O’ZBEKISTON RESPUBLIKASI OLIY VA O’RTA MAXSUS

TA’LIM VAZIRLIGI

BUXORO DAVLAT UNIVERSITETI

TABIIY FANLAR FAKULTETI
KIMYO KAFEDRASI

ULUG’BEK IKROMOV

BITIRUV MALAKAVIY ISHI

TABIIY VA SINTETIK POLIMERLAR ASOSIDA BIOLOGIK PARCHALANADIGAN KOMPOZITSION MATERIALLAR YARATISH

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«Tasdiqlayman»

Kafedra mudiri _____________

«____» ________________yil

BUXORO DAVLAT UNIVERSITETI

BITIRUV MALAKAVIY ISHI BO’YICHA TOPSHIRIQ

1. Kafedra ***Kimyo***

2. Ish mavzusi: **Tabiiy va sintetik polimerlar asosida biologik parchalanadigan kompozitsion materiallarni yaratish**

3. Bajaruvchi**:** ***Ulug’bek Ikromov***

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5. Yakunlangan ishning topshirish muddati

6. Bitiruv malakaviy ishni bajarish uchun talabaga berilgan topshiriqlarning qisqacha mazmuni va bajarish muddati:

a) Mavzuga oid bulagn adabiyotlarni to’plash, tahlili qilish 2019 oktyabr

b) Ishga oid jarayonlar kimyoviy va texnologik asoslarini o’rganish 2019 dekabr

v) O’zbekistondagi mavzuga oid texnologik jarayonlarni o’rganish 2020 yil fevral

g) Bitiruv malakaviy ishning 2 va 3 bo’limlarini yozib, tayyorlash 2020 aprel

d) Bitiruv malakaviy ishini kafedra oldi ximoyasiga tayyorlash 2020 may

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Talaba imzosi _____________________________

ANNOTATSIYA

Tadqiqot mavzusining dolzarbligi. Bugungi dunyoda polimer sintetik materiallarga talab barqaror o'sib bormoqda. Keng imkoniyatlarga ega sintetik polimerlardan biri bu polivinilxlorid (PVX) bo'lib, u plastmassa va poliolefinlarni qurgandan so'ng dunyo ishlab chiqarishida uchinchi o'rinni egallaydi. Amaliy xarakteristikalarning sezilarli diapazoni qadoqlash materiallari ishlab chiqarishda PVXni ajralmas holga keltiradi: har xil turdagi plyonkalar, konteynerlar va boshqalar. Kimyoviy beqarorligi va barqarorligi tufayli, qattiq, egiluvchan yoki naycha shaklida bo'lsin, PVXni qadoqlash sifatida qo'llashning eng muhim sohalari oziq-ovqat sanoati va tibbiyotdir. Polivinilxloridga asoslangan mahsulotlar xilma-xildir, juda oson ishlab chiqariladi va sterilizatsiya qilinadi, yorilib ketmaydi va oqmaydi va jonli ravishda ishlatilishi mumkin.

PVX kimyoviy tuzilishining barqarorligi va tabiiy sharoitlarda juda sekin parchalanishi tufayli, bir necha o'n yilliklar davomida, asosiy masala materialning ishlash muddati tugaganidan keyin uni yo'q qilishdir. Bir martali ishlatiladigan qadoqlash materiallari atrof muhitga zararli ta'sir ko'rsatadi, ular parchalanish paytida zaharli moddalarni chiqaradi, tuproq va er osti suvlarini ifloslantiradi.

Hozirgi vaqtda polimer chiqindilarini, birinchi navbatda, yoqish, ko'mish, kompostlash va utilizatsiya qilishning bir qancha usullari mavjud. Shu bilan birga, ushbu usullarning har biri bir qator muhim kamchiliklarga ega, ular past samaradorlik va qayta ishlashning tayyorgarlik bosqichidagi qiyinchiliklar va atrof-muhitga zarar etkazish, ishlab chiqarishda texnologik qiyinchiliklar va boshqalar.

Shuning uchun tashqi omillar (tuproq mikroorganizmlari, yorug'lik, kislorod, suv va boshqalar) ta'siri ostida mahsulotlarning ishlash muddati tugaganidan keyin kuchga kiradigan, buziladigan xususiyatlarga ega bo'lgan PVX asosidagi polimer kompozitlarni yaratish uchun kompozitsiyalar va texnologiyalarni ishlab chiqish juda muhimdir.

Atrof-muhitning tezlashtirilgan fizik-kimyoviy va biologik o'zgarishlariga

duchor bo'lgan materiallarning rivojlanishi zamonaviy ishlab chiqarishga faol joriy etilib, biopolimerlar yoki mineral plomba moddalari yordamida o'zgartirilgan polimer kompozitlarni yaratish tamoyillariga asoslanadi. Shu bilan birga, materialning yanada tez parchalanishiga hissa qo'shadigan plomba moddalarini PVXga kiritish, uning operatsion xususiyatlarining sezilarli darajada pasayishi bilan birga keladi. Shunday qilib, qisqa umr va maqbul xususiyatlarga ega parchalanadigan PVX plyonkalarni ishlab chiqarish uchun eng maqbul texnologik parametrlarni tanlash toza, ekologik toza qadoqlash mahsulotlariga o'tishda muhim vazifalardan biridir.

Tadqiqotning maqsad va vazifalari. Ushbu ishning maqsadi qadoqlash materiallariga zamonaviy talablarga javob beradigan, sozlanishi quvvat xususiyatlariga ega va fizik-kimyoviy xususiyatlar to'plamiga ega bo'lgan PVX asosida parchalanadigan kompozitsion materiallarni ishlab chiqish edi. Maqsadga muvofiq quyidagi vazifalarni hal qilish kerak edi:

- retsept va texnologik parametrlarning ta'sirini aniqlash: plomba moddalarining nisbati - pektin, kraxmal va bentonit, yumshatish vaqti va harorat PVX asosidagi plyonkalarning mustahkamligiga, termal, optik va maxsus xususiyatlariga;
- polivinilxloridli kompozitlarning "tuzilish - tuzilish - mulk" aloqasini aniqlash, o'rash materiallari sifatida foydalanish uchun fizik va mexanik parametrlarni aniqlash;
- kompozitsion PVX plyonkalarning degradatsiyasiga UB nurlanishi, plazma-kimyoviy ishlov berish va kompostlashning ta'sirini aniqlash;
- ishlab chiqilgan to'ldirilgan polimer kompozitlaridan biologik parchalanadigan qadoq sifatida foydalanish samaradorligini baholash.

Mavzuni o’rganilganlik darajasi. Parchalanadigan PVX asosidagi materiallar sohasidagi tadqiqotlar qabul qilinadigan ishlash xususiyatlariga ega bo'lgan buziladigan polimer kompozitlarni yaratishning samarali usullarini izlash va turli xil plomba moddalarining polimer matritsasining xususiyatlariga ta'sirini aniqlash, to'ldirilgan kompozitsiyalarning tarkibi, tuzilishi va asosiy xususiyatlari o'rtasidagi naqshlarni o'rnatish bilan bog'liq. Biroq, bugungi kunga qadar, sanoat tomonidan buzilib ketadigan materiallarning kompozitsiyalari ishlab chiqilmagan va ularning ekspluatatsion xususiyatlarini yo'naltirilgan tartibga solish imkoniyatlari aniqlanmagan.

Tadqiqotning Ilmiy yangiligi.

- PVX ning mineral va polimer to'ldiruvchilar bilan modifitsirlangani asosida buziladigan qadoqlovchilar sifatida foydalanishi mumkin bo'lgan polimer kompozit materiallar tarkibini ishlab chiqiladi;
- yangi kompozit materiallarni ishlab chiqarish uchun retsept parametrlarining asosiy operatsion, mexanik va issiqlik xususiyatlariga ta'sirini o'rganish. Tarkibni past konsentratsiyada kiritish - 1 vt%% barcha o'rganilgan kompozitsiyalar uchun eng maqbuldir;
- Ko'rsatilganidek, PVX kompozitlarining issiqlik xususiyatlari polimer plyonkaning to'kiladigan plyonkadan farqli ravishda uning qaynash vaqtiga bog'liq. PVX bilan qoplangan plyonkalarning yanada yaxlit tuzilishini olish uchun to'ldirilmagan plyonkalarni ishlab chiqarishning standart usulidan farqli o'laroq, vaqtni 5 minutga ko'paytirish kerakligi aniqlandi, bu vaqt 2 minutni tashkil etadi;

Tadqiqot predmeti va obyekti. Tadqiqotda asosan polivinilxlorid, bentonitlar va pectin hamda kraxmal asosida turli tarkibli kompozit materiallar ob'yekt sifatida tanlangan bo'lib. Tadqiqot predmeti sifatida ana shun kompoztlarning olinish jarayonlari, tarkibi va tuzilishi hamda xossalarini o'rganish bosqichlarini olingan.

Ishning nazariy va amaliy ahamiyati. Ishning nazariy ahamiyati tarkibiga va ishlab chiqarish sharoitiga qarab bentonit, kraxmal va pektin bilan o'zgartirilgan degradatsiyaga uchraydigan PVX asosidagi polimer kompozit plyonkalarning fizik-mexanik parametrlarini bashorat qilish va hisoblash usullarini ishlab chiqishdan iborat.

Ishning hajmi va tuzilishi. Bitiruv malakaviy ishi 67 betdan iborat bo'lib, kirish, adabiyotlar tahlili, eksperimental qism, olingan natijalar tahlili va xulosa qismlardan tashkil topgan. Ishda 9 ta jadval, 12 ta rasm keltirilgan. Ishni rasmiylashtirish jarayonida 75 nomdagi ilmiy adabiyotlardan foydalanildi.

MINISTRY OF HIGHER AND SECONDARY SPECIAL EDUCATION OF
THE REPUBLIC OF UZBEKISTAN BUKHARA STATE UNIVERSITY
FACULTY OF NATURAL DISCIPLINES DEPARTMENT OF CHEMISTRY

ULUGBEK IKROMOV

GRADUATE PROFESSIONAL WORK

CREATION OF BIOLOGICAL DIVIDEDCOMPOSITION MATERIALS ON THE BASIS OF NATURAL AND SYNTHETIC POLYMERS

5140500-direction of chemistry education

Supervisor: dots. M. S. SHARIPOV

Permission granted: “ ” 2020 year

Chair holder: dots H. T. AVEZOV

BUKHARA 2020

OUTLINE

CHAPTER 1. REVIEW OF MODERN SCIENTIFIC AND TECHNICAL LITERATURE

CHAPTER 2. OBJECTS AND METHODS OF SYNTHESIS AND RESEARCH OF PVC COMPOSITES

CHAPTER 3. INFLUENCE OF RECIPE PARAMETERS ON CHARACTERISTICS OF POLYMER COMPOSITE FILMS

INTRODUCTION

In today's world, the demand for polymer synthetic materials is growing steadily. One of the large-capacity synthetic polymers with a wide range of applications is polyvinyl chloride (PVC), which occupies third place in terms of world production after building plastics and poly olefins. A significant range of operational characteristics makes PVC indispensable for the production of packaging materials: various types of films, containers, etc. Due to its chemical inertness and stability, the most important areas of application of PVC as packaging, whether rigid, flexible or in the form of a tube, are the food industry and medicine. Products based on polyvinyl chloride are diverse, fairly easily manufactured and sterilized, do not crack or leak, and can be used in vivo.

Due to the stability of the chemical structure of PVC and the extremely slow decomposition under natural conditions, over several decades, the main issue is the disposal of the material after the end of its life. Of particular environmental hazard are single-use packaging materials that release toxic substances during their decomposition, polluting the soil and groundwater.

Currently, there are several ways to dispose of polymer waste, first of all, incineration, burial, composting and recycling. However, each of these methods has a number of significant drawbacks, including low efficiency, difficulty in the preparatory stages of processing and environmental hazard, and technological difficulties in production, etc.

That is why it is urgent to develop compositions and technologies for producing PVC-based polymer composites with degradable characteristics that come into force after the end of the life of the products under the influence of external factors (soil microorganisms, light, oxygen, water, etc.).

The development of materials undergoing accelerated physicochemical and biological changes in the environment, actively being introduced into modern production, is based on the principles of creating polymer composites modified either with biopolymers or with mineral fillers. However, the introduction of fillers in PVC, contributing to a more rapid decomposition of the material, is accompanied by a significant decrease in its operational characteristics. Thus, the selection of optimal technological parameters for the production of degradable PVC films with a short life and acceptable characteristics is one of the most important tasks in the transition to clean, environmentally friendly packaging products.

The degree of elaboration of the topic. Research in the field of degradable PVC-based materials is associated with the search for effective ways of creating destructible polymer composites with acceptable performance characteristics and establishing the effect of fillers of various nature on the properties of the polymer matrix, establishing patterns between the composition, structure and basic properties of filled compositions. However, to date, industrially produced compositions of degradable materials have not been developed and the possibilities of directional regulation of their operational characteristics have not been identified

The goals and objectives of the study. The aim of this work was the development of degradable composite materials based on PVC with adjustable strength characteristics and a set of physicochemical properties that meet modern requirements for packaging materials.

In accordance with the goal, it was necessary to solve the following tasks:

- establish the influence of prescription and technological parameters: the proportion of fillers - pectin, starch and bentonite, rolling time and temperature on the strength, thermal, optical and special properties of PVC-based films;
- to identify the relationship "composition - structure - property" for polyvinyl chloride composites in order to predict acceptable, for use as packaging materials, physical and mechanical parameters;
- establish the effect of UV irradiation, plasma-chemical processing and composting on the degradation of composite PVC films;
- evaluate the effectiveness of the use of developed filled polymer composites as biodegradable packaging.

Scientific novelty.

- developed compositions of polymer composite materials based on PVC, modified with mineral and polymer fillers for use as a degradable packaging;

- a study of the influence of prescription parameters for the production of new composite materials on the main operational, mechanical and thermal properties. It was shown that the introduction of filler in low concentrations - 1 wt.% Is most optimal for all studied compositions;
- It is shown that the thermal properties of PVC composites depend on the rolling time of the polymer film, in contrast to the unfilled film. It was found that in order to obtain a more uniform structure of PVC filled films, it is necessary to increase the rolling time to 5 minutes, in contrast to the standard method for producing unfilled films, where the time is 2 minutes;
- it is shown that under UV and plasma chemical exposure in an argon-oxygen medium, the surface morphology of the composite materials changes, which can be further used as one of the possible stages of the process of recycling polymer waste;
- it has been established that the introduction of fillers, pectin, starch and bentonite, into the PVC composition contributes to the degradation of the material in the model landfill - compost, where, presumably, under the influence of microorganisms and external factors (humidity, temperature), oxidative degradation and dehydrochlorination of the polymer composite occur simultaneously.

Theoretical and practical significance of the work. The theoretical significance of the work lies in the development of methods for predicting and calculating the physic mechanical parameters of degradable PVC-based polymer composite films modified with bentonite, starch and pectin, depending on the composition and production conditions.

Based on the obtained experimental data, a process flow diagram for producing PVC composites with fillers — bentonite, pectin, starch — that are degraded in natural conditions is proposed. A scientific and technical groundwork has been created for the development of new biodegradable packaging plastics.

Methodology and research methods. In the course of the research, modern methods for diagnosing materials were used: IR Fourier spectroscopy, optical microscopy, differential scanning calorimetry, thermomechanical and thermos gravimetric analysis, potentiometer, impedance conductivity meter and piercing methods using a TA. TX plus texture analyzer. The surface of the films was modified by reactive ion-plasma etching by low-temperature anisotropic plasma in the RIE-1701 complex.

Bioassay of PVC-based polymer films with various excipients was carried out by studying the changes in the vital activity of test microorganisms Lactobacillus. The study of biodegradation of the studied polymer composites was carried out by composting.

Protection provisions:

- The influence of prescription and technological parameters: time and temperature of rolling of composite PVC films on the production of degradable packaging materials with adjustable physical and mechanical characteristics.
- The influence of the nature and amount of fillers on the production of PVC films by rolling, as well as on the operational and special properties of the studied composites.
- Patterns of the processes of degradation of PVC-based materials, modified by fillers - bentonite, starch and pectin, under the influence of UV, plasma chemical processing and composting.
- Test results of developed PVC filled composites as packaging materials with an accelerated life cycle.

The personal contribution of the author to the work consists in active participation in the formation of the goals and objectives of the study, in the organizational and technical planning and conduct of research, in the processing and interpretation of the results, summarizing them in the form of articles and reports, and formulating scientific conclusions.

Reliability level and approbation of results. The reliability of the results is confirmed by the reproducibility of experimental data obtained using modern research methods and the use of mathematical apparatus, as well as comparability with data from other authors.

CHAPTER 1. REVIEW OF MODERN SCIENTIFIC AND TECHNICAL LITERATURE

1.1 THE CONCEPT OF BIODEGRADABLE POLYMERIC MATERIALS, THEIR CLASSIFICATION AND RESEARCH METHODS

In countries with advanced plastics industry, waste polymer materials slowly decomposing in natural conditions constitute a serious threat as a source of pollution the environment. Currently, ~ 30% of polymer waste is burned, 30% is recycled, 30% is not disposed of ruts.

Waste polymer materials can be burned, but then it is necessary capture released gases for the purpose of their use or neutralization. After cleaning, polymer debris may be exposed to recyclable. Such processing requires a certain training and includes the following activities:

1) creating a reliable system for collecting waste from the population in agriculture;
2) the development and implementation of a perfect and cost-effective technology of their processing;
3) the creation of an appropriate production potential;
4) expanding the themes of fundamental and applied follow-up on the replacement of primary raw materials with secondary for production output;
5) the availability of markets for products from this type of raw material. A certain proportion of polymer waste is the so-called polymer packaging, i.e., consumer goods. By different sources, from 10 to 15% of all polymers produced are used to make containers. Japanese experts carried out forecasting increase in the amount of plastic waste with and without taking into account activities aimed at reducing waste (Fig. 1.1). Judging by this dependence, the most effective a way to reduce polymer waste is to develop biodegradable polymers, i.e. polymers that retain performance only during the period consumption, and then undergo physicochemical and biological

The chemical transformations under the influence of environmental factors (light, temperature, moisture, water) are easily included in the metabolism of natural bio systems (bacteria, yeast, fungi, algae). In this case, high molecular weight substances decompose into low molecular weight (water and carbon dioxide), substances and biomass. Thus, the natural cycle of substances is performed, which is able to maintain ecological balance in nature.

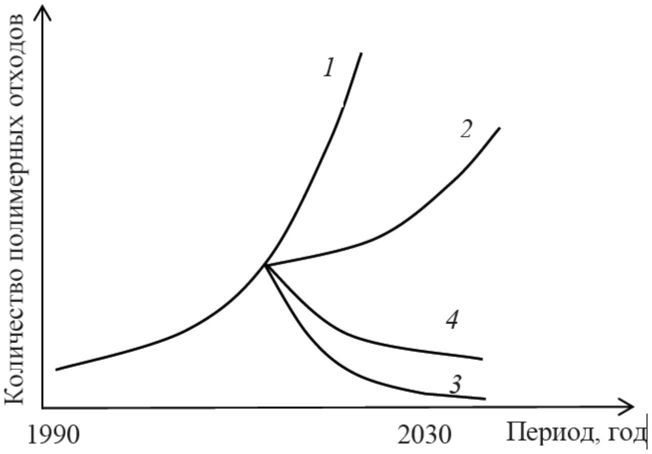


Fig. 1.1. Prediction of the growth of plastic waste:

1 - lack of control in waste growth; 2 - use of state and legislative measures to control this waste; 3 - the use of polymeric materials, whose life is 2 months; 4 - the use of polymeric materials, whose life is 2 months, provided that the amount of waste doubles

Creation and use of biodegradable polymer materials aims at the economic and environmental benefits of:

- utilization and processing of plastic waste, the volume of they grow every year;
- low cost of polymers from renewable raw materials;
- reduced need for synthetic polymers, worsening sewing environmental conditions;
- reduction of greenhouse fumes by 15-60% when replacing past generation polymeric materials for biodegradable polymers (BPM).

The term “biodegradable” is used to refer to a polymer destruction, the deterioration of the former qualities of which may be called at least partially by the biological system. Overall polymer degradation construction includes primary heat absorption processes and light, diffusion of the components of the medium in the material, its fouling microorganisms. Micron enzymes initiate further reactions of breaking chemical bonds in a macromolecule. The tendency of polymers to biodegradation is determined not only chemical structure, the presence of branches, macro size chains, but also their supramolecular micro- and macrostructure.

Benefits of biodegradable polymers:

a) the possibility of processing, like conventional polymers, into standard equipment;

b) low barrier to the transmission of oxygen, water vapor (optimal for use in food packaging);

c) resistance to decomposition under ordinary conditions;

d) rapid and complete degradability with specially designed or in vivo - no disposal problems waste;

e) independence from petrochemical raw materials.

Disadvantages of biodegradable polymers:

a) high cost (so far an average of 2-5 euros per 1 kg). However it should be noted that the economic value in addition to the price of The product also contains the costs of disposal and use. In this sense, biodegradable polymers are preferable: renewable resources necessary for their production, more profitable. It is also important to note that the high price of the material is temporary phenomenon until the production of biopolymers massive and the process of their release is not fully debugged. Over time the cost of bioplastics will decrease, and they will become affordable for a wide range of enterprises;

b) limited opportunities for large-capacity production leadership;

c) the difficulty of regulating the decay rate in landfills under exposure to environmental factors;

d) technological difficulties in production.

According to the construction and technological characteristics of BPM, you can cleverly divide into 3 classes:

1) biodegradable plastics based on natural polymers;
2) chemically and microbiologically synthesized highly molecular compounds (IUDs) whose structure is similar biopolymers;
3) composite materials.

There are 3 main areas of polymer production adjustable life - synthesis of photodegradable, biodegradable and chemically degradable polymers.

1. Photo degradation. Under the influence of UV radiation breakable polymers first crack, then coat continuous network of cracks and finally crumble into pieces various sizes, which later turn into powder. This is a powdered product that has a molecular mass 500 and below, is destroyed by the action of microorganisms.

The most sensitive to this type of degradation is polyolefin are produced. To enhance the efficiency of Photo degradation use the following techniques:

- the addition of special additives to the biopolymer formulations wok - initiators of photochemical reactions (benzophenone, diphenyl disulfide). These substances are called sensitizers;
- the introduction into the polymer as a result of copolymerization of the composition units including aldehyde and ketone groups, t. e. a weak link is introduced (they are used as comonomer vinylketon);
- change in the composition of the polymers by the inclusion of a large number of carbonyl groups that absorb ultraviolet radiation;
- the introduction into the polymer of additives containing metals (Cu and Fe).

Microbial and photo degradation biopolymers find use in the production of disposable mulch and crop cover for protection against frost.

2. Bacterial degradation. Bacterial degradation Plastics are carried out under the influence of bacteria and water. Dan-Natural polymers are subject to this type of bio degradation containing natural components. Besides, another approach to bacterial degradation should be highlighted biopolymers associated with the cultivation of microorganisms for the specific purpose of the decomposition of polymer plastics. It is more intensive and expensive process, which allows at the same time break down plastics synthesized from petroleum products

3. Chemical degradation. Some biodegradable poly dimensional materials undergo rapid dissolution when are exposed to certain aqueous solutions on a chemical basis. First, the polymer dissolves product in an aqueous solution. Further, like photo degradation, polymer, there is a complete biodegradation of water solution due to microbial digestion. Relevant microorganisms are usually found in cleaning plants Wastewater. The fastest structural breakdown of material occurs in an alkaline environment. The ability of polymers to decompose and absorb microorganisms depends on a number of their structural characteristics. The most The chemical nature of the polymer, the molecular mass, branching macro (presence and nature of lateral groups), supramolecular structure. Natural and synthetic polymers containing bonds that are easily hydrolysis, have a high biodegradability. Present-The presence of substituents in the polymer chain often contributes to biodegradation. The latter also depends on the degree of place the chain and the length of its sections between functional groups, the flexibility of macromolecules. Therefore, biodegradable polymers must:

1) be hetero-chain and contain biodegradable bond lengths: R = CH2; R = CH – R1; R – CH2 – OH; R – CH (OH) –R; R – CO – H; R – CO – R1 and others;
2) contain fragments that include in a row no more 5 groups of CH2;
3) have voluminous substituents in the composition. More volume substituent, the faster the polymer is destroyed;
4) include in the macromolecular chain natural products - starch, cellulose, lactose, magnesium, urea, which can be used as fillers, and then microorganisms absorb them.

Polymers with an amorphous supramolecular structure always less resistant to biodegradation than crystalline. It's related so that the compact arrangement of structural fragments onion crystalline and crystalline polymers limits their swelling in water and prevents the penetration of enzymes into the polymer matrix, complicating the effects of enzymes not only to the main carbon chain of the polymer, but also to biodegradable parts of the chain. An important factor that determines the resistance of the polymer to biodegradation, is the size of its molecules. While monomers or oligomers can be affected by a microorganism mi and serve as their source of carbon, polymers with large molecular weight resistant to microorganisms. Biodegradation of most technical polymers, as a rule, initiate processes of a non-biological nature (thermal sky, photo oxidative, mechanical degradation, etc.). UP-prolonged degradation processes lead to a decrease in the molecular the mass of the polymer. In this case, low molecular weight fragments having hydroxyl, carbonyl or carboxyl groups.

Resistance of polymeric materials to microorganisms also depends on their constituent plastic, fillers, stabilizers, other technological additives, and also to what extent these substances can before microorganisms, a source of carbon, nitrogen and other biogenic elements. Inorganic components are known (silicates, sulfates, phosphates, carbonates) do not support mushroom growth.

There are various technological approaches to creating biodegradable polymers. Among them, the following should be highlighted:

General directions:

1) selection of special strains of microorganisms, able to carry out the destruction of polymers. This direction only with respect to polyvinyl alcohol was successful. Japanese scientists isolated Pseudomonas sp., that produce an enzyme that breaks down polyvinyl alcohol. After decomposition of the polyvinyl alcohol macro chain fragments are completely absorbed by bacteria. In recent years Pseudomonas bacteria are added to activated sludge for water treatment facilities for more complete wastewater treatment from this polymer;

2) the synthesis of biodegradable polymeric materials having chemical structure similar to the structure of natural polymers. An example of such a synthesis is a biodegradable aliphatic complex polyester having a chemical structure similar to that of Polyoxyacetobutyrate cellulose.

3) the creation of compositions containing in addition to high molecular weight Organic fillers (starch, cellulose, amylose, amylopectin, dextrin, etc.), which are nutritious medium for microorganisms. The material obtained from such a mixture is partially biodegradable, since the matrix is synthetic.

The polymer breaks up into pieces. When mixing carrier with a synthetic polymer at the micro level (particle size less than 10 microns) the components of the mixture form interpenetrating mesh structure that provides polymer effect of additional destruction. As you know, weed can accumulate in less ordered areas polymer. In addition, the packing density of macromolecules in the outer layers of the polymer-filler system are approximately half as much as in the rest of the disordered polymer. Therefore, when the filler is destroyed by bacteria, easier access of microorganisms to a less stable relative biologically degradation of part of the polymer. Thus, the ability of polymeric materials to bio destructor due primarily to their chemical composition, structure and properties of macromolecules.

However, on a stable biodegradability of polymers is a big influence have some macro structure characteristics (on porosity, uniform distribution of additives in the polymer mass, features of surface treatment of products, etc.), as well as the technological parameters of the manufacture of the material and its processing into packaging. The aim of the latest developments in the field of biodegradation of plastics is the establishment of general patterns in the selection of components and technological parameters during production of materials combining a high level of operation specific characteristics (strength, low gas permeability, environmental safety, good formability, etc.) with biodegradability, and fundamental principles regulation of their destruction processes to ensure fast and safe degradation of the packaging at the end of its life. There are two main classes of biodegradable polymers:

- natural (starch, cellulose, chitin, chitosan);
- synthetic, and this class of BPM can be two types - polymerization (polyethylene, polypropylene, polystyrene, polyvinyl chloride) and poly condensation (polyesters, etc.).

Biodegradable polymer materials based on nature polymers. In the production of biodegradable packaging, polysaccharides are most widely used. First of all, starch, dextrin, chitosan, cellulose, wood processing waste.

Known packaging materials based on starch of corn, peas, wheat and other plants. In its pure form, as a rule, starch is hardly processed into products on technological equipment for thermoplastics. It is advisable to use it in conjunction with plasticizers. The property of starch to contain up to 30–40% of bound moisture makes it possible to consider water as the most affordable plasticizer. Plasticization of starch is carried out under the simultaneous influence of temperature and mechanical stresses. The result is a significant change in its physical and mechanical properties. Urea, mono-, di- and polyethylene glycols also have a plasticizing effect on starch. By extrusion technology, foam materials are made that are used as soundproofed packaging. By extrusion of mixtures of corn starch and microcrystals of cellulose and methyl cellulose with or without additives of plasticizers, BPMs are obtained for protecting food products from weight loss and spoilage.

Biodegradable films are prepared from aqueous solutions of mixtures of starch and sodium salts of carbo x y methyl cellulose. Chitin and chitosan are gaining increasing importance as a basis for bi-degrading materials. Mixtures of chitin and chitosan are considered promising polymeric materials for the production of packaging films, textile fibers. Chitosan-based films are formed from acetic acid solutions by adjusting the solubility and swelling of the films by chitosan crosslinking with glutaraldehyde or oligomer di epoxide.

Composite biodegradable polymers. The progressive direction of obtaining BPM is the creation of such materials based on blends of polymers with the necessary set of properties. When creating biodegradable polymer mixtures, as a rule, the following principle is applied: add bio degradable natural materials to a synthetic polymer binder polymer mixtures (starch, cellulose, chitin) or synthetic sky. The biodegradation of polyolefin in the presence of starch is a very complex process, in which a variety of factors play an important role, including oxidation reactions of carbo macromolecules.

For example, a set of valuable characteristics inherent in poly chitin saccharide: low density, layered structure, method tendency to film formation, a tendency to selective interaction action with microorganisms, radio absorption and radio protective properties, suggests the possibility of developing biodegradable electromagnetic screens based on its mixtures with polyethylene (PE). For example, biodegradable copolymers of the product of co-polymerization of ethylene with caprolactam were prepared by graft copolymerization methods. By extrusion, mixtures of waxy maize starches with a copolymer of ethylene and caprolactam are obtained.

Currently already created and implemented in industrial presence of developed countries in the world of BPM based on starch and PE, its copolymers. For the first time in the Republic of Belarus, studies on the development of formulations and manufacturing technologies for composite BPM, namely films based on starch and PE, were launched at the Institute of Mechanics of Metal-Polymer Systems (Gomel) in early 2000.

1.2. MECHANISMS OF DESTRUCTION OF BIOPOLYMERS

To describe the terminology of biological decomposition, there are a number of definitions that are not significantly different from each other, the essence of which is that biodegradation is a process caused by biological activity, which leads to the production of natural end products of metabolism when the chemical structure of the material changes. Modern research activities in the field of Biodegradable materials are produced in two directions:

- development of polymeric materials and auxiliary materials substances that under the influence of microorganisms quickly decompose and completely mineralize. In this case, polymers can be obtained from both petrochemical and renewable raw materials;
- development of polymeric materials and auxiliary materials substances without rapid decomposition requirements. Classic examples are rubber, casein polymers and cellulose acetate. New products, among others, are net polymers based on polysaccharides and proteins for insulating materials and particle boards.

For optimal biodegradation a specific set of environmental factors: temperature, pressure, humidity in the liquid or gas phase, the type and concentration of salts, the presence or absence of oxygen (aerobic or anaerobic decomposition), the availability of alternative electron acceptors, the presence of trace elements and nutrients, the pH value, redox potentials, stability or change in environmental conditions, opposing microorganisms, inhibitors, alternative carbon sources, light intensity and wavelength. At this prerequisite is the presence of a minimum water content. In all cases of bio deterioration, interaction is observed. Vie living organisms and polymers (composite materials fishing). Bio deterioration can be caused by the following factors:

- macro organism (animals, higher plants);
- microorganisms (bacteria, fungi). Most aggressive of these, mold fungi belonging to the genera Aspergillus, Penicillium and Tricoderma are active.

The biodegradation mechanism varies depending on the type polymer, microorganisms and environmental conditions. There are three types of exposure of microorganisms to polymeric materials:

- mechanical;
- the effect of metabolic products (organic acids, enzymes, amino acids, pigments) on the basic physicochemical and technological properties of materials;
- bio contamination of polymeric materials and products from them.

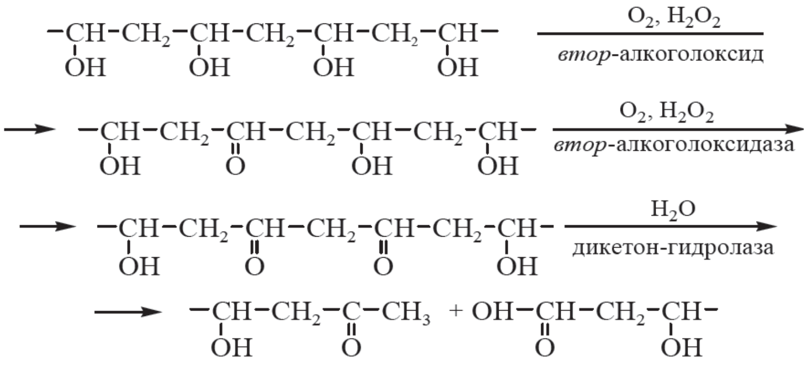
The mechanical destruction of polymers occurs due to fungus mycelium plants (similar to grass piercing as). Mushroom mold for its growth can use very thin cracks and pores of the material formed at the junction of plastic and particle components.

Bio pollution occurs due to the direct presence of effects of spores, copyids or individual parts of the mycelium on various products. In the process of life on polymeric materials -molds and bacteria can secrete a huge amount of
the variety of metabolites that are negative affect the properties of materials. Oxidative Fermentation, Challenges caused by molds and oxidizing bacteria,
possible due to the fact that microorganisms secrete special oxidized recovery enzymes.

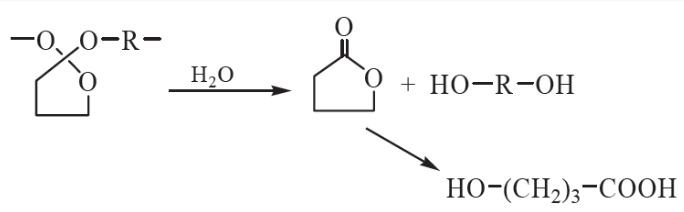
The action of metabolic products promotes the passage of basically two processes leading to biodegradation: hydrolysis and oxidation. So, the metabolism of degradation products of polymers based on lactic acid in the body is studied quite well. At the initial stage and outside living organisms, biodegradation occurs due to hydrolysis with a decrease in molecular weight. Hydrolytic decomposition at pH <1.5

occurs slightly distinctly, and at pH> 7.5 - quickly. Responsible for biodegradation proteinase, ficin, esterase and trypein.

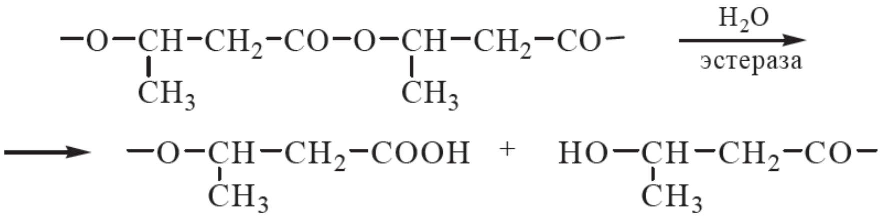
Microbiological reactions conversion of hydrocarbons are mainly oxidized real processes. As a result of their course, alcohols, aldehydes, keto and hydroxy acids subject to long-further oxidation and fragmentation. For example, below is mechanism of enzymatic de polymerization of polyvinyl alcohol:



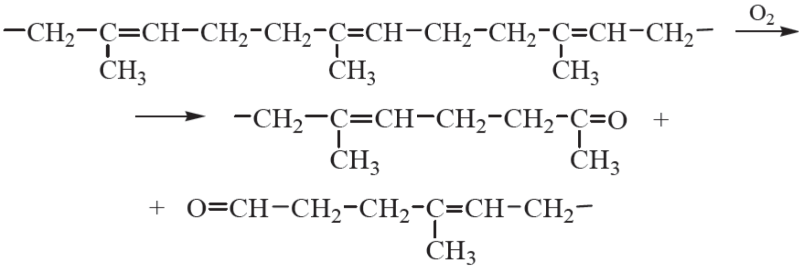
The mechanism of enzymatic decomposition of polyorthoester opioid is given by the following equation:



Hydrolytic and enzymatic decomposition of poly hydroxy fatty acids proceed according to the scheme:



Enzymatic de polymerization of natural rubber:



Upon oxidation of the β-carbon atom of the alkane chain, alcohols and ketones. The decomposition of ketone leads to the formation of primary alcohol, the chain length of which is two carbon atoms sort shorter than the parent compound. This alcohol can then undergo oxidative dehydrogenation followed by β-oxidation of the resulting fatty acid.

Oxidation of unsaturated hydrocarbons by enzyme microorganism excreted through education alcohols, aldehydes, keto and hydro acids with further conversion lowering them into dibasic acids, which are then subjected to β-oxide laziness.

Cleavage by microorganisms of aromatic hydrocarbons Dov is accompanied by the formation of phenols, which are further oxidized are added to neutral dibasic acids. Alkyl-substituted aromatic compounds are benzyl oxidation with fungi Aspergillus niger, Aspergillus sclerotiorum, Penicillium adametri.

Cleavage by microorganisms of cellulose leads to the development of oligo- and monosaccharides, CO2, and polyimide - to degrade the imide cycle; upon decomposition of polyethylene terephthalate a change in the absorption bands in the regions 1720, 1330, 990 and 730 cm – 1, corresponding to the groups C = O, CH2, C – O and ben ash ring.

The presence of acetic, propeon, oil, fumar, amber, apple, lemon, tartaric, gluconic and oxalic acids. Organic acids play a double role: on the one hand, act on polymer materials as aggressive media that can lead to their physical and mechanical characteristics, on the other hand, are carbon source for the further development of fungi.

Polymers are affected by the following main types of organisms: fungi - A. niger, A. versicolor, A. flavus, A. amstelodamii, A. ruber, Pen. purpurogenum, Pen. brevi-compactum, Pen. commune, Cladosporium, Fusarium, Paccllomyces, A. wamori, A. oryzae, Tricoderma, etc. Mushrooms A. niger, Candida lipolitica, Sporatrichum sp. able to oxidize olefins by hydration reaction a double bond with the formation of monobasic alcohols; by reaction pits as a result of which epoxy compounds are obtained; by reaction holes leading to the formation of diols.

To protect polymer products, it is especially often used compounds exhibiting fungicidal properties: salicilanlid, zinc salicylanilide, copper 8-hydroxyquinolate, derivatives of zeros, quaternary ammonium compounds, trilane, trichloroethyl phosphate, 1-fluoro-3-bromo-4,6-dinitrobenzene, phenyl-salicylate mercury, phenyl-mercury phthalate, pentachlorophenol and others. As antiseptics for wood use sodium fluoride, di nitro phenol, wood resin, ammonium tetra fluoroborate, bolide, naphtha copper tenat, donalite. It was found that iron oxide in the composition composite polymer materials stimulates the growth of of organisms, titanium dioxide is inert, and zinc oxide slows down his.

Of the fillers, asbestos and talc are increased, and carbonate calcium reduces the growth rate of microorganisms. Bottom-some mushroom resistance of a number of composite materials is associated with the presence in their composition of magnesium oxide with hygroscopic personality, which leads to swelling that promotes the active development of microorganisms. To protect polymer materials from bio deterioration as biocides used organometallic, organochlorine, quaternary ammonium-high and inorganic compounds.

Of particular interest are limited fungicides the validity of their toxicity, since with the expiration of product operation removes the question of their toxicity. These fun hybrids can be divided into four groups:

- inorganic compounds Zn O, $CuSO_4$, Na F, NH_4BF_4,Ca $(CN)_2$;
- organic compounds (phenol derivatives, phosphorus holding compounds, amines, etc.); - organometallic compounds containing mercury, lead, tin, sodium, silver; - multifunctional additives - synthetic biological bioactive bio-degradable compounds due to the reduction of internal stresses due to the implementation mesomorphic supramolecular level of organization, leading to the participation in the adhesive-cohesive interaction of the most more active functional groups, their regular local distribution in the system.

Thus, for complete biodegradation of the poly material requires three key elements: microorganisms selectively acting on polymeric materials themselves; relevant environmental conditions living environment. If one of these elements is missing, then bio decomposition does not occur. An example would be newspapers or food products that after a long stay in the ground or in landfills almost completely preserved.

The degradable polymer must satisfy specific requirements. So, in particular, the polymer chain must contain chemical fragments subjected to hydro- lysis or oxidation. The most sustainable are poly measures that contain no more than 10 atoms in the monomer unit carbon.

The hydrophobicity ratio has an additional effect and hydrophilicity. At the same time, layering of positive effects (for example, if the rate of hydrolysis correlates with milling material).

Resistance to the action of microorganisms of polymer materials depends on the plasticizers used, carriers, stabilizers, and also to what extent these substances organisms can be a source of carbon for microorganisms, nitrogen and other nutrients. Inorganic components - silicates, sulfates, phosphates, carbonates - Do not support mushroom growth. It is shown that mushroom resistance PVC samples do not mean their bacterial resistance. For example, shale PVC – mushroom resistant, but destroyed by di nitrophic and hydrocarbon-oxidizing bacteria.

Now there are no absolutely resistant to the action of living organisms.
of polymeric materials. As shown by in Japan studies materials such as neoprene and nylon, which, according to American data, are not affected by mold fungi, in fact, under the influence of A. niger, A. flavus markedly worsened their properties. Opinions of researchers also apply to a number of other polymers: kapron, polyurethane, cellulose acetate, cellulose acetate butyrate, phenol aniline-formaldehyde resin, melamine-formaldehyde-Noah resin.

Environmental factors must be selected so that to create optimal conditions for microorganisms for bio-decomposition, such as temperature, humidity in liquid or gas phase, the presence of salts (type and concentration), the presence or absence of the action of oxygen (aerobic or anaerobic decomposition). Wherein a prerequisite is the presence of a minimum holding water.

So, the main habitat of microorganisms is soil. Their species composition and quantity depend on the type of soil, its structure,fertility and other causes. The most saturated microorganism Mami soil layer at a depth of 5-15 cm. Here 1 g of soil contains up to108 units of microorganisms. As a rule, the more lives in the soil of organic residues, the more microorganisms.

Soil metabolism depends on a system of relationships within microbial community. In the study of microorganisms, prisoners from any soil, their diversity and the fact that they are often opposite and incompatible for one habitat properties.

The process of decomposition of organic substances in the soil is carried out through sequential reactions involving various groups of microorganisms replacing each other and supplied soil from its colossal reserve - a microbial pool. Mik fungi are cosmopolitan organisms of all types of soils of the genera Penicillium, Aspergillus and bacteria Bacillus mycoides, Bacillus megaterium. They are united by one common property- ability secrete enzymes. Without enzymes in nature is not created and not a single substance is destroyed.

Any splitting of the dead of a substrate is an enzymatic process, as a result of whose simple chemical compounds are released, subsequently disposed of as microorganisms themselves, and higher plants. Successful solution to a problem is largely related to development ideas about the nature of the real process of microbiological damage to materials and with the presence of objective quantitative information about the patterns of occurrence and Kania of this process.

Therefore, a relevant and promising method of obtaining biodegradable synthetic plastics, for example based on polyethylene, polypropylene, polystyrene, which are the most large-capacity, their modification is special special additives introduced into the polymer at the stage of its conversion work in the processes of extrusion and casting.

There are additives that allow you to get polymer biodegradable materials for 1-3 years depending on the composition of the additive and the specific formulation of the poly dimensional composition. For example, the action of d2w is based on the oxidation polymeric material under the influence of factors such as ultraviolet light, oxygen. This supplement is accelerator of the oxidation process. Polymer decomposition process of material with d2w is called OXO decomposition (with the participation of oxygen), and a polymer material containing d2w, -OXO-degradable polymer material.

Hydro degradable polymeric materials are polymers, obtained on the basis of plant materials, including dairy acids. Hydro biodegradable plastics can be classified as sti and synthetic plastics, for example polyethylene, poly propifla, which contain special additives (starch) and trans are formed into degradable products by hydrolysis without oxygen access. One of the features of such plastics is-The fact that methane is released during their biodegradation. It due to the fact that in an atmosphere devoid of oxygen, the complete oxidation of carbohydrates and fats to CO is impossible. As seen from fig. 1.2, decomposition of OXO and hydro degradable materials, non-looking at the course of various chemical processes, leads to the formation of the same substances: carbon dioxide, water and biomass. In both cases, at the stage of oxidation and hydro- low molecular weight fractions which under the action of microorganisms, bacteria turn into CO2, H2O and biomass. Biomass is the total mass of plant and animal here microorganisms. In fig. 1.2 shows the principle of operation OXO additives on the example of decomposition of polyethylene, where There are two processes: 1) under the action of an oxidation catalyst (d2w additives), dimensional molecule breaks up into many low molecular weight fragments; 2) low molecular weight fragments are assimilated (assimilated bacteria), which gives CO2, water and biomass. Wherein microorganisms grow on the surface of the polymer after the oxidation process.

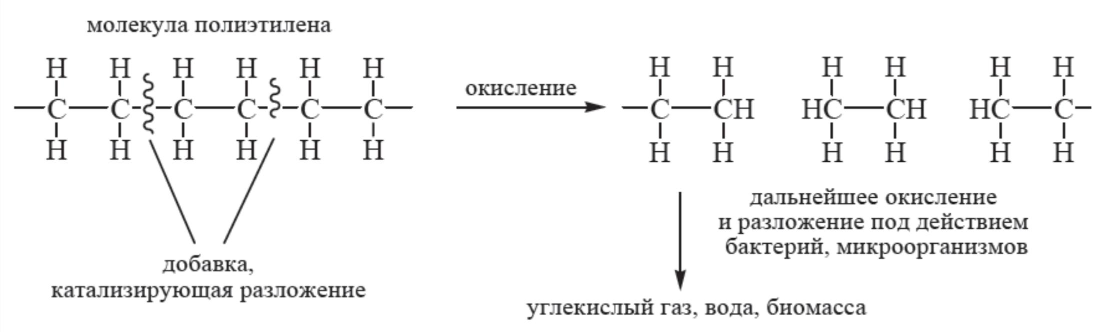


Fig. 1.2. The principle of action of OXO-additives

In contact with the environment, soil on top of the oxidized polymer does not have hydrophobic properties you inherent in the primary polymer material, and therefore easily exposed to water, bacteria.

The use of OXO-degradable plastics provides environmental benefits:

- can be easily obtained compositions by compounding the addition of additives with the starting polymer in the process of extrusion, casting;
- are recycled;
- their pyrolysis is possible in order to obtain starting materials or fuel;
- are transformed into biodegradable fragments worn under the influence of light and heat;
- slow conversion to carbon dioxide;
- maximum conversion to biomass during decomposition composting or in soil;
- do not form methane.

One of the most important benefits of OXO-biodegradable plastics is their inability to form methane, since the biodegradation of these plastics is an aerobic process, caused by oxygen, heat and light. Anaerobic the process is inherent in hydrobiologically degradable plastics, primary the decomposition stage of which is hydrolysis. This process carried out without oxygen. In fig. 1.3 presented two processes - aerobic and anaerobic.

Fig. 1.3. The process of decomposition of polymeric materials

The specificity of polymer degradation by multi-enzyme com- pounds plexi. Polysaccharides play an important role in life microorganisms are one of the main sources nutrients and energy. Recycling natural polis-environmental scharydes, microbes synthesize their hydrocarbons -polymers that are the building material of the cell (e.g., chitin) or are delayed in intracellular reserve nutrients (e.g. glycine). In this regard, microorganisms produce complex compositions of extracellular and cytoplasmic enzymes with pre-property orientation of the first group on catalysis of destanual transformations, and the second on the regulation of the course processes of constructive and energy metabolism Maybe-microbiological synthesis of polymers, although they attract researchers' attention, but at present stupid the practice of using full conversion processes or bio modification of feedstock.

Among the bio catalysis there are several hundreds of de polymerase enzymes, whose new function is the degradation of polymer substrates to mono- and oligomers with a relatively small degree polymerization. These enzymes vary:

- according to the type of chemical reaction catalyzed by them - hydro- lysis, transfer of certain chemical groups, dehydration, isomerization, etc.);
- a method of acting on a polymer substrate;
- specificity to the nature of the monomer polymer residues;
- specificity to the type of bonds connecting monomeric links of the substrate, etc.

The complexity of studying the mechanism of action of de polymerase Slovenia heterogeneous polymeric materials, a whole range of substrates with different reaction ability, an example of this are complex in structure natural macromolecular compounds of hemicelluloses, pectina, starch, etc. At the same time, the patterns of enzyme degradation of their constituent polymers are quite similar and determined mainly by the supramolecular structure of the substrate and active centers of de polymerases.

The destruction of any polymer is usually carried out in as a result of the coordinated action of a whole group of enzymes, the name of the multi-enzyme complex (IEC). Part IEC usually includes enzymes of three or more types with different the liable mechanism of breaking bonds in macromolecules, the specificity of which is determined by the structure of the active center biocatalyst.

According to modern ideas, the active center enzyme de polymerase has the form of an active cavity, which may be in the form of a “pocket” directed deep into the protein molecule, or located on the surface of a protein globule -"Hollows." In fig. 1.4 presents the interaction scheme active center of enzymes with certain areas of macro-polymer molecules. "Pocket" allows you to accommodate a certain the number of terminal monomer units of the substrate. In the "hollow" fragments of the middle part of the polymer can be accommodated.

The form active cavity, determines the affinity (affinity) of the bio catalyser a specific section of the substrate macromolecule. In correspondence with existing ideas about various Under the influence of de polymerase enzyme groups exo-and endoductions. Exodepolymerases are active in with respect to the terminal (external) sections of the polymer, by cleaving one or two monomeric units of the macromolecule polymer. The endodepolymeras group preferably acts into the middle (inner) sections, splitting the bonds remote from end of the macromolecule. The combined effects of components Enzyme system provides maximum speed

biopolymer conversion.

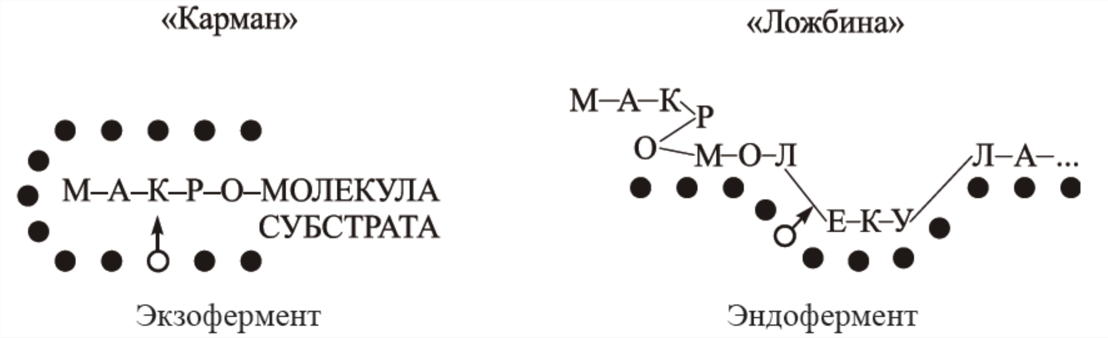


Fig. 1.4. Forms of the active center of the globule of de polymerase enzymes

The destruction of polymer substrates in the presence of poly ment complexes is carried out, as shown in Fig. 1.5, in the course of series-parallel catalytic transformations under the influence of endo- and exodepolymerases

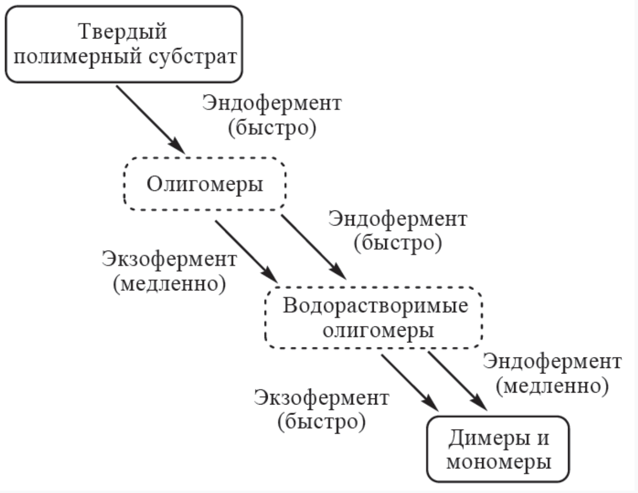


Fig. 1.5. Conversion of polymer substrates under the action of de polymerase enzymes

Endozymes exhibit a high substrate specific relative to the insoluble substrate, and destruction relatively small degree of polymer hydrolysis products polymerization under their influence occurs less intensively. The action of endoenzymes is not only complemented by the destruction of zoenzymes, but it is also an indispensable condition for manifestation effects of the latter, since exodepolymerase is significantly active against solid phase substrates due to the presence of steric difficulties when approaching the end sections macromolecules. At the same time, fractions of water-soluble oligome the moat is cleaved by exoenzymes at a higher rate, rather than endodepolymerase. Joint action of both groups enzymes provides fast and complete conversion of raw materials to monomer products.

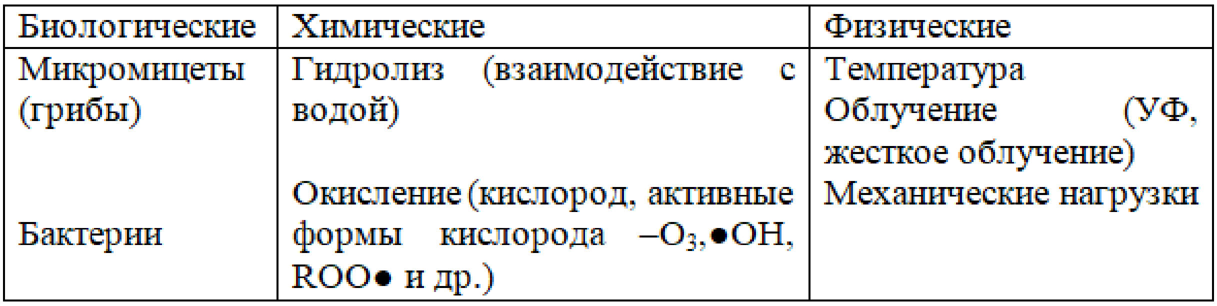
To obtain monomolecular nutrients naturally programmed natural strains of organisms. Therefore, in the products of their cultivation exofer cops are contained in significant quantities. If it is needed to partially hydrolyze the polymer compound, then becoming enzymes must be changed, i.e., genetically adjust the functions of their biosynthesis by microbiological.

1.3 DEGRADABLE MATERIALS

The main goal in creating a degradable material is to ensure that the resulting substance can degrade either by physicochemical or biological mechanisms. In the review [41], factors that can cause the destruction of polymers are given — Tab. 1.2.

The proportion of polymer materials entering the soil is high. Therefore, the question arises of creating biodegradable (biodegradable) materials that could be disposed of in the natural environment independently or with the help of microorganisms without harm to the environment [42].

Table 1.2 - Factors causing degradation of polymers in nature



Биологические	Химические	Физические
Микромицеты (грибы)	Гидролиз (взаимодействие с водой)	Температура Облучение (УФ, жесткое облучение)
Бактерии	Окисление (кислород, активные формы кислорода –O_3,•OH, ROO• и др.)	Механические нагрузки

Biodegradable material can degrade under natural conditions (in aerobic or anaerobic) under the action of microorganisms, ultraviolet radiation, radiation, which subsequently leads to the absorption of this material by microbes [43]. In other words, the polymer becomes food for soil microorganisms. The decomposition rate of such materials depends on a number of factors: the type of polymer, the concentration of decomposing materials, environmental conditions, etc. [44]. Most often, the decomposition products are carbon dioxide, water, biomass (in the case of anaerobic decomposition, carbon dioxide, methane and biomass), which are naturally utilized in the future [45].

At the same time, it is necessary to distinguish between the concepts of biopolymer and biodegradable plastic, since the first material is created from natural components, but is not always biodegradable, while biodegradable plastic can be made from either hydrocarbon raw materials or natural ones, but it has the ability degrade in the natural environment [46].

The main factors affecting the biodegradation process are: temperature and humidity of the environment, as well as microorganisms and / or enzymes that trigger the process. As a result of the process of biodegradation, as a rule, processes of oxidation and hydrolysis proceed in parallel [47]. Changing the length of polymer chains leads to destruction macromolecules, and as a consequence of the deterioration of the strength characteristics of the material [48].

The main advantages of biodegradable plastics are that they can be composted with organic waste to enrich the soil [49]. Their use allows not only to reduce injuries of wild animals caused by dumping of ordinary plastics, but also to reduce labor costs for removing plastic waste from the environment, since they will decompose naturally [50]. Their decomposition can increase the durability and stability of landfills by reducing the volume of garbage, and they can also be processed into useful monomers and oligomers [51].

Obtaining biodegradable materials is possible in several ways: both the use of biopolymers (cellulose, starch, natural rubber, etc.) and the introduction of bio additives [52], see Fig. 1.10. Traditional polymers are made from petrochemical raw materials. These include: polyethylene, polypropylene, polyvinyl chloride and others. Decay time in nature of objects made from these materials more than 100 years [53].

Bioplastics are an analogue of traditional polymers, but are made on the basis of plant or animal raw materials [54]. The most promising bioplastics at the moment is considered to be polyactide (polylactic acid, PLA) - a condensation product of lactic acid [55]. However, the widespread use of this material is constrained by the low productivity of technological lines and the high cost of the final product, and the high diffusion coefficient of carbon dioxide prevents the use of PLA bottles for storing carbonated water [56].

Полимеры, изготовленные путем глубокой переработки растительного сырья и обладающие свойствами традиционного пластиков

Полимеры, изготовленные из растительного сырья и соответствующие требованиям директивы ЕС по срокам разложения (6 месяцов)

Полимеры, изготовленные из нефтепродуктов, срок распада в природе — до 100 лет

Полимеры, изготовленные из нефтепродуктов, с добавлением спецдобавок для контролируемого по срокам биоразложения

Figure 1.10 - Types of raw materials for bioplastics

Also known today is the technology for creating (in small volumes) traditional polymeric materials that contain TDPA — Tottaly Degradable Plastic Additive — an additive (it is different for different companies) that completely decomposes plastic in the light in the presence of oxygen [57]. However, this component merely crushes the initial polymer into dust and complete decomposition of the polymer still does not occur [58]. Such materials, due to their obvious non-environmental friendliness, are not widely used.

The next group of biodegradable polymers includes plastics that contain starch, protein, cellulose, or chitosan [59]. The largest of these materials is used and investigated materials with starch and pectin, with the introduction of plasticizers (polyoxyethylen glycol or glycerin) and polyester [60] into the composite material. However, an increased concentration of starch increases the fragility of the film. Therefore, the main task of scientists in the direction of obtaining films from natural fillers is the creation of composites with performance characteristics similar to traditional polymers, and it has not yet been fully solved [61].

The materials mentioned above are mainly produced on a non-industrial scale in small private enterprises. There are also methods to impart biodegradation properties. large tonnage industrial polymers [62]. This is achieved by the introduction of additives accelerating the photo degradation of the composite. Often degraded natural additives are introduced into polymers, initiating, at a certain moment, the decomposition of the entire composite, or the polymer is modified with a biodegradable filler by some physicochemical method in order to reduce the length of the polymer units [63]. For example, copolymers of ethylene with carbon monoxide are photodegradable, vinyl ketone monomers initiate photo degradation of polyethylene and polystyrene [64]. The introduction of polyethylene or polypropylene polyethylene phthalate cellulose or fragments containing carbonyl groups into the composite accelerates the photo and biodegradation of films [65]. It is worth noting that the issue of introducing natural materials into synthetic polymers to impart biodegradation properties is in stagnation and is not particularly developing at the moment.

The article [66] describes the modification of composites based on PVC and pectin and chitosan by electron beam etching for medical purposes to create an antibacterial wound cover. The work [67] presents studies of plasma processing of polyvinyl chloride films with argon and oxygen with different positions of the samples in the etching chamber and the exposure time of the samples under the plasma. It was found that the greatest destruction of the polymer was achieved by treating the samples with oxygen — the surface was covered by pits and craters, relatively evenly distributed over the film area. The result of spectroscopic analysis showed that oxygen etching increases the intensity of the peaks in the bands of 1720 cm-1 and 3400 cm-1 - which corresponds to O-H vibrations. Together, both of these factors indicate an increase in the ability of PVC samples to absorb and adsorb moisture, which subsequently accelerates the destruction of the polymer, since the untreated plasma PVC sample is hydrophobic and not subject to biological destruction [68].

Thus, in work [69], polyvinyl chloride samples and samples from poly acrylic acid were processed with low pressure argon plasma in order to remove the side chains of vinyl groups in polymers. The samples were studied by infrared absorption spectroscopy. As a result of the work done, it was concluded that argon plasma processing of vinyl polymers entails the appearance of unsaturated carbon-carbon bonds.

In [70], the destruction of PVC samples with plasticizers, diethyl phthalate and dimethyl phthalate after etching with low pressure oxygen and argon plasma was studied using vibrational SFG and X-ray photoemission spectroscopy; as well as spectroscopy of coherent anti-Stokes Raman scattering.

CONCLUSION ON CHAPTER 1

According to the results of the analysis of scientific and technical literature, it can be concluded that the study of materials based on PVC is promising. The prevalence of the use of PVC and its derivatives gives the prospect of creating degradable materials to reduce the environmental burden on the environment.

CHAPTER 2. OBJECTS AND METHODS OF SYNTHESIS AND RESEARCH OF PVC COMPOSITES

2.1 OBJECTS OF RESEARCH

In this work, the objects of study were polymer films based on an industrial PVC composition developed by Klokner Pentaplast Rus LLC (St. Petersburg, Russia) with various fillers with a concentration of 0 ÷ 15 wt.%.

As fillers were used:

1) Potato starch (K) (premium, CAS No. 9005-84-9, CJSC Becton)
2) Apple pectin (GOST 29186-91, Yantai Andre Pectin Co. Ltd.) (P)
3) Bentonite

Two types of bentonite were used in the work: Bentonite of Navbahor (BN) (obtained at the Navoi district, (Uzbekistan) and Aszkomar bentonite produced at the Bukhara region (B).

In addition, 6 series of polymer PVC composite films (PVC + B and PVC + P) were obtained with different rolling times: 2, 5 and 10 minutes.

The objects of study were also PVC filled films modified with low-temperature plasma.

2.2 TECHNOLOGY OF PREPARATION OF COMPOSITE FILMS

The technology for preparing composite films consisted of two stages: mixing the components and rolling [71].

The industrial composition included the following components: suspension polyvinyl chloride (Fikentchera constant 57-58, mass fraction of volatiles 0.04%), organotin thermos stabilizator 0.2-1.5 wt.%, modifier of the polymer mixture 2.0-4.0 wt.%, paraffin (as a lubricant) 0.1-0.5%. The fillers were introduced on a paddle mixer with a stirring speed of 4000 rpm for 4 minutes.

The preparation of polymer composite films was carried out on industrial roll equipment Poly mix 150U (SCHWABENTHAN, Germany) (Figure 2.1).

Figure 2.1 - Industrial rollers Polymix 150U

The temperature of the rollers was 165-170 ° C. The mixture of components was processed on rollers for 2, 5 and 10 minutes. These parameters (rolling time and temperature of the rollers) were varied to select the optimal preparation technology for the objects of this study. The film thickness was determined by the distance between the rollers and was 350 мкм.

2.3 MODIFICATION OF THE SURFACE OF POLYMERIC MATERIALS BY THE METHOD OF ION-PLASMA ETCHING

In the course of this study, the surface of polymer films was modified by ion-plasma etching. Reactive etching of low-temperature anisotropic plasma was carried out in a RIE-1701 apparatus (NORDSON MARCH, USA). Samples of PVC films with different fillings were etched for 5 and 10 minutes at atmospheric pressure under the influence of a low-temperature plasma of a high-frequency discharge.

During the experiment, an argon-oxygen gas mixture was used with an argon: oxygen ratio of 20:80. During plasma-chemical etching, the surface was subjected to the process of cold evaporation at a speed of 2 microns per minute.

2.4 STUDY OF PROPERTIES OF PVC FILMS

2.4.1 OPTICAL-SPECTRAL METHODS OF STUDYING PVC FILLED FILMS

2.4.1.1 RESEARCH OF POLYMER COMPOSITIONS BY IR FOURIER SPECTROSCOPY

The structure of polymer composite films was studied by IR Fourier spectroscopy on a Tensor 37 spectrometer (Bru0ker, Germany) using the MI Racl TM Pike Technologies ATR attachment equipped with a diamond coated Zn Se crystal.

The measurements were carried out with a spectral resolution of 2 cm – 1, averaging over 32 scans. The spectra were recorded and processed using the OPUS program, version 7.02 (Bruker)

2.4.1.2 STUDY OF THE STRUCTURE OF POLYMERIC COMPOSITES BY THE METHOD OF OPTICAL MICROPHOTOGRAPHY

The surface of polymer composite films and the distribution of filler in them were studied using the optical microscopy method on an STM6 instrument (OLYMPUS, Japan)

Microphotographs of the studied materials were obtained by the methods of bright field in reflected light and polarization contrast.

2.4.1.3 RESEARCH OF POLYMERIC FILLED FILMS BY SPECTROFLUORIMETRY METHOD

The structure of polymer-filled PVC films was studied by fluorimetr using an SM-2203 instrument (SOLAR, Belarus). For this, Rayleigh light scattering spectra in the wavelength range from 230 to 700 nm and synchronous fluorescence excitation spectra in the same wavelength range with a shift of the emission wavelength relative to the excitation — 30, 40, 60, or 85 nm — were previously recorded.

2.4.1.4 METHOD FOR DETERMINING COLOR AND SHINNING OF PVC FILMS

The color of the obtained films was measured using a SPECTRO-GUIDE 45/0 gloss spectrophotometer (SPECTRO-GUIDE, Germany) according to the standard method DIN 5033 “Colorimetry-Part 7: Measuring conditions for object colors” and DIN 5039 “Licht, Lampen, Leuchten - Begriffe, Einteilung "[72,73].

The study of color is based on determining the brightness of the color L (0-100%), as well as color indicators a - from green to red and b - from blue to yellow, in degrees, for each -120 °: + 120 °.

2.4.1.5 METHOD FOR DETERMINING HAZARDS AND FILM TRANSMISSION RATE OF PVC FILMS

The optical parameters — turbidity and total light transmission — were determined in accordance with the standard ISO 13468 Plastics - Determination of the total luminous transmittance of transparent materials method using a HAZE-GARD spectrophotometer (BYK-Gardner GmbH, Germany) [74].

Total light transmission is the ratio of the light transmitted by a sample to the light incident on it. This parameter is affected by the absorbing and reflecting properties of the material. Completely transmitted light consists of directly transmitted and diffused components. Transparent plastic will look different depending on the angular distribution of the scattered part. Measurement and analysis of turbidity and transparency It guarantees a uniform and uniform quality of the product and helps to analyze the influencing process parameters and material properties, for example, like cooling rate or raw material compatibility.

2.4.1.6 STUDY OF ROUGHNESS OF THE SURFACE OF COMPOSITE FILMS

The study of surface roughness is one of the main operational parameters of PVC film to determine the suitability of its further use as a package. The roughness of the test surface is measured in small areas.

The main parameters characterizing the surface roughness have a certain letter designation. In the course of our work, we determined the values of RZ, which is the height of the measured irregularities, calculated from 10 basic points, microns.

The study of the roughness of PVC films was carried out according to the standard method using a Surftest SJ-210 profilometer (MITUTOYO, Japan) according to the standard method DIN EN 10049 Measurement of roughness average Ra and peak count RPC on metallic flat products” [75].

2.4.2 RESEARCH OF THERMAL CHARACTERISTICS OF COMPOSITES BASED ON PVC

2.4.2.1 STUDY OF POLYMER FILMS BY THE DIFFERENTIAL SCANNING CALORIMETRY METHOD

The thermal properties of polymer composite materials were studied by differential scanning calorimetry (DSC) using a DSC 204 F1 Phoenix instrument (NETZSCH, Germany). The DSC scheme is presented in Figure 2.6. The experiment was carried out in closed aluminum crucibles in a stream of nitrogen (consumption as a protective gas 40 ml / min; flow rate as working gas 20 ml / min). Samples were heated to 150 ° C at a rate of 3 ° K / min.

A sample of the polymer film was placed in a disk-shaped crucible until it was completely filled, while the reference crucible was left empty.

2.4.2.2 THERMOGRAMMETRIC ANALYSIS

Thermal destruction of polymer composites was studied by thermos gravimetric analysis using a TG 209 F1 Libra thermal balance (NETZSCH, Germany)

The experiment was carried out in closed crucibles in a nitrogen medium, the gas flow rate through the working chamber was 20 ml / min. The samples were heated in the range from 25 ° C to 500 ° C at a rate of 10 ° C / min.

A variable in thermos gravimetric analysis is the mass of the material subjected to degradation. The rate of change of mass of a substance is described by the equation:

$$-\frac{\mathbf{dW}}{\mathbf{dT}} = \mathbf{kW^n} \qquad (1)$$

where W- is the mass of the sample that has reacted; k- is the reaction rate constant; n -is the reaction order; t- is the time;

This equation describes very well the kinetics of thermal decomposition of solids.

Since heating occurs at a constant rate $\beta = \frac{dT}{dt}$ from differentiation in time, we can proceed to differentiation in temperature.

$$-\frac{dW(T)}{dT} = \frac{k}{\beta} W^n(\mathrm{T}) \qquad (2)$$

Logarithm both sides of the equation:

$$ln\left(-\frac{dW(T)}{dT}\right) = lnk - ln\beta + n \cdot lnW(T) \qquad (3)$$

Building addiction $ln\left(-\frac{dW(T)}{dT}\right)$ от $lnW(T)$ From the slope of the straight line, we determine the order of the reaction of thermal decomposition n and, at the point of intersection with the ordinate axis, the constant of thermal decomposition rate k.

The dependence of the reaction rate constant on temperature is described by the Arrhenius equation, according to which

$$-\frac{dW}{dt} = A \cdot exp\left(-\frac{E}{RT}\right) \cdot W^n \qquad (4)$$

where A -is the preexponential factor; R- is the universal gas constant; T- is the temperature.

$$-\frac{dW}{dT} = A_T \cdot exp\left(-\frac{E}{RT}\right) \cdot W^n \qquad (5)$$

where AT = A / β; β -is the heating rate of the sample.

At the inflection point of the TGA curve, the second derivative $\frac{d^2W(T)}{dT^2} = 0$ Then, taking into account formula (5), we obtain:

$$-\frac{d^2W(T)}{A_T dT^2} = exp\left(-\frac{E}{RT}\right) \cdot n \cdot W^{n-1} \cdot \frac{dW}{dT} + W^n \cdot exp\left(-\frac{E}{RT}\right) \cdot \left(\frac{E}{RT^2}\right) = 0$$

At the inflection point, we have the meanings $W_0, T_0, \frac{dW_0}{dT},$ based on which, according to equation (6), the imaginary reaction order can be calculated $n = \frac{E \cdot W_0}{R \cdot T_0^2 \cdot \frac{dW_0}{dT}}$ according to the Reich and Fuoss methods.

The E / R ratio is found from the slope of the dependence $ln\left(-\frac{dW}{dT}\right) \text{от} \left[\frac{W_0}{-\frac{dW_0}{dT} \cdot T_0^2} \cdot lnW - \frac{1}{T}\right]$ near the value of T = T0.

$k = -\frac{dW_0}{dT} \cdot \frac{\beta}{W_0^n}$ where β is the heating rate.

2.4.2.3 THERMOMECHANICAL ANALYSIS IN THE STUDY OF POLYMER COMPOSITIONS

The thermomechanical characteristics of filled PVC-based polymer films were also studied by thermomechanical analysis using a TMA 402 F1 Hyperion analyzer (NETZSCH, Germany)

The experiment was carried out using a tensile attachment (Figure 2.8). A sample of a polymer film 2 * 2 mm in size was heated at a speed of 1 K / min and a static force of 0.5-1 N was applied until it was completely tensile (tear). An inert gas, nitrogen (flow rate 40 ml / min), was used as the working gas, and the instrument shaft was cooled using liquid nitrogen.

2.4.2.4 METHOD OF DETERMINING THE THERMAL STABILITY OF FILLED PVC FILMS

The thermal stability of the samples was evaluated by the initial color of the obtained films, as well as by the yellowing index of the samples tested during the statistical thermal test. Aging at a temperature of 190ºC was carried out in a specially designed thermostat.

2.4.3 RESEARCH OF MECHANICAL CHARACTERISTICS PVC COMPOSITE MATERIALS

The mechanical properties of the obtained films were investigated. by piercing on a TATX plus texture analyzer (STABLE MICROSYSTEMS, England). Mechanical size puncturing was 150 * 150 mm. To study the properties of polymer films were used: nozzle with holder for XTP / FSP film and spherical probe P / SS Ø5mm. The probe lowering rate was 1 mm / s

After the test, the film strength upon piercing $\sigma_{p\,r}$ was calculated as

$$\sigma_{np} = \frac{F_{np}}{S_{np}},$$

Where:

F p r is the peak of the piercing force of the sample (N);

S p r = 19.625 mm2 - area of load distribution.

The elongation when piercing ε p was determined as relative sample deformation according to the equation

$$\varepsilon_{np} = \left(\frac{\sqrt{a'^2 + d^2} + r}{a} - 1 \right) \times 100, \qquad (7)$$

Where:

α ‘= 2.5 mm - the linear size of the sample between the probe and the edge openings of the working area of the film holder;

α = 5 mm is the radius of the loaded circle of the sample before the test;

d is the distance traveled by the probe to the piercing point;

r = 2.5 mm is the radius of the probe tip.

CHAPTER 3. INFLUENCE OF RECIPE PARAMETERS ON CHARACTERISTICS OF POLYMER COMPOSITE FILMS

3.1. INFLUENCE OF ROLLING CONDITIONS ON PERFORMANCE CHARACTERISTICS OF PVC MODIFIED FILMS

The main parameters that determine the behavior of PVC during its processing include the characteristics of the polymer, the dispersit and nature of the surface of the particles, thermal stability, etc.

In the course of the work, the influence of the conditions for obtaining PVC composite films with different filling on the operational characteristics of the materials was studied. The main factors affecting the structure and, accordingly, the properties of the final material are the rolling time and temperature, as well as the quantitative ratios of the reagents.

Figure 3.1 shows the dependences of the influence of rolling time on the strength characteristics of polymer compositions depending on the rolling time and the proportion of filler - natural bentonite.

PVC films without filler have a puncture strength of 13.3 MPa. As can be seen from Figure 3.1, when PVC is filled with natural bentonite in an amount of 5 wt.%, An increase in the rolling time to 10 min slightly affects the change in strength characteristics. In this case, in the general case, an increase in the rolling time leads to an increase in the strength characteristics of the films by an average of 10–15%, which is explained by the strengthening effects that occur during the formation of the films.

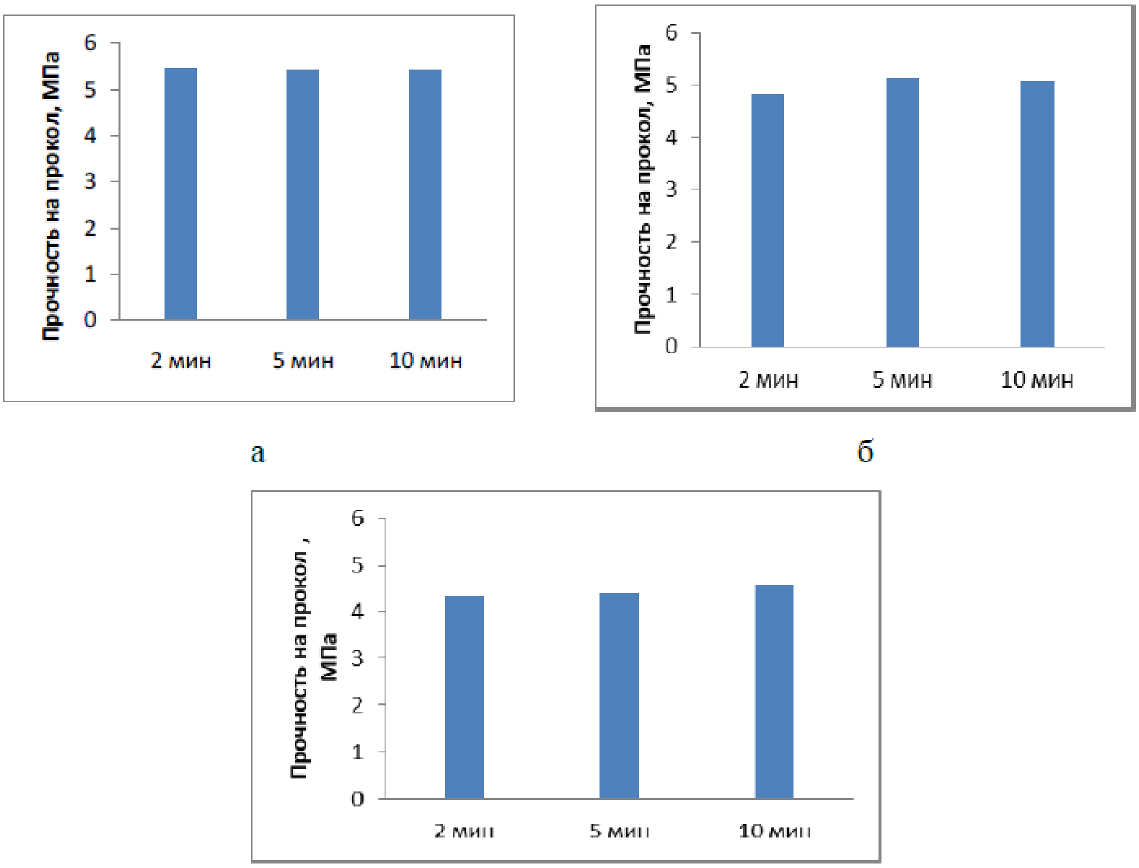
Puncture strength dependencies of PVC films filled with bentonite are described by the following exponential equations:

– for a concentration of bentonite of 5 wt.%: $\Sigma = 5.5e-0.01\tau$;

– for a bentonite concentration of 10 wt.%: $\Sigma = 4.8e0.02\tau$;

– for a concentration of bentonite of 15 wt.%: $\Sigma = 4,2e0,03\tau$,

where σ is the puncture strength, MPa; τ - rolling time, min.



а б

в

Figure 3.1 - Effect of rolling time on puncture strength PVC composite films filled with bentonite (wt.%): a - 5, b - 10, c - 15

Appearance of polymer PVC-filled bentonite films presented in figure 3.2.

However, increasing the rolling time to 10 minutes leads to significant changes in the structure of the PVC composite. In the spectra of the PVC-bentonite composite shown in Figure 3.3, with an increase in the rolling time, there is an increase in the intensities of the absorption bands of carbonyl, carboxyl groups, 1543 cm-1 and 1762 ν (C = O) COO-, respectively, as well as vibrations in the region of 3200 - 3400 cm - 1, corresponding to the presence of a hydrogen bond, which, first of all, is associated with the processes of thermal degradation of the PVC polymer matrix.

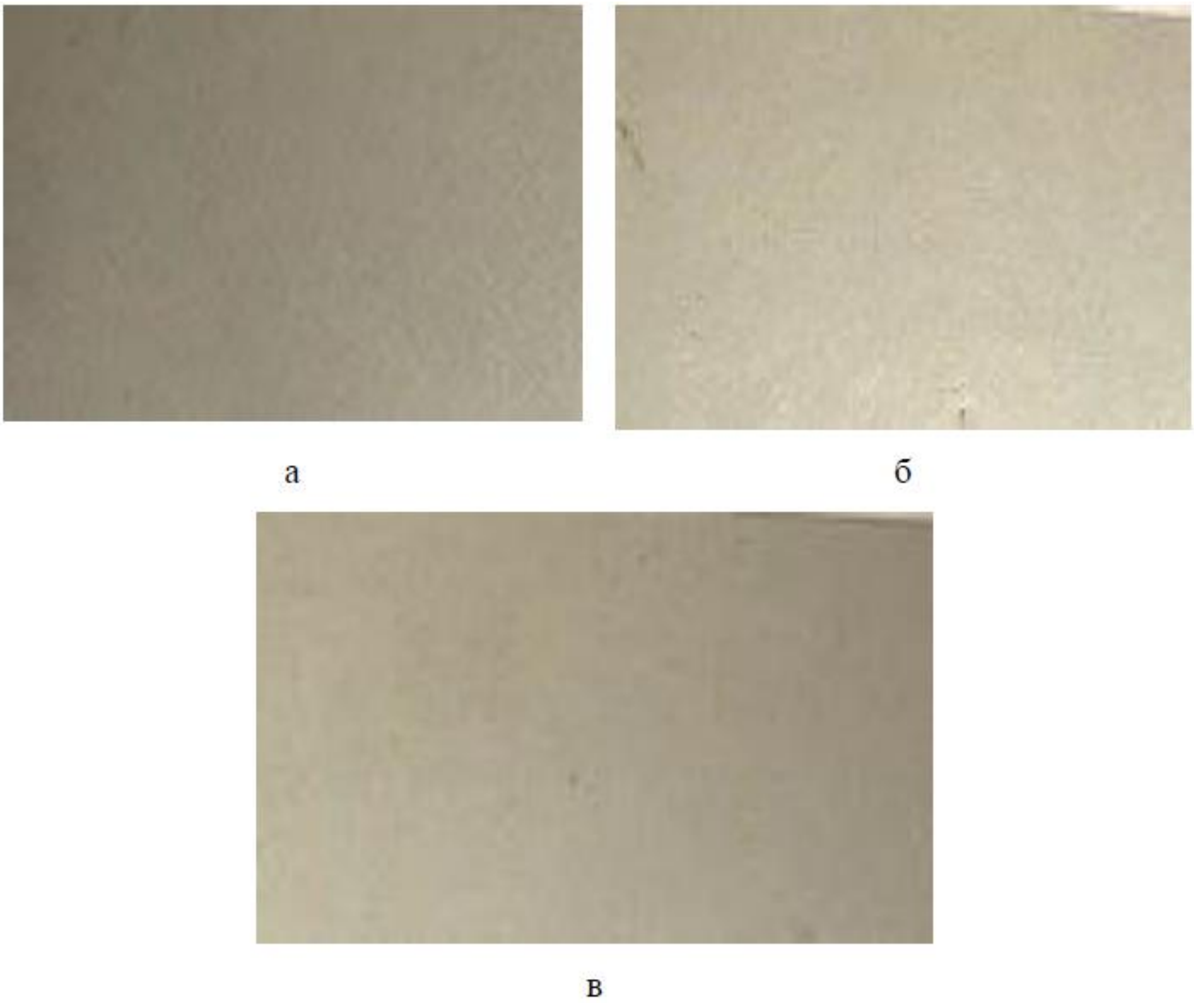


Figure 3.2 - Finished samples of films made on the basis of PVC with bentonite, wt.%: A) 1; b) 5; at 10

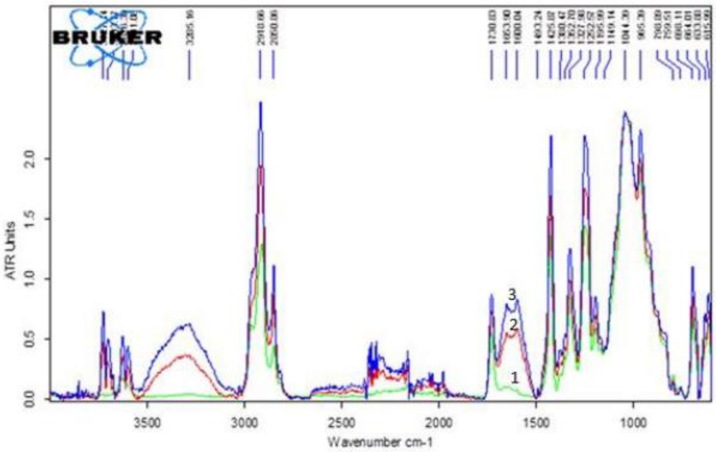


Figure 3.3 - IR spectra of polymeric PVC composites with filling of 15 wt.% Bentonite at different rolling times

In this case, an increase in the rolling time results in a more uniform and finely dispersed structure of the samples, as can be seen from Figure 3.4.

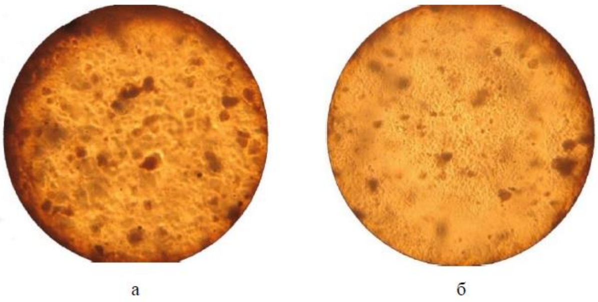


Figure 3.4 - Photographs of bentonite-containing PVC films, with a filler concentration of 15 wt.%, Obtained at different rolling times, min: a - 2; b - 10

As can be seen from Figure 3.5, an increase in temperature does not significantly affect the increase in the strength characteristics of polymer films, on average, by 5-10%, however, the appearance of the material slightly deteriorates, see Figure 3.6, so the temperature of 165 ° C was chosen optimal.

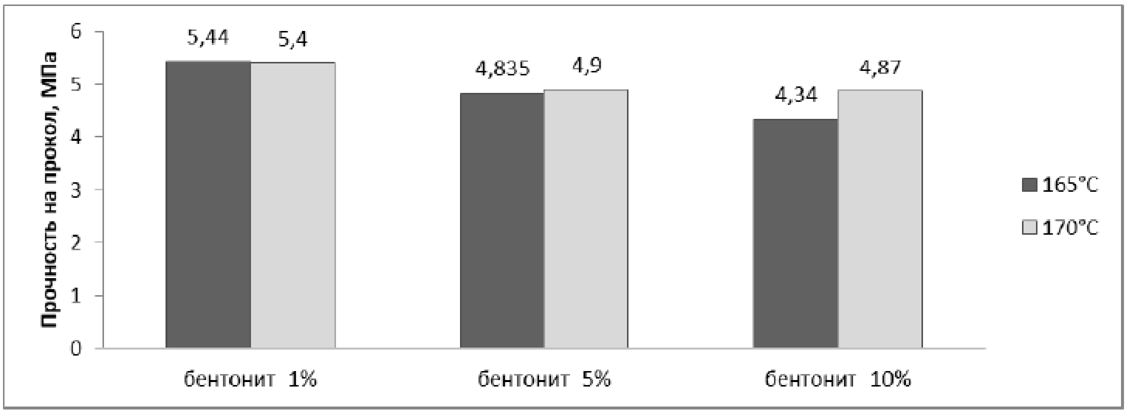


Figure 3.5 - Dependence of the strength of polymer PVC-filled bentonite films at various molding temperatures: 1 - 165 ° C; 2 - 170 ° C

Figure 3.6 - A sample of a film made on the basis of PVC with bentonite, at a temperature of 170 ° C

To obtain a high-quality polymer film, the introduction of fillers took place, in all cases, not during rolling (as standard technology provides), but at the preliminary mixing stage. The components of the composition, as well as the filler used, in the required mass ratio, were intensively mixed on paddle mixer at a speed of 4000 rpm for 4 minutes. The introduction of an additional stage gives a more uniform polymer material with improved performance.

For a comparative assessment of the influence of the composition, as well as the reduction in the cost of the process, natural bentonite from Aszkomar bentonite, Navoi, was used as a filler. In this case, during the mixing process, a rather inhomogeneous material was obtained, which can be seen from micrographs of polymer films obtained by filling with bentonite at a concentration of 1 wt.%, Manufactured by various companies, shown in Figure 3.7. Natural bentonite has a high dispersion and phase heterogeneity, which affects the quality of polymer films obtained on their basis.

The use of pectin as a filler, as well as bentonite and starch, in the General case, reduces the strength characteristics of polymeric PVC films, compared with unfilled materials. However, a general decrease in the strength of composite films leaves their operational characteristics acceptable for use as packaging.

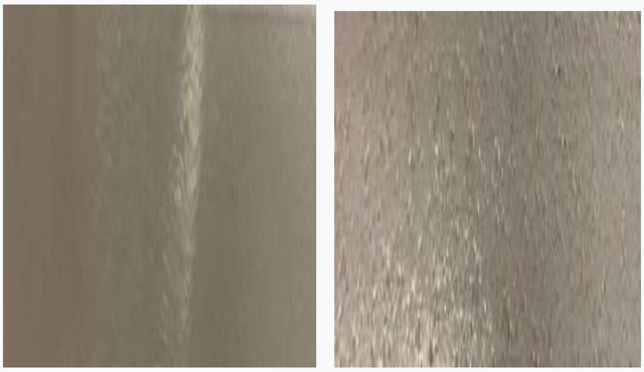


Figure 3.7 - Microphotographs of polymeric films based on PVC with bentonite filler: a –Navbahor’s bentonite; b - natural, Aszkomar bentonite

As when filling polymer films with an inorganic filler, when modifying polyvinyl chloride samples with pectin, an increase in the puncture strength of polymer composite materials is observed with an increase in rolling times of 0.5 - 1.5

times, which is associated with mechanochemical and structural changes in the material, see Figure 3.8.

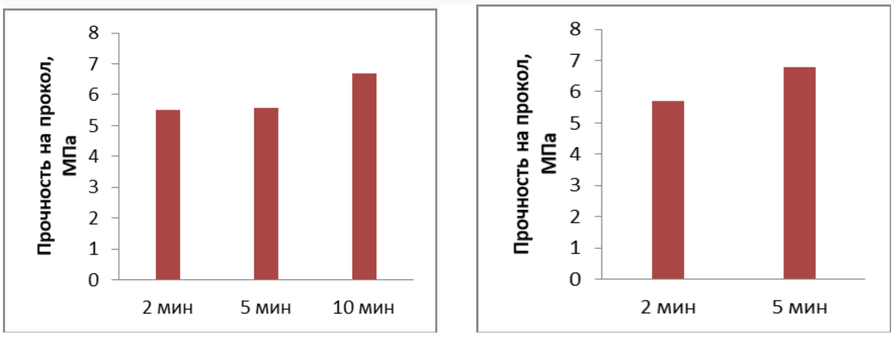


Figure 3.8 - The effect of rolling time on the puncture strength of polymer composite films based on PVC filled with pectin, wt.%: A) 5; b) 10

However, for the polymer composition PVC-pectin with a concentration of 5 wt.%, Destruction of the material was observed when processing on rollers for more than 6 minutes, and when filled with pectin 10 wt.%, Destruction was observed within 4 minutes of the process.

The dependences of the puncture strength of PVC films filled with pectin are described by the following exponential equations:

- for a pectin concentration of 5 wt.%: $\Sigma = 4.8e0.1\tau$;
- for pectin concentration of 10 wt.%: $\Sigma = 4.8e0.2\tau$;

where σ is the puncture strength, MPa; τ - rolling time, min.

The appearance of polymeric PVC films filled with pectin is shown in Figure 3.9.

a b c

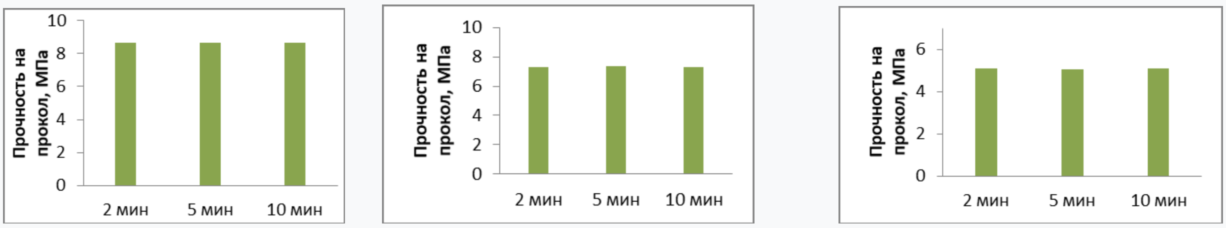
Figure 3.9 - Finished samples of films made on the basis of PVC and pectin with a mass concentration of 5% at different rolling times, min: a) 2; b) 5; at 10

A change in the color of PVC-filled pectin films is expected, and depends not only on the properties of the filler used, color, nature, etc., but also on the processing process. The high yellowness of pectin film samples, see Figure 3.9, can be caused in addition to the Maillard reaction, dehydration processes, chain breaks or the formation of dicarbonyl compounds and hydroxymethyl furfural at the initial stage of the destruction of composites.

An increase in the rolling temperature to 170 ° C during the manufacturing of PVC films filled with pectin, unlike composite films filled with bentonite, leads to degradation of pectin during rolling, which makes it impossible to obtain a polymer film (see Figure 3.10).

Figure 3.10 - Photographs of a film sample made on the basis of PVC and pectin at a temperature of 170 ° C

The use of starch films as a PVC filler leads to a more insignificant decrease in the strength characteristics of the obtained composite material compared to unfilled PVC films, as well as to an insignificant dependence of the physico mechanical parameters on the rolling time (see Figure 3.11).



a b c

Figure 3.11 - The effect of rolling time on the puncture strength of polymer composite films based on PVC filled with starch, wt.%: A) 1; b) 5; c) 10

Figure 3.12 shows photographs of finished PVC films modified with starch with a filling of 5 wt.% And obtained at different rolling tim

a b c

Figure 3.12 - Samples of films made on the basis of PVC and 5 wt.% Starch obtained at different rolling times, min: a) 2; b) 5; c) 10

The dependences of the puncture strength of PVC films filled with starch are described by the following exponential equations:

- for a starch concentration of 1 wt.%: $\Sigma = 8.7e\text{-}0.01\tau$
- for a starch concentration of 5 wt.%: $\Sigma = 7.3e0.001\tau$;
- for starch concentration of 10 wt.%: $\Sigma = 4{,}5e0{,}001\tau$;

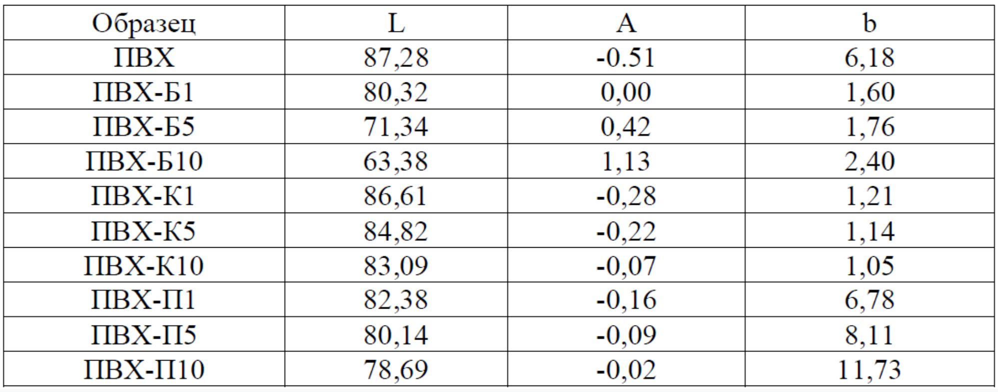
where σ is the puncture strength, MPa; τ - rolling time, min.

3.2. STUDY OF COLOR AND OPTICAL CHARACTERISTICS OF FILLED PVC FILMS

The properties and application of finished materials based on PVC largely depend on the method of their preparation. In the course of the work, the color characteristics of polymeric PVC films filled with bentonite, starch and pectin of various concentrations were determined. The results are presented in table 3.1.

L represents the coordinate of lightness, varies from darkest to lightest, and accordingly, varies within 0 ÷ 100, a and b are the chromatic components described by Cartesian coordinates; a - indicates the position of the color in the range from green to red, b - from blue to yellow.

Table 3.1 - Color characteristics of polymer filled films based on PVC



Образец	L	A	b
ПВХ	87,28	-0.51	6,18
ПВХ-Б1	80,32	0,00	1,60
ПВХ-Б5	71,34	0,42	1,76
ПВХ-Б10	63,38	1,13	2,40
ПВХ-К1	86,61	-0,28	1,21
ПВХ-К5	84,82	-0,22	1,14
ПВХ-К10	83,09	-0,07	1,05
ПВХ-П1	82,38	-0,16	6,78
ПВХ-П5	80,14	-0,09	8,11
ПВХ-П10	78,69	-0,02	11,73

The introduction of fillers, in the General case, slightly reduces the luminosity of the PVC filled films and significantly affects the color gamut of the obtained polymer PVC samples. Films with pectin are more yellow in color, and a material containing 1 wt.% Pectin is most similar in value to b to unfilled PVC films. Thus, depending on the type and amount of filler, it is possible to obtain polymer composite films of various colors.

It is well known that irregularities on the surface of a material arise, first of all, due to the resulting deformations of the upper film layer during processing. In the general case, the surfaces of the obtained polymeric vinyl chloride-filled films filled with bentonite, pectin and starch have a small roughness, which increases on average by 1.5–3 times with an increase in the proportion of filler in the composite. When comparing the results presented in Figures 3.13, 3.14 and Table 3.2, it is seen that the introduction of organic fillers leads to a material with a greater surface roughness than when using bentonite from Navbahor Bentonite as a filler.

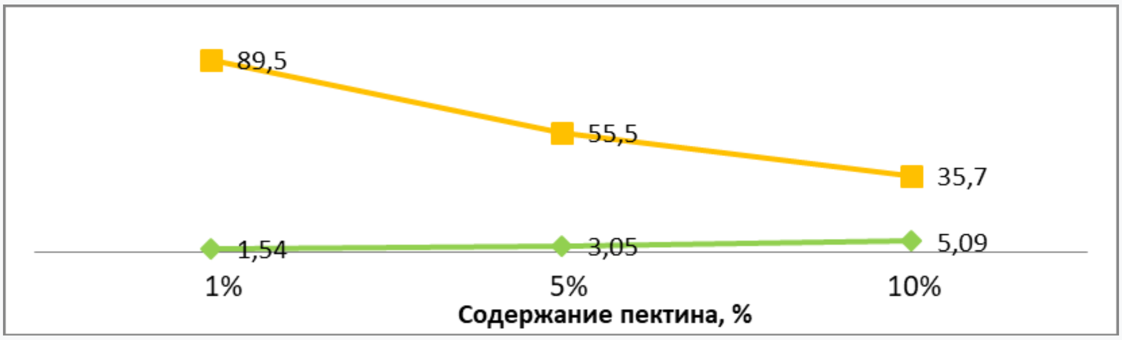


Figure 3.13 - The dependence of the optical characteristics and surface properties of PVC composites on the percentage of pectin: a - gloss, b - roughness

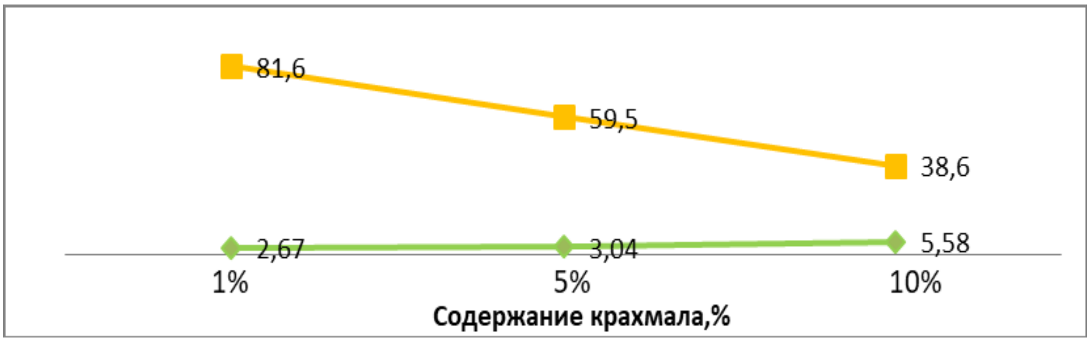
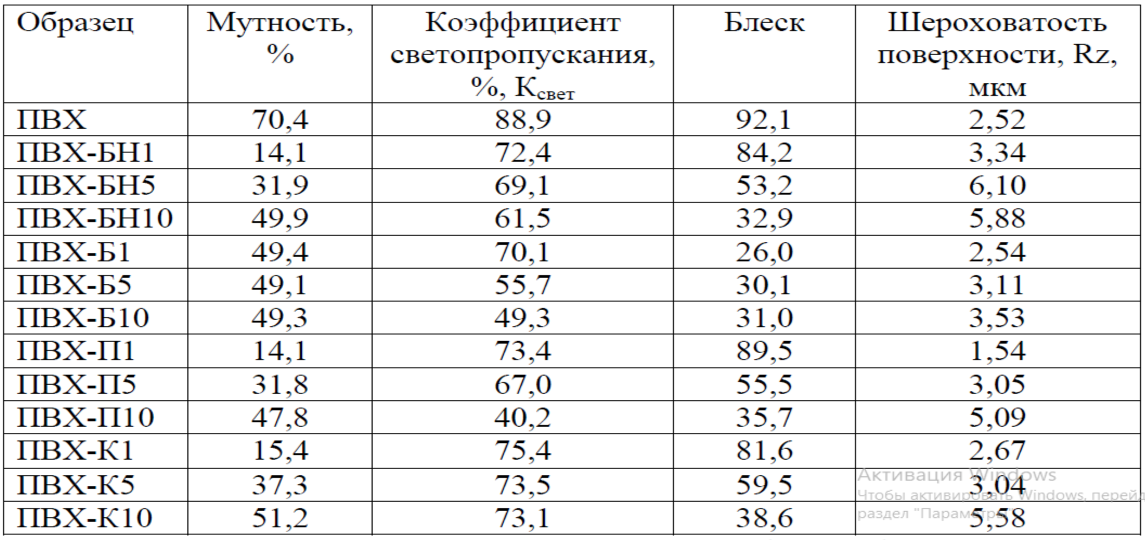


Figure 3.14 - The dependence of the optical characteristics and surface properties of PVC composites on the percentage of starch: a - gloss, b – roughness

In this connection, we can say that bentonite particles have a low tendency to migrate to the surface of polymer films, which is also confirmed by the data on the brightness of the samples under study (see Table 3.2). Samples of PVC films filled with natural bentonite have the highest roughness.

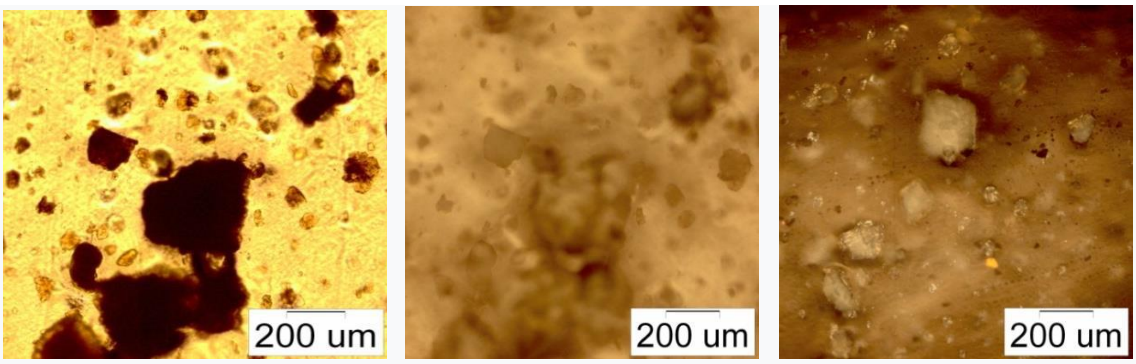
Table 3.2 - Characteristics of polymer filled films based on PVC



Образец	Мутность, %	Коэффициент светопропускания, %, $K_{свет}$	Блеск	Шероховатость поверхности, Rz, мкм
ПВХ	70,4	88,9	92,1	2,52
ПВХ-БН1	14,1	72,4	84,2	3,34
ПВХ-БН5	31,9	69,1	53,2	6,10
ПВХ-БН10	49,9	61,5	32,9	5,88
ПВХ-Б1	49,4	70,1	26,0	2,54
ПВХ-Б5	49,1	55,7	30,1	3,11
ПВХ-Б10	49,3	49,3	31,0	3,53
ПВХ-П1	14,1	73,4	89,5	1,54
ПВХ-П5	31,8	67,0	55,5	3,05
ПВХ-П10	47,8	40,2	35,7	5,09
ПВХ-К1	15,4	75,4	81,6	2,67
ПВХ-К5	37,3	73,5	59,5	3,04
ПВХ-К10	51,2	73,1	38,6	5,58

Figures 3.15 and 3.16 show microphotographs of PVC films without filler and with bentonite concentration of 5 wt.%, Obtained in various modes.

Figure 3.15 - Photo of a PVC film without filling



a b c

Figure 3.16 - Photographs of the surface of PVC films with bentonite concentration of 5 wt.%, Obtained on: a) clearance; b) reflection; c) reflection with a polarizer

As can be seen from the microphotographs when natural bentonite is introduced into the PVC, the formation of agglomerates with sizes from 30 to 230 microns is observed, which leads to a less uniform and more rough surface of the polymer films. Such PVC-filled films scatter light strongly. That is why the inorganic filler bentonite used can be used as an anti-blocking agent when creating a PVC composite, giving less adhesion of the films to each other.

As can be seen from figures 3.13, 3.14 and table. 3.2 the gloss of polyvinyl chloride films filled with starch and pectin is reduced by an average of 1.5 - 2 times. It should be noted that for PVC films filled with Sigma Aldrich bentonite, the introduction of bentonite increases the brightness value, but at the same time, these values are minimal, of all the studied composites, and vary within 26 ÷ 31.

In the above figures (3.13 and 3.14), the dependences of the roughness and gloss of films filled with biopolymers are the same, which allows us to conclude that when creating biopolymer composite materials based on PVC and pectin or starch, the nature of the filler does not significantly affect the performance properties of the films.

One of the most important characteristics of the packaging material is transparency. Manufacturers of containers are trying to make polymeric material almost invisible so that the consumer can see the “product face”. For this, the polymer films used as packaging should have minimum roughness, turbidity and maximum light transmission. Therefore, these values play a decisive role in determining the operational characteristics of polymeric PVC films proposed for use as packaging.

The dependence of the light transmission coefficient is expected to decrease with increasing filler concentration, see Figures 3.17 and 3.18. The lowest transmittance is possessed by samples with the addition of bentonite

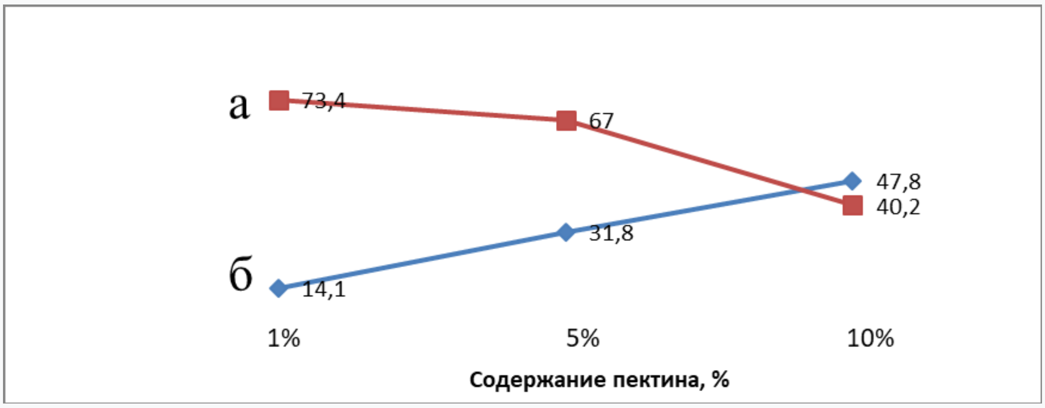


Figure 3.17 - The dependence of the optical characteristics of the surface of biodegradable PVC composites on the percentage of pectin: a - turbidity, b – transmittance

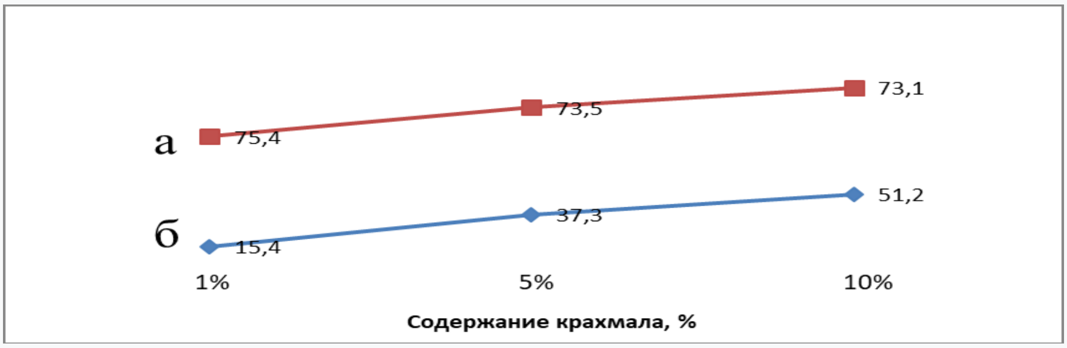
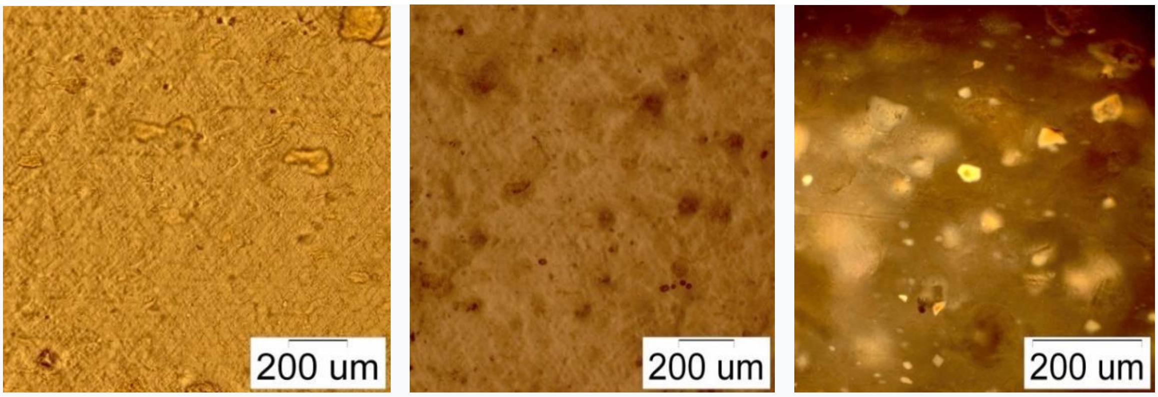


Figure 3.18 - The dependence of the optical characteristics of the surface of biodegradable PVC composites on the percentage of starch: a - turbidity, b - transmittance

The turbidity of the studied PVC films is caused, first of all, by the scattering of light by the structures inside the film itself or by the roughness of its surface.

Photos of the surface of PVC films with pectin at a concentration of 1 wt.%, See Figure 3.19, demonstrate the preparation of the most homogeneous material, while only the boundaries of transparent agglomerates are visible in the light, which is also confirmed by the good optical characteristics of the sample (see Table 3.2).



a b c

Figure 3.19 - Photos of the surface of PVC films with pectin concentration of 1 wt.%, Obtained on: a) clearance; b) reflection; c) reflection with a polarizer

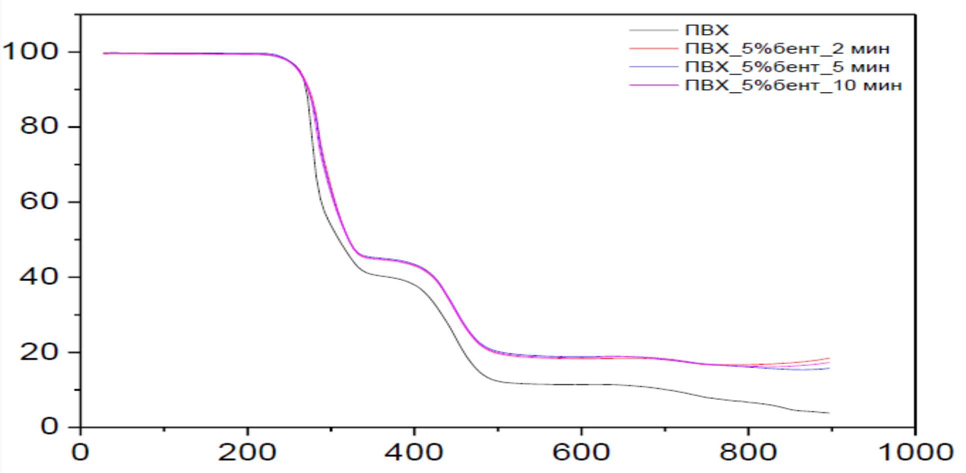
Thus, the introduction of fillers leads to a decrease in the turbidity of the polymer material, while an increase in the proportion of filler, in the General case, leads to a decrease in the turbidity of PVC-filled films by an average of 1.5 to 3 times. The degree of turbidity of the films obtained from solutions of mixtures of various polymers can also serve as a measure of the compatibility of polymers. In our case, the use of starch and pectin as fillers in a concentration of 1 wt.% Leads to a more compatible structure.

3.3. CHANGE OF THERMAL PARAMETERS OF POLYMER FILMS BASED ON PVC, DEPENDING ON TECHNOLOGICAL PARAMETERS

The study of thermograms allows not only to determine the temperatures of the beginning and stages of polymer degradation, but also makes it possible to calculate their kinetic parameters — the reaction order and activation energy. In the course of the work, the laws governing the occurrence of thermo-oxidative degradation of PVC composite films and the influence of rolling conditions on the thermal characteristics of materials were studied. One of the most important parameters, talking about the thermal stability of the studied PVC samples, is the value of the effective activation energy of thermal decomposition (Eact).

For a better understanding of the laws governing the occurrence of thermo-oxidative degradation, the first and last stages of degradation of PVC films filled with bentonite, starch and pectin were studied depending on the rolling time of the material and the proportion of the filler of the polymer material.

Figures 3.20, 3.21, as well as Figures A.1-A.4 of Appendix A show thermograms of PVC films filled with bentonite of various concentrations depending on the rolling time.



Temperature, °C

Figure 3.20 - Thermogravimetric curves of polymer composites on based on PVC and 5 wt.% bentonite at different rolling times

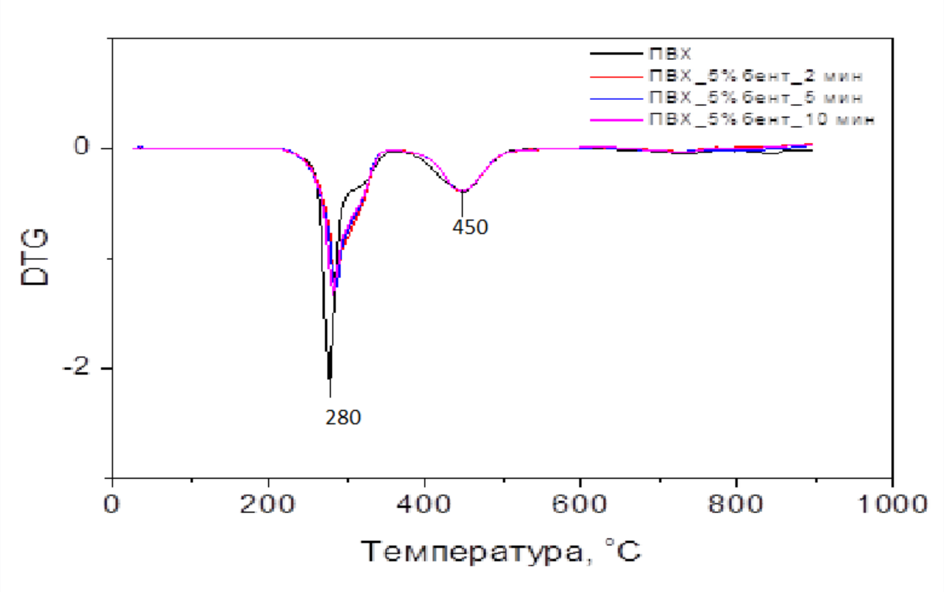


Figure 3.21 - DTG-curves of polymer composites based on PVC and 5 wt.% bentonite

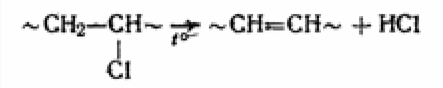
Kinetic parameters of the process of thermal degradation of composite PVC films with different filling ratios and rolling times for the I and II stages of the material resolution process, calculated by the Reich-Fuoss method are presented in table 3.3.

Table 3.3. - Kinetic characteristics of thermal degradation of PVC composites calculated by the Reich-Fuoss method

Образец	τ, мин	I стадия термической деструкции			II стадия термической деструкции		
		n	K	E, кДж/моль	N	K	E, кДж/моль
ПВХ	2	3,9	$5,83\cdot10^{-7}$	224,56	2,2	0,00291	214,25
ПВХ-Б5	2	4,1	$1,22\cdot10^{-7}$	176,30	4,5	$3,083\cdot10^{-7}$	239,16
	5	4,0	$1,93\cdot10^{-7}$	176,58	4,0	$2,00\cdot10^{-6}$	202,88
	10	4,3	$5,066\cdot10^{-8}$	184,80	4,3	$5,766\cdot10^{-7}$	224,69
ПВХ-Б10	2	3,8	$4,117\cdot10^{-7}$	174,80	5,2	$1,279\cdot10^{-8}$	222,19
	5	5,2	$7,286\cdot10^{-8}$	189,05	4,6	$1,426\cdot10^{-7}$	217,73
	10	3,3	$5,09810^{-6}$	182,08	5,4	$7,305\cdot10^{-9}$	226,77
ПВХ-Б15	2	4,7	$6,147\cdot10^{-9}$	202,83	6,2	$2,49\cdot10^{-10}$	224,42
	5	4,3	$6,476\cdot10^{-8}$	201,24	5,3	$8,363\cdot10^{-9}$	211,52
	10	4,1	$1,158\cdot10^{-7}$	173,03	3,4	$7,94210^{-6}$	160,00
ПВХ-П5	2	4,7	$1,205\cdot10^{-8}$	183,26	3,3	$3,124\cdot10^{-5}$	205,61
	5	4,3	$8,320\cdot10^{-8}$	184,65	3,4	$2,00110^{-6}$	202,88
ПВХ-П10	2	4,9	$5,081\cdot10^{-9}$	199,59	3,5	$1,674\cdot10^{-5}$	199,40
	5	5,0	$3,306\cdot10^{-9}$	187,44	4,6	$1,426\cdot10^{-7}$	217,73
ПВХ-П15	2	4,9	$5,043\cdot10^{-9}$	187,27	4,9	$5,043\cdot10^{-9}$	187,27
ПВХ-К1	2	3,4	$1,988\cdot10^{-9}$	147,47	2,0	$0,002\cdot10^{-9}$	153,80
ПВХ-К5	2	5,0	$2,527\cdot10^{-9}$	187,83	2,0	0,00391	177,61
ПВХ-К10	2	5,2	$8,958\cdot10^{-10}$	194,22	2,3	0,00124	178,76

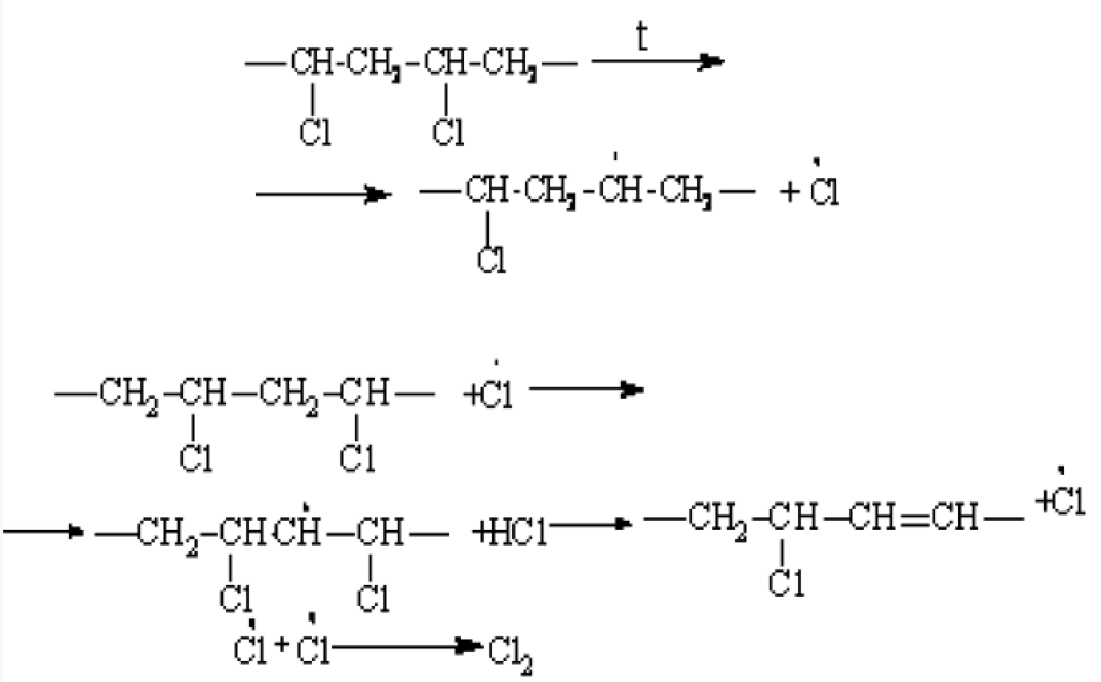
As can be seen from the results presented in table 3.3, the effective activation energy of thermal decomposition for unfilled PVC is higher than Eact for polymer composites based on it, and is 224.56 kJ / mol. Thus, the introduction of fillers helps to simplify the destruction of the material.

The predominant process of thermal degradation of PVC-based composites is dehydrochlorination, which proceeds by reaction:



$$\sim CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}\sim \xrightarrow[t^{\circ}]{} \sim CH{=}CH\sim + HCl$$

The reaction is radical:



It is noteworthy that the reaction order of the first stage of thermal degradation of the material, calculated by the Reich-Fuoss method, takes values within 3-5, which testify to the occurrence of several parallel processes.

In all cases, PVC films obtained with a rolling time of 2 minutes have a higher activation energy than for similar composites obtained with a longer time: 5 and 10 minutes. The activation energy of the degradation reaction for pectin-modified polyvinyl chloride composite films is 1.5-2.5 times lower in the first stage than the Eact value for unfilled PVC.

The thermomechanical behavior of samples of PVC films filled with bentonite with different rolling times is shown in Figure 3.22. It is important to note that as the rolling time increases, the shape of the TMA curves approaches the dependence characteristic of unfilled PVC samples. In this case, there is a narrowing of the temperature range at which the polymer composition is in a highly elastic state.

A rolling time of 2 minute results in a less uniform internal structure of the material compared to PVC composites obtained with a rolling time of 5 and 10 minutes. This is also evidenced by the strength characteristics of PVC composites obtained at different rolling times, as described previously.

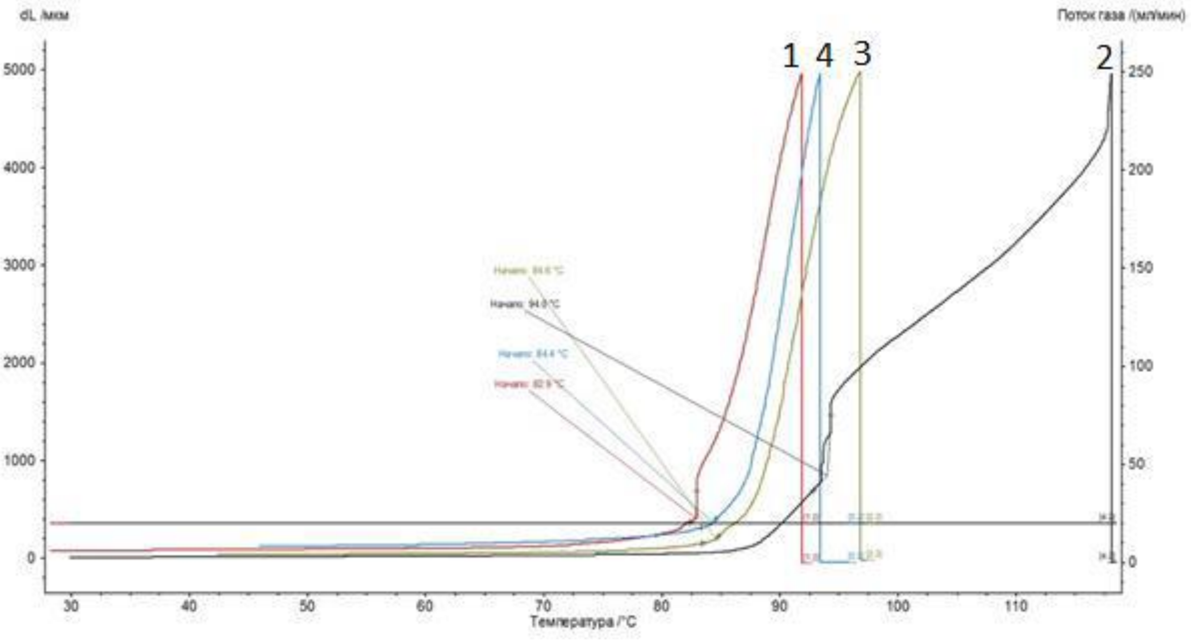
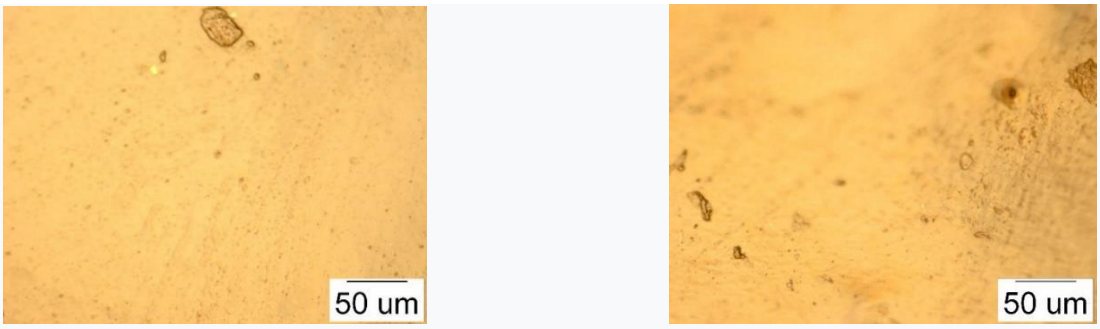


Figure 3.22 - Relative strain versus heating temperature for PVC films containing 5 wt.% Bentonite at different rolling times: 1 - PVC without filling, 2 - PVC-B5 rolling time 2 min, 3 - PVC-B5 rolling time 5 min, 4 - PVC-B5 rolling time 10 min

This can be explained by taking into account the wide range of interactions of the polyvinyl chloride matrix with filler particles - bentonite. Thus, the adsorption of polymer chains on the surface of the filler leads to their immobilization and a decrease in segmental mobility, which will require a greater thermal effect than for non-adsorbed molecules. Therefore, the higher the set of such polymer-filler interactions differing in energy, the devitrification of the polymer will occur in a larger temperature range. With on the other hand, an increase in the rolling time leads to hardening of the structure, which is primarily associated with crosslinking processes.

Figure 3.23 shows microphotographs of films based on PVC and bentonite with a concentration of 1 and 5 wt.% At a rolling time of 2 minutes. As can be seen from the photographs, the surface of the sample containing 1 wt.% Of the filler has a more defective surface, therefore, higher internal stresses.



a b

Figure 3.23 - Microphotographs of PVC composites at a rolling time of 2 minutes with a bentonite content, wt.%: A - 1; b - 5

As the homogeneity of the PVC composition increases with an increase in rolling time, the shape of the TMA curves becomes less complicated by additional kinks in the region of the highly elastic state or by jumps during the transition from glassy to highly elastic.

Figure 3.24 - Dependence of the glass transition temperature of PVC-based composites containing 5 wt.% Bentonite on the rolling time

Figure 3.24 shows the dependence of the glass transition temperature, Ts, PVC polymer films containing 5 wt.% Bentonite, on the rolling time. Samples of composite PVC prepared at a rolling time of more than 2 min are characterized by close glass transition temperatures to T of pure PVC, which suggests that the rolling time of 2 min is not enough to obtain a homogeneous composite structure, while any longer mixing time is sufficient.

CONCLUSIONS

1.The prevalence of the use of PVC and its derivatives gives the prospect of creating degradable materials to reduce the environmental burden on the environment. The use of biopolymers as well as mineral fillers is relevant as fillers for polyvinyl chloride films.

2. The development and study of PVC structures with fillers that do not change their operational properties and at the same time decompose in the soil are a promising area in science and production.

3. The use of pectin as a filler, as well as bentonite and starch, in general, reduces the strength characteristics of polymeric PVC films, as compared to unfilled materials. However, a general decrease in the strength of composite films leaves their operational characteristics acceptable for use as packaging.

4. Thus, the introduction of fillers leads to a decrease in the turbidity of the polymer material, while increasing the proportion of filler, in the General case, leads to a decrease in the turbidity of the PVC-filled films by an average of 1.5 to 3 times. The degree of turbidity of the films obtained from solutions of mixtures of various polymers can also serve as a measure of the compatibility of polymers.

5. Samples of composite PVC prepared at a rolling time of more than 2min are characterized by close glass transition temperatures to Ts of pure PVC, which suggests that the rolling time of 2min is not enough to obtain a homogeneous composite structure, while any longer mixing time is sufficient.

6. A rolling time of 2 minute results in a less uniform internal structure of the material compared to PVC composites obtained with a rolling time of 5 and 10 minutes. This is also evidenced by the strength characteristics of PVC composites obtained at different rolling times described in this paper.

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