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Development of a technology for processing waste plastic bottles and bags to obtain various types of biodegradable polymer films

Abstract. Currently, one of the most important problems in the world is waste bottles made of polyethylene terephthalate, the number of which is currently growing every hour, polluting the environment. One of the ways to protect the environment from polyethylene terephthalate waste is the invention of biodegradable polymer materials from PET waste. Currently, several methods for processing polyethylene terephthalate waste have been proposed, but the work on the production of biodegradable materials has not been fully solved. Currently, various technologies for recycling plastic bottles and bags are being developed. The most promising technology in this direction is chemical processing, which is based on obtaining the final product in the form of a monomer or oligomer, which can be used as a new raw material for the synthesis of polymers. In this work, these polyethylene terephthalate wastes were chemically degraded with ethylene glycol solvent in the presence of zinc acetate catalyst and bis-hydroxy ethylene terephthalate was obtained. This work aims to obtain bis-2-hydroxyethyl terephthalate (BHET) by glycolysis of polyethylene terephthalate (PET) waste for the synthesis of various types of biodegradable polymer films. Biodegradable films based on polyvinyl alcohol and BHET have been synthesized. Water-soluble copolymers based on BHET and PVA were obtained by grafted copolymerization. (PVA) polyvinyl alcohol (5; 15; 25 wt. %) was dissolved in distilled water at 75-80°C until complete dissolution, ammonium persulfate, used as an initiator, was added to the initial mixture and biodegradable films based on PVA and BHET were obtained for the first time. It has also been proved that the resulting biodegradable films are formed by hydrogen bonds using IR spectroscopy.

Key words: PET, depolymerization, recycling, biodegradable films, BHET.

Introduction

In recent years, intensive work has been carried out to obtain biodegradable polymer materials that do not harm the environment and the human body. The problem of environmental protection is global, so the increase in the amount of synthetic plastic waste hourly raises serious concerns. The most suitable way to solve these problems is to create environmentally friendly biodegradable polymer materials. Currently, many methods have been proposed for the development of biodegradable polymer materials, but the production of biodegradable polymers has not been completely solved [1-5]. Recycling of used plastic materials is the main problem of polymer production, mainly due to the harmful effects of plastic waste on the environment. Plastic materials are stored for a long time under normal conditions due to their high resistance to environmental influences. We can consider the recycling of plastic materials as an important economic factor, since the material and energy are reused. This will reduce the cost of raw materials, reduce the use of the necessary energy source, and bring economic benefits. In the global world, various types of recycling are offered [5-12].

Currently, mechanical and chemical methods of recycling are used. In addition, during chemical processing, monomers are removed, and then new polymer raw materials, chemicals and fuel are obtained. Methods of incineration and disposal of waste polymer materials have lost their importance, as new directions of methods of processing polymer materials are being introduced. Currently, strategies for the processing of biodegradable polymers and the secondary use of polymer materials are being considered [13-16].

The following incentives are necessary for the implementation of secondary use: legal requirements, low price, consumer demand, environmental aspect. Recycling of polyethylene terephthalate waste in the global world has received rapid development and is just beginning in Kazakhstan.

Materials and methods

Development of a technology for processing waste plastic bottles and bags to obtain various types of biodegradable polymer films. Obtaining bis-2-hydroxy ethylene terephthalate by glycolysis of polyethylene terephthalate waste from plastic bottles. Currently, different technologies are developed for the recycling of waste plastic bottles and bags. The most promising technology in this direction is chemical processing, which is based on obtaining the final product in the form of a monomer or oligomer, which can be used as a new raw material for the synthesis of polymers.

The aim of this work is to obtain bis-2-hydroxy ethylene terephthalate (BHET) by glycolysis of polyethylene terephthalate waste (PET) for the synthesis of various types of biodegradable polymer films. After the mechanical rinsing with acetone and methanol, removing glue and other substances, the beverage bottles produced by Bonaqua™ were crushed into small pieces.

Depolymerization of PET waste was carried out in a three-necked flask equipped with a thermometer, a refrigerator, and a mechanical stirrer, in the temperature range 140 ÷ 190°C at a mass ratio of ethylene glycol to PET equal to 1:1, in the presence of a catalyst – zinc acetate (0.5% by weight PET), is the most effective catalyst for PET glycolysis. The degree of PET degradation (or conversion) was determined gravimetrically. For this, samples were taken at regular intervals, weighed with an accuracy of 0.0002 g, and calculations were performed. The reaction was carried out until the complete glycolysis of PET, after which distilled, water was added to the resulting destructive at a ratio of 1:100. For the complete precipitation of BHET, the contents of the flask were kept for at least 24 hours. The formed precipitate was filtered off, after which the filtrate containing water was concentrated by evaporation of water at a temperature of 80-90°C, and then cooled in a refrigerator at a temperature of 3-5°C. The filtration residue was dried in a vacuum oven to constant weight. The output of BHET is 77%.

Figure 1 presents data on the study ща the effect of temperature on the conversion of PET in the presence of zinc acetate. The results showed that as the temperature rises from 140 to 190°C, there is a regular increase in PET conversion. Thus, the complete glycolysis of PET at 140ºC takes 2 times longer than at 160°C and 3 times longer than at 190°C.

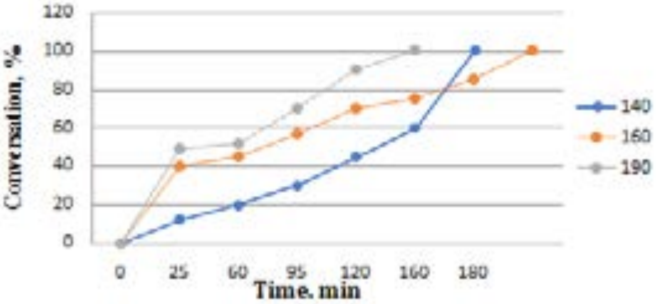

Figure 1 – Effect of temperature on PET conversion
in the presence of zinc acetate as catalyst

The synthesis of biodegradable films is based on copolymers of polyvinyl alcohol and bis-2-hydroxyethyl terephthalate

Synthesized biodegradable films based on polyvinyl alcohol and BHET. Water-soluble copolymers based on BHET and PVA (FlukaChemie GmbH (Switzerland), Mw = 145000 kDa) were prepared by the graft copolymerization method. PVA (5 wt. %) was dissolved in distilled water at 75-80°C, till complete dissolution, ammonium persulfate, used as an initiator, was added to the initial mixture. A 15% aqueous solution of BHET was added through a dropping funnel at a rate of 20 drops/min. To adjust the pH of the reaction mixture (the optimum pH of the reaction medium is 3.8), a certain amount of glacial acetic acid was added to the reactor, the reaction mixture was heated for 2 hours at 75°C. At the end of the process, the reaction mixture was cooled to room temperature. In this case, a white homogeneous mass is obtained.

Results and discussion

The obtained PET Glycolyzed production is the form of a white crystalline powder with a melting point of 108°C. To confirm the structure of the obtained product, IR spectroscopy was investigated (Fig. 2).

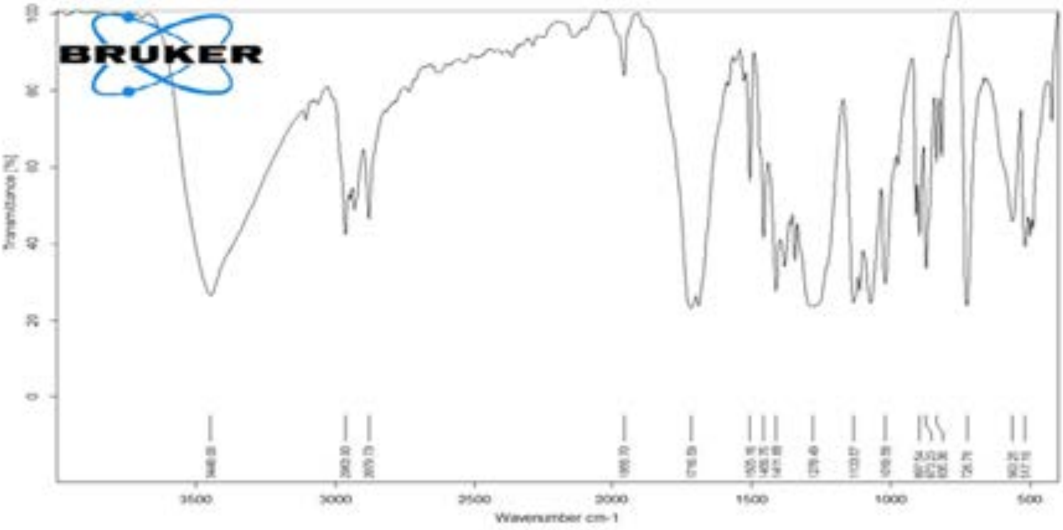

Figure 2 – IR spectrum of bis-2-hydroxyethyl terephthalate.

Thus, by the glycolyzed PET waste, bis-2-hydroxyethyl terephthalate was obtained for the synthesis of various types of biodegradable polymer films. Figure 2 shows the IR spectrum of the BHET of the pure product obtained. If we compare the spectra of the obtained copolymer and BHET, it turns out that the monomers are obtained in pure form and do not have chemical bonds. Benzene rings are located in the spectrum of the BHET, demonstrating the absorption of 1716-1677cm^{-1} and 726-875cm^{-1}, and 1133cm^{-1} C-O-C bonds were also observed. Two vertices connected in the spectrum at 3447cm^{-1} and 2931cm^{-1} showed us the existence of hydroxyl groups, i.e., they manifested themselves acutely, which tells us about the elongation of the O-H groups in the composition of the CH$_2$-CH$_2$-OH bonds and can serve as a basis for the fact that we have obtained a pure monomer.

To confirm the interaction reaction between PVA and BHET, IR spectra analysis was studied. As shown in Figure 3, the obtained films based on PVA and BHET showed an absorption band at about 3265.13 cm^{-1}, attributed to OH groups. The band at 1712 cm^{-1} characteristic of the carbonyl group (C = O) is related to the presence of residual acetate groups in the copolymer, which remained after the preparation of PVA by hydrolysis of polyvinyl acetate. The absorption bands at 1126 and 1066 cm^{-1} are due to stretching vibrations of the C – O, C – O – C groups, and the band at 724 cm $^{-1}$ refers to the C – H$_2$ groups. In addition, at 1712 cm^{-1}, an absorption peak characteristic of the carbonyl group of acetic acid is observed, and at 568 and 670 cm^{-1}, a band of vibrations of C-H groups characteristic of aliphatic compounds appears.

Polymer films of the obtained copolymers were prepared by pouring a 4% aqueous solution of copolymers into polyethylene Petri dishes, followed by evaporation of the solvent at room temperature and keeping in a vacuum drying oven at 30°C until constant weight. Photographs of the obtained films based on PVA and BHET copolymers are shown in Figure 4. It can be seen that films based on PVA and BHET interpolymers are equally homogeneous and elastic.

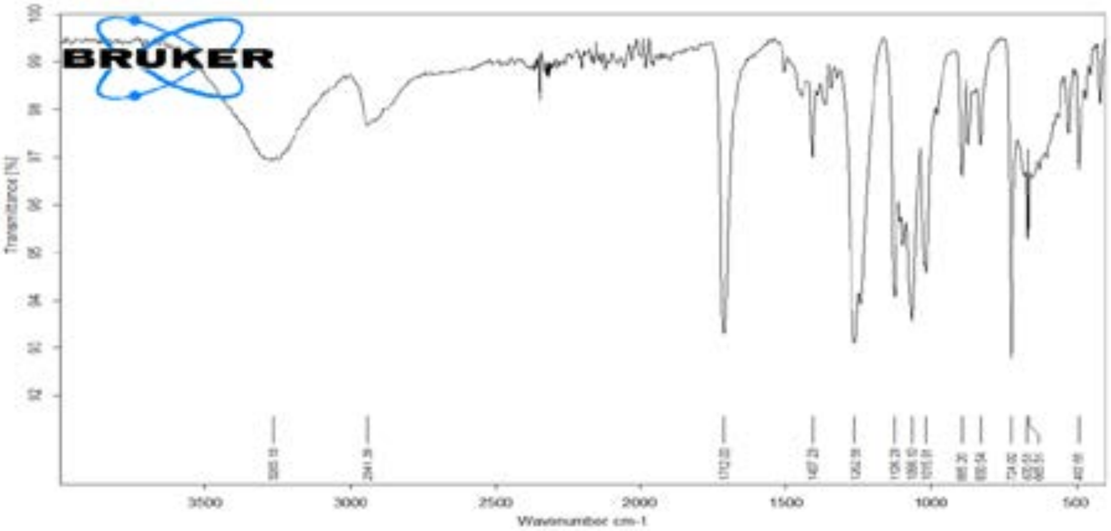

Figure 3 – IR spectra of P(PVA-co-BHET)

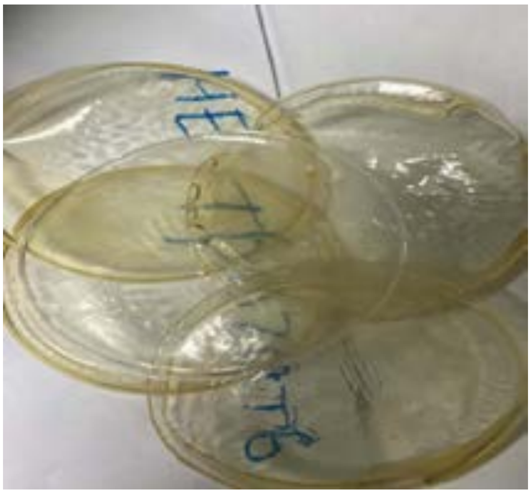

Figure 4 – Photographs of films based on P(PVA-co-BHET)

Development of a technological scheme for the processing of waste plastic bottles and bags

Completed work:

- A technological scheme for the processing of waste plastic bottles and bags has been developed.

These studies, showed the fundamental possibility of obtaining secondary BHET by glycolysispolyethylene terephthalate from waste, and indicate the advantage of the ethylene glycol solventless over water.

The optimal conditions for the PET destruction process are:

- temperature – 190°C;
- the mass ratio of ethylene glycol and PET, equal to 1: 1;
- catalyst – zinc acetate (0.5% to the weight of PET).

Based the laboratory results, a technology for producing BHET from secondary PET was proposed. This technology includes several stages (Figure 5):

- in the reactor at a temperature of 180-190°C and a pressure of 1 MPa for 1 h, PET is mixed with ethylene glycol in the presence of zinc acetate as a catalyst;
- separation of unreacted PET from the solution;
- separation of BHET from ethylene glycol and water is carried out by filtration in a drum vacuum filter;
- separation of a mixture of ethylene glycol with water is carried out in a column separation at a temperature of 200°C, where part of the ethylene glycol is returned to the first stage of processing to soften PET.

Shredded polyethylene terephthalate is fed into the reactor (R-1) from the vessel (B-1), zinc acetate is pumped from the tank (E-2) by the pump (N-3), and recycled ethylene glycol at the temperature of 206°C is also pumped into the reactor. In the reactor (R-1), the process of glycolysis polyethylene terephthalate occurs at a temperature of 190°C.

To maintain the temperature of the process, due to the exothermicity of the target reaction, the reactor (R-1) is equipped with a jacket, into which water vapor is supplied with a pressure of 2.4 MPa.

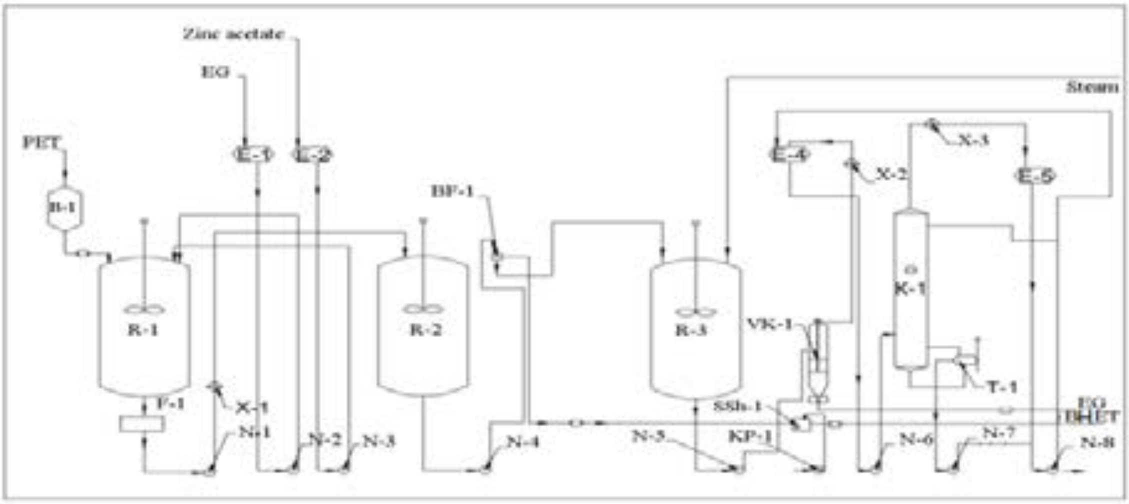

Figure 5 – Flow diagram of the process of obtaining BHET from glycolysis polyethylene terephthalate.
Note: B-1 – storage hopper; BF-1 – drum filter; VK-1 – evaporator-crystallizer; E-1, 2, 3, 4, 5 – containers; K-1 – rectification column; KP-1, 2 – compressors; N-1, 2, 3, 4, 5, 6, 7, 8 – pumps; R-1, 2, 3 – reactors; SSh-1 – drying apparatus; T-1 – heat exchanger; X-1, 2, 3 – condenser refrigerator; F – filter

From the reactor (R-1), the mixture is fed to the filter (F-1), where the unreacted PET is separated from the solution. The solution after F-1 is cooled in a refrigerator X-2 to a temperature of 2-3°C and transferred to receive BHET in the reactor (R-2), in which BHET is released at a temperature not exceeding 60°C and pressure at 101.3 kPa.

The mixture of reaction products from the reactor (R-2) is pumped out by using the pump (N-4) into the vacuum drum filter (BF-1), where the BHET is separated from the liquid part of the mixture. A mixture of water and ethylene glycol is fed to the R-3 reactor. Then BHET goes for drying to the dryer (SSh-1), where the air is supplied by the compressor (KP-1). The dried BHET is removed from the plant as a finished product.

From the R-3 reactor, the resulting mixture of water and ethylene glycol is fed to the VK-1 crystallizer through the H-5 pump and cooled in the x-3 refrigerator, and the mixture is fed to the K-1 Steam column through the H-6 pump. Water vapor is removed from the top of the column, which condenses in the (X-2) refrigerator. Water condensate enters the (E-4) tank, from which the (H-8) pump is pumped to the sewage system. From the bottom of the (K-1) column, the (N-7) pump pumps out ethylene glycol, part of which is heated in the (T-1) heat exchanger with water vapor, returns to the K-1 column cube as irrigation, and the other part enters the(R-1) reactor. The balance amount of EG is removed from the installation.

Process flow diagram of the production process of biodegradable polymer films based on PVA and BHET

To obtain polymer films based on CPL PVA-BHET, the method of casting films from solutions on a substrate ("dry" method) was used. This method is economic and technological advantages, firstly, the "dry" method is more industrially applicable due to the prostate equipment and low cost, and secondly, it allows you to obtain films with high-performance characteristics.

The basic and principle of this method is to form a viscous polymer solution. The mixture is thoroughly mixed, the excess air is removed under a vacuum. A film is formed from the resulting solution, dried and then cut to the required size.

The production of film materials consists of two technological lines for the production of water-soluble and grafted films. The main stages of the technological process of forming water-soluble films:

– Dissolution of copolymers;

– Preparation of copolymer solutions (solution filtration);

– Deaeration of the molding solution;

– Forming a film on the surface of the dryer belt;

– Film stretching and drying;

– Reception, winding and cutting of finished film;

– Stamping, packaging, and marking of finished products.

In the production of grafted films, the stages of thermal grafting and saturation of films with drugs are additionally included.

For the pilot production of new water-soluble films based on CPL of polyvinyl alcohol and BHET, a technological scheme has been developed, shown in Figures 6 and 7.

From the measuring tank – dispenser (MD-1), the pure polyvinyl alcohol dissolves in distilled water in the mixer (C-1) with a corrosion-resistant inner coating, equipped with a frame mixer. As a solvent, CPL PVA and BHET uses water, which is obtained from a metering meter (MD-2). The loading of the CPL PVA and BHET into the mixing apparatus is carried out with the mixer operating. First, using a pump N-1, water is supplied in an amount of 10-20% of the total volume of the solvent and CPL PVA-BHET is loaded in small portions through the hopper, then after a short stirring, half of the water is introduced through the dispenser. After swelling of the CPL PVA and BHET, the remaining amount of solvent water is fed into the mixer. The dissolution process lasts 12 – 24 hours with constant stirring at a temperature of 65-70°C. The prepared solution of CPL PVA and BHET is fed by a gear pump (N-2) under a pressure of several atmospheres to multistage filter presses (PF-1) to remove undissolved particles of CPL PVA and BHET.

In the filtration process of the solution, an increase in pressure is observed due to the clogging of filters. When the critical pressures are reached, the flow is switched to a backup filter press, and the clogged one is washed with water and then blown with compressed air.

To produce a water-soluble film, the filtered PVA and BHET solution was transferred to the mixer (C-1) and (C-2) to obtain a homogeneous molding solution. After prolonged mixing, a plasticizer is added to obtain homogeneous solution. The duration of the preparation of the film-forming solution at a stirrer speed of 40 – 60 rpm is 2 hours.

The mixing process of solutions can inadvertently introduce air bubbles into the liquid, therefore deaeration is a prerequisite for obtaining a homogeneous polymer solution. The film-forming solution is evacuated in a deaerator (D-1) and (D-2) for 4-6 hours and fed into the storage tank (E-1) and (E-2).

From the container (E-1), the copolymer solution is fed into the container of the smearing die (MF-1), from which it is applied to the surface of the moving continuous belt of the casting machine (FM-1). The forming speed is 1-5 m/min. The optimal drying mode was experimentally established at 28-30°C. The drying process takes 24 hours.

In the casting machine, the film is dried to a residual solvent content of 15 – 20%, after which the film is removed from the substrate with a knife and enters the drying chamber (KD-1), where, passing through a system of rollers, it is pulled out for hardening and finally dried with heated air.

After that, the film transfers to the cutting unit (PM-1). It passes through a shaft equipped with a trimming device, after which it enters the winding machine, where it is cut along the web into 6 × 3 plates, first packed in plastic bags then into paper boxes, marked and sent to the finished product warehouse. Waste is recycled.

The formation of a polymer solution to obtain grafted films is carried out in a mixer (C-2). At the beginning, the filtered copolymer solution enters the mixer, and then the dissolved grafting agent and plasticizer are introduced. The duration of the solution formation at a stirrer speed of 40-60 rpm is 2 hours.

The molding solution is transferred to the deaerator (D-1), where it is processed for several hours, and then under pressure is fed into the container of the smearing die. The die ensures the formation of a layer of polymer solution of a given thickness and distributes it evenly over the entire width of the ground surface of the metal substrate strip stretched over the surface of the casting machine.

The solution layer is dried to a residual solvent content of up to 15-20%, the film is separated from the substrate surface and through a tear-off roller and a compensator is directed into a heat chamber (T-1) formed by several electric heating plates located in a horizontal plane. The film, passing through the rollers of the speed control system, is captured at the edges by using clamping clips and transported through the chamber using Gall roller chains. The speed of the chains is synchronized with the speed of the belt of the forming apparatus. The temperature in the chamber is 100°C; the duration of the stay of the film in the chamber is 4 hours. After the heating chamber, the film is directed into the bath (VO-1) to wash off the ungrafted part of the polymer. Then the film enters the drying chamber (VN-1).

The dried film is cut into oval-shaped plates 10 × 20 mm in size, 10 plates are packed in contour-cellular packaging made of PVA film and aluminum foil and marked.

All packed boxes are gas sterilized with ethylene oxide and then sent to the warehouse.

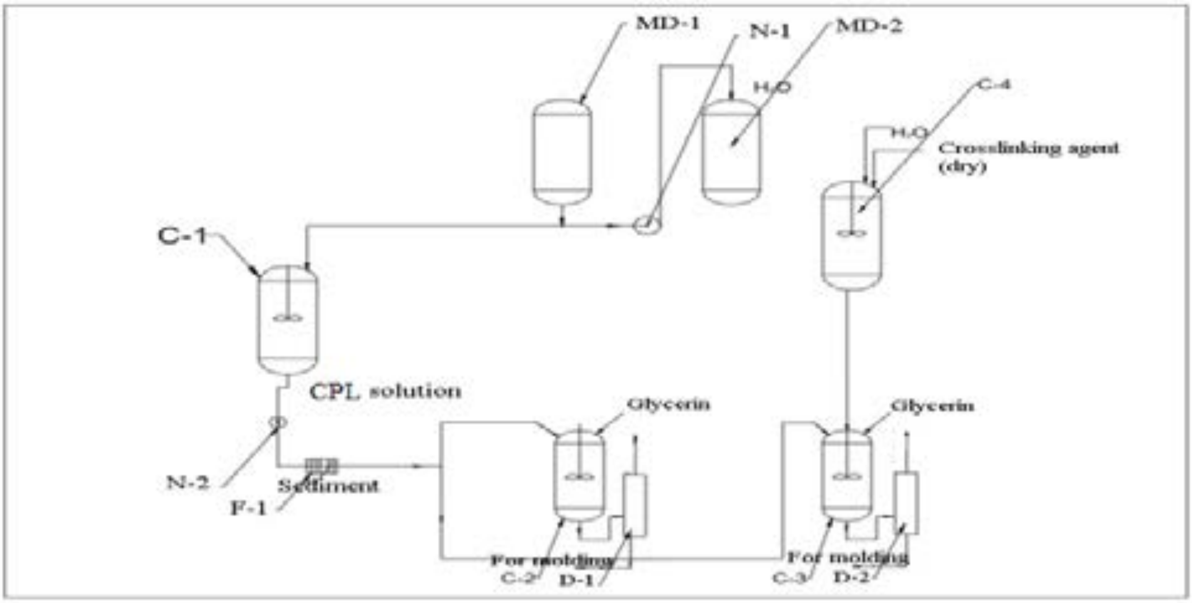

Figure 6 – Technological scheme of pilot production of linear and grafted films based on CPL PVA and BHET.
Note: MD-1, 2 – measuring tank-dispenser; C-1, 2, 3, 4 – mixer; H-1, 2 – centrifugal pump; F-1 – filter press; D-1, 2 – deaerator

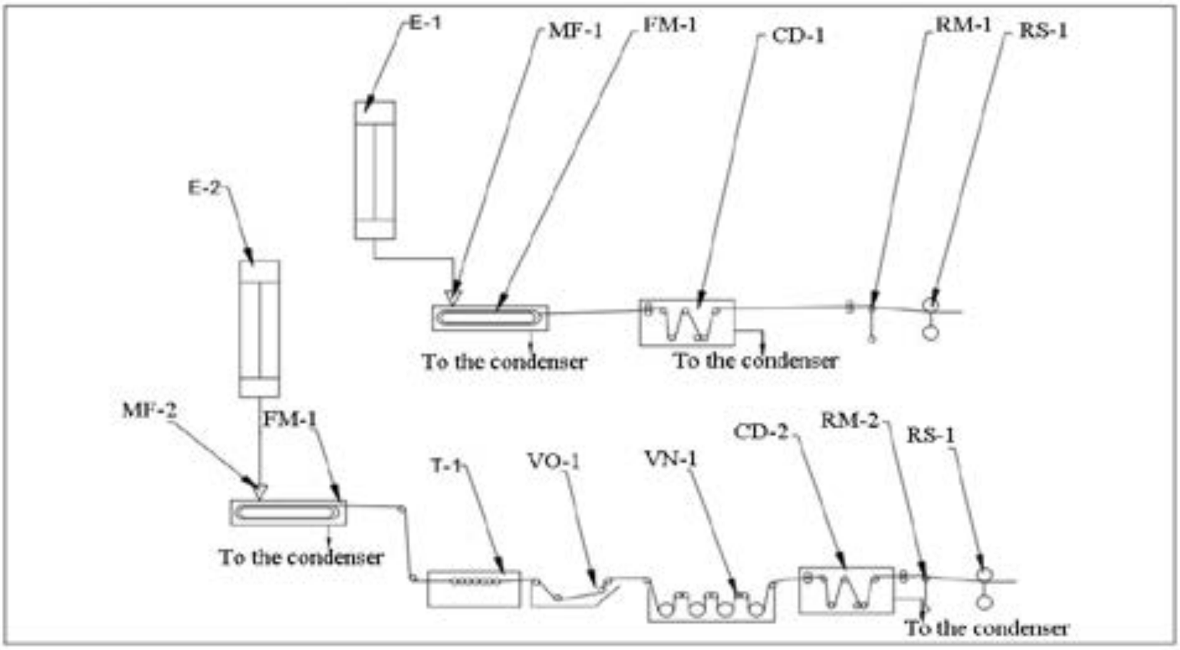

Figure 7 – Technological scheme of pilot production of linear and grafted films based on CPL PVA and BHET.
Note: E-1, 2-storage capacity; MF-1, 2-smearing die; FM-1,2-forming machine;
CD-1, 2-drying chamber;RM-1, 2-stretching machine; RS-1, 2-cutting machine;
T-1-heat capacity; VO-1 – bath for washing; VN-1-bath for saturation

Conclusion

In this article, the method of secondary chemical treatment of polyethylene terephthalate waste is studied. The remains of PET bottles were first sorted by color and cleaned, disassembled into flexi. Optimal conditions for the chemical method of processing polyethylene terephthalate waste have been determined, i.e. it has been established that PET waste is destroyed in the presence of ethylene glycol solvent and zinc acetate (0.5% to the weight of PET) as a catalyst. In addition, 190°C was designated as the optimal destruction temperature. Biodegradable films based on polyvinyl alcohol and bis-hydroxy ethylene terephthalate were obtained by graft copolymerization, during which ammonium persulfate was used as an initiator. This method of obtaining biodegradable films based on PVA and BHET has not yet been considered in scientific research at all. Optimal conditions for the production of films based on polyvinyl alcohol and bis-hydroxy ethylene terephthalate have been established, i.e. the optimal temperature is 75-80°C and with a ratio of PVA and BHET 1:3 and pH = 3.8-4.0, it has been established that in the presence of glacial acetic acid, very strong and flexible, water-soluble films are obtained. It has been established that biodegradable films based on PVA and BHET are interconnected by hydrogen bonds along the IR spectrum and can attract water to it as a result of the presence of C-O-C bonds in the composition, and a technological scheme of a biodegradable film based on PVA and BHET. In addition, biodegradable films based on PVA and BHET were obtained for the first time.

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