposed to high temperatures or humidity [49][50], UV radiation [51][52], various acids, bases, salts, etc. [53]. The parameters, which are dependent on the particular test conditions, must be decided upon as the initial stage in constructing an accelerated aging technique [54]. The ability to manage whether environmental elements are increasing or decreasing has a significant impact on the test's dependability [55]. In a perfect scenario, the environmental elements that the experiment simulates would be as similar to those in the natural state as possible, and the experiment's duration would be kept to a minimum. The level of testing that is being conducted now, however, is still far below what is optimal for experiments.

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