

# Caspian Corrosion Control

journal home page: <http://ccc-az.com>

## ANALYSIS OF POLYMER DESTRUCTION PROCESSES

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### Abstract

Destruction reactions are one of the most important reactions for high molecular weight compounds. They are also used to study the structure of high-molecular compounds, as well as to obtain low-molecular compounds from natural polymers (for example, glucose from cellulose and starch). During the destruction reactions, a decrease in the molecular weight is observed due to the breakdown (breaking) of the molecular chain without changing the chemical composition of the polymer. In this case, the functional groups located at the end of the macromolecule are not taken into account.

### Keywords:

Lewis acid;  
Polyolefin;  
Cation;  
Destruction;  
Free radical;  
Alkyl- radical;  
Carbocation.

### Introduction

Sometimes destructive reactions are used to facilitate the processing of a polymer or its use for practical purposes. For example, solutions of products obtained in the production of varnishes based on cellulose esters have a very high viscosity, so it is important to pre-destroy the original pulp. By partially destroying natural rubber, the rubber can be made easier to obtain. In addition, it is possible to obtain a new polymer due to the free macroradicals obtained during the destruction processes. In addition to all this, the destruction of polymers is considered as an unpleasant intermediate reaction that occurs during their chemical transformation, processing and operation. As a result of studying the mechanism of destructive reactions and their conformity to the basic laws, it is possible to regulate (increase or decrease) them in accordance with any process. Destruction of polymers reactions can occur under the influence of chemical agents (water, acid, alcohol, oxygen, etc.) or certain physical factors (heat, light, ionizing radiation, mechanical energy, etc.) [3,6].

### The experimental part

Chemical destruction is even more characteristic for heterozygous polymers. Thus, in this case, the destruction occurs by breaking the carbon-heteroatomic bond in the chain, and the initial monomer is obtained as the final product of the reaction. C-C bonds in carbon-chain polymers are more resistant to chemical agents than in

heterocyclic polymers. They can be chemically destroyed only under harsh conditions or in the presence of side groups (losses) in the polymer chain that can weaken the strength of C-C bonds. The process of destruction of the polymer as a result of mechanical action and its mechanism have been widely studied in recent years. The results show that the destruction processes that occur under the influence of different types of energy are very close in their mechanisms.

Many types of physical destruction, such as mechanical and high-energy particles, are widely used in engineering. Just as a reaction in a polymerization process is characterized by a degree of polymerization, so a reaction in a destruction process is characterized by a degree of destruction:

$$R = a/n$$

Where:  $R$  - the degree of destruction;

$a$  - the number of broken valence bonds in the main chain;

$n$  - is the total number of valence bonds.

As it was mentioned earlier, chemical destruction involves the destruction of various agents: water, oxygen, acids, amines, alcohols, and so on. may occur under the influence of [1,2].

One of the most common types of chemical destruction is oxidative destruction by oxygen and ozone. Oxidation destruction is activated by heat, light rays and mechanical energy, and the types of thermal, photo and mechanical oxidation of destruction are known, respectively. As a result of these destructive reactions, the composition and structure of the polymer change, ie it «ages». Aging of a polymer means a change in its physicochemical, physical and

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<http://dx.doi.org/10.54787/CCC LLC 20220400024>

mechanical properties during operation. The fastest oxidative destruction of polymers occurs by the chain mechanism (with free radicals), as in low-molecular hydrocarbons. The oxidation process of polymers without double bonds in the chains is weak, and the formation of peroxide groups is not always observed in them. This process consists of three stages (formation of the active center, lengthening and breaking of the chain). It is known that oxidation begins with the formation of peroxides. The active centers are obtained by the decomposition of peroxides.

Depending on the structure of the polymers, different products can be obtained at the end of the reaction as a result of changes in the rate of oxidation destruction. For example, unsaturated high- molecular hydrocarbons are more oxidized by oxygen than saturated hydrocarbons. This difference in the rate of oxidation reactions is due to the fact that unsaturated compounds form peroxide compounds quite easily. For this reason, the rate of formation of active centers is high [3,4,8].

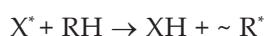
The reason for the intensive development in the field of polymer destruction is explained by the fact that research on destruction leads to the longevity of polymer construction and the creation of a scientific basis for their stabilization.

Destruction as a method is invaluable in the field of recycling of polymers, use of waste and giving them new properties. At present, destruction is widely used in the field of modification of polymers, which leads to the expansion of the synthetic potential of polymers.

There are many methods of destruction, and the following can be noted:

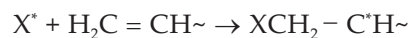
1. Destruction of polymers with the help of radical initiators is more widespread. In many cases, synthetic polymers cause molecular cleavage during operation. This is a free-radical chain mechanism. The source of radical centers are the polymers themselves. Thus, they create destruction by breaking the C - H and C - C bonds. The discovery of the nature of these transformations is due to the study of the mechanism of disintegration, its kinetics is associated with structural changes and plays an important role in determining their longevity.

Alkyl radicals formed in the process of destruction are involved in the free radical transformation of polymers, which ultimately determines not only their molecular weight but also their structure. It should be noted that the radical chain destruction of polyolefins saturated with alkyl radicals or the removal of hydrogen from the polymer:



or initiates its bonding to the final double bond

of the polymer.



Here:  $X^*$  alkyl is a radical;

~ RH is a polymer.

Kinetic studies of the alkyl radical hexyl reaction show that the activity energy (for the first reaction) is 50 kC/mol (temperature 363-383 K).

2. Thermal destruction occurs most often as a result of thermal and thermo oxidative decomposition during the operation of polymers.

It has been found that the rate of destruction and activity energy of polyolefins depends on the structure and molecular weight of the polymer.

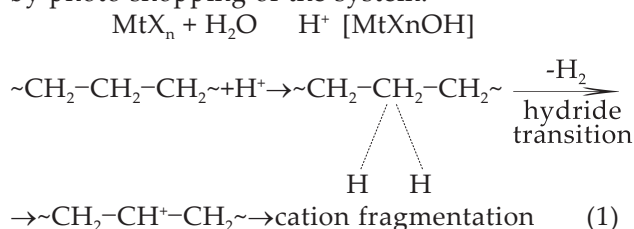
The rate of destruction of a branched polymer is higher than that of a linear polymer, but the activity energy of the destruction of a branched polymer is lower than that of a line. The dependence on the molecular mass is as follows: as the molecular mass of a linear polymer increases, the activity energy of its destruction also increases, but the rate of destruction decreases [8,11].

The mechanism of radiation decomposition of polymers consists of the stages of absorption of radiant energy, transfer of excitation energy to areas where chemical bonds are more likely to break, and the formation of free valence as a result of breaking chemical bonds. The formed free radicals can reunite to restore the bond or stabilize and complete the cleavage process.

One of the interesting aspects of the destruction process is full understanding the «chemistry» of catalytic destruction.

The reaction of catalytic destruction of polyolefins by Lewis acids can be considered as a cationic process. This is similar to the reactions of organic compounds with Lewis acids. According to accepted assumptions, the catalytic destruction of polyolefins is carried out by the following two mechanisms.

However, it should be noted that as the order of destruction of carboxylic polymers decreases, for example, during the complex MX<sub>n</sub> reaction or the inclusion of radical acceptors in the reaction mixture (J<sub>2</sub>, methylstyrene), the destruction of polymers is determined by a radical mechanism. The fact that the destruction has been carried out by a radical mechanism can also be confirmed by the fact that the order of destruction is increased by photo shopping of the system.



$\sim\text{CH}=\text{CH}_2+\text{H}^+\rightarrow\text{C}^+\text{H}-\text{CH}_3$  cation fragmentation (2)

Based on these indicators, the existence of an alternative mechanism of catalytic destruction of polyolefins under the influence of Lewis acids (radical-chain mechanism) is confirmed. [10].

The results: Thus, it can be concluded that the continuation of research on the mechanism of catalytic destruction can reveal the existence of new alternative routes for the detection of fragmentation of macromolecules [9].

The solution of theoretical problems of catalytic destruction under the influence of Lewis acids can lead to the creation of a scientific basis for the processes of processing and modification of polymers.

From the analysis of the literature it can be concluded that the reactions of catalytic destruction of polymers under the influence of Lewis acids are less studied than the destruction of free radicals. Given the high catalytic activity of Lewis acids and their occurrence in various reactions (eg, isomerization, cracking, destruction, alkylation, complex formation, polymerization, etc.), it is important to study their interaction with different polymers in nature. .

The formation of active centers has been also confirmed by the EPR method, and free macroradicals has been detected and their density has been determined.

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## Анализ процессов разрушения полимеров

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### Реферат

Реакции деструкции являются одними из наиболее важных реакций для высокомолекулярных соединений. Их применяют для изучения строения высокомолекулярных соединений, а также для получения низкомолекулярных соединений из природных полимеров (например, глюкозы из целлюлозы и крахмала). В ходе реакций деструкции наблюдается уменьшение молекулярной массы за счет разрыва (разрыва) молекулярной цепи без изменения химического состава полимера. При этом не учитываются функциональные группы, расположенные на конце макромолекулы.

**Ключевые слова:** кислота Льюиса; полиолефин; катион; деструкция; свободный радикал; алкил-радикал; карбоксилирование.

## Polimerlərin destruksiya proseslərinin analizi

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### Xülasə

Destruksiya reaksiyaları yüksəkmolekullu birləşmələr üçün ən mühüm reaksiyalardan biri hesab olunur. Onlardan yüksəkmolekullu birləşmələrin quruluşunu öyrənmək həmçinin, təbii polimerdən aşağı molekullu birləşmələri almaq (məsələn, sellülozanın və nişastadan qlükoza- almaq) üçün istifadə olunur. Destruksiya reaksiyaları zamanı polimerin kimyəvi tərkibi dəyişmədən molekulyar zəncirin parçalanması (qırılması) hesabına molekul kütləsinin azalması müşahidə olunur. Bu zaman makromolekulun sonunda yerləşən funksional qruplar nəzərə alınmır.

**Açar sözlər:** Lyuis turşusu; poliolefin; kation; destruksiya; sərbəst radikal; alkil-radikal; karbokation.