PROSPECTS AND RELEVANCE OF THE SYNTHESIS OF AN ENVIRONMENTALLY FRIENDLY PLASTICIZER

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ABSTRACT:

Production of environmentally friendly polymeric materials intended for the manufacture of medical equipment, children's toys is one of the important problems in chemical technology. For the production of these products, phthalates are widely used as plasticizing additives to polymers, in particular dibutyl phthalate, dioctyl phthalate, which are considered non-toxic. However, it is known that they have a hazard class - II. The article provides a literature review on the use of vegetable oils as plasticizers for polymers. The authors propose a method for obtaining an environmentally friendly plasticizer for PVC compositions from castor oil, present the results of research in this area, provide optimal options for the method for obtaining an environmentally friendly plasticizer, as well as a technological scheme for the production of a plasticizer and its description.

INTRODUCTION. As you can see, the chemical industry of our country is rapidly growing, and the manufactured products must also meet the requirements of the time. With the exception of some chemical companies, there is no industrial production of PVC additives as such in the Republic. The problem is explained by the lack of not only modern technologies, but also raw materials used in the production of high-quality PVC compounds.

Abroad, the situation is somewhat different, but there are also shortcomings that should be addressed.

Some of the first PVC manufacturers were German manufacturers, who launched large-scale industrial production back in the 30s of the 20th century [1; 992-997]. However, at that time, PVC was a rather scarce product on the market in Russia.

1912 is considered to be the year of the discovery of polyvinyl chloride. That year, Klatte reported on the PVC production process. However, the history of PVC began a century earlier. In 1795, four Dutchmen, Dieman, Trotsvik, Bondt and Laurenverburg, produced a substance named after them "Dutch chemists' oil" (dichloroethane). The nature of this substance became a subject of debate in chemistry; was it a simple combination of equal parts of chlorine and ethane or was it a more complex compound? Several chemists began to work on this question. [2; 23-p.].

Because of their chemical stability, versatility, lightness and limited cost in relation to other classes of materials (e.g. metals and ceramics), polymers have found widespread use in recent decades. Applications in many technological fields such as construction, electronics, packaging and healthcare. Worldwide plastics production in 2017 was 354 million tons, and about 26% of polymers were produced in China [3; 59-63-p.]

Even if the interest in polymer blends is constantly increasing, the history of polymer alloys is quite long and related to the development of various polymer matrices. In fact, the possibility of mixing two or more matrices can lead to the development of new polymers with individual properties, different from the constituents, thus overcoming the problems due to the synthesis of new types of polymers. At a general level, five different methods, i.e. melt mixing, solution mixing, latex mixing, partial block- or graft copolymer formation and synthesis of interpenetrating polymer networks, can be used for the processing of polymer blends. Practically speaking, melt mixing is the most common technology for the production (and processing) of polymer blends, and according to this method, the components of the blend are mixed in the molten state through extruders or melt compounders. This method is preferred over others due to the use of well-defined components and the versatility of the mixing devices, since the same equipment can be used to prepare a wide range of polymer blends. On the other hand, this technology involves increased energy consumption and is generally not suitable for performing chemical modification of the composition of the mixture [3; 59-63-p.].

Plastics have made our lives easier. From household items to medical equipment, plastics are an integral part of our lives. They can be designed with customized properties and resist degradation by the environment and time. Medical plastics are developed for specific applications; they have revolutionized the industry mainly because of their ease of processing and can be easily functionalized to impart desired chemical or functional properties. Medical instruments made of steel, ceramics or glass have now been replaced by plastics, which have proven to be economical and durable. Plastics can be given any shape and size in the production of medical disposables. They are lightweight and can be mixed with additives or fillers to fine-tune their flexibility or surface properties [4; 199-208-p.].

Phthalates play an important role in the plastics and rubber industry worldwide, accounting for over 80% of all PVC plasticizers, with DEHP accounting for at least 60% of this amount due to its good performance and low cost. Esters come in a variety of molar masses and have been used for a variety of purposes for over 50 years due to their superior properties and cost.

Some studies conducted in the 90s showed that some plasticizers of the phthalate family caused genetic changes in mice, which were not observed in humans. However, the precautionary concept was applied to low molecular weight phthalates such as BBP, DIBP, DIHP and DEHP, limiting their use in some products. On the other hand, high molecular weight phthalates such as DINP and DIDP have no restrictions on use.

In line with this trend, plasticizers from renewable sources such as modified vegetable oil, modified and epoxidized vegetable oil, glycerol acetate blends, glycerol monoester, and di(2-ethylhexyl) terephthalate – DEGT are emerging alternatives for PVC stretch film [5; 272-278-p.]. A large number of excellent works describing the investigation of PVC thermal stabilizers [6; 426-429-c.] and lubricants are mentioned in the specialized literature [7; 15-17-c.].

In recent years, there has been a rapid increase in the use of vegetable oils to prepare a wide range of polymers to replace petroleum-based polymers to minimize the environmental impact. Inedible castor oil (CO) can be obtained from the castor plant, which grows easily even in arid areas. CO is a promising source for the development of several polymers such as polyurethanes, polyesters, polyamides and epoxy polymers. Several synthesis routes have been developed and various properties of the polymers have been studied for industrial applications. In addition, fillers and fibers, including nanomaterials, have been incorporated into these polymers to improve their physical, thermal and mechanical properties. This review highlights the development of CO-based polymers and their composites with attractive properties for industrial and biomedical applications [8; 4639-4662-p.]. Synthesis of non-toxic plasticizers derived from rosin processing industry waste can reduce environmental pollution and promote the full utilization of rosin waste. In this study, four kinds of sustainable branched plasticizers derived from biomass resource, eugenol (obtained from rosin production waste), were synthesized by solvent-free one-pot polymerization and used for plasticization of polyvinyl chloride (PVC). Internally plasticized PVC was prepared using thiolated DPE (eugenol-based branched plasticizers).

Thermal stability, tensile properties, microstructure, volatility and solvent extraction resistance of plasticized PVC were investigated. Compared with the commercial plasticizer dioctyl phthalate, the thermal stability, plasticization efficiency and migration resistance of the branched plasticizers were superior. The acute oral toxicity of each branched plasticizer was extremely high at 5000 mg/kg body weight, with no mortality in the experimental animals. Compared to externally plasticized PVC, internally plasticized PVC showed zero weight loss in the volatility and leaching tests, despite its less efficient plasticization. All branched plasticizers have potential applications in plastic products [9; 104-331-p.].

Castor oil hydrolysis using the lipase enzyme is carried out in a batch reactor at room temperature (35-400C). In order to reduce the cost of the enzyme-catalyzed reaction, water in an oil emulsion and an oil to water ratio of 3:1 are selected. The enzyme concentration in the reaction mixture is optimized. The effect of various additives, such as solvent and salt, which can increase the reaction rate, is studied. It is found that glycerol does not have any effect on oil hydrolysis. The possibility of reusing the lipase enzyme was also tested. The yield of enzymatic hydrolysis of castor oil is compared with the yield of coconut and olive oils [10; 93-99-c.].

The chemical industry of our country is rapidly gaining momentum, and the products manufactured must also meet the requirements of the time. With the exception of some chemical companies, there is no industrial production of PVC additives as such in the Republic. The problem is explained by the lack of not only modern technologies, but also raw materials used in the production of high-quality PVC compositions. To improve the environmental friendliness of polymeric materials, the authors of the article propose using vegetable oils as a plasticizer for PVC compositions.

Along with existing plasticizers and other additives to PVC, which is used to produce the necessary medical equipment, children's toys, linoleum, and leatherette, scientists are continuously working to synthesize newer, environmentally friendly, and economically not inferior plasticizers for general and special purpose polymers.

The authors are working in this direction, proposing to use vegetable oils as additives that could replace such plasticizers as dioctyl phthalate (DOP), dibutyl phthalate (DBP), etc.

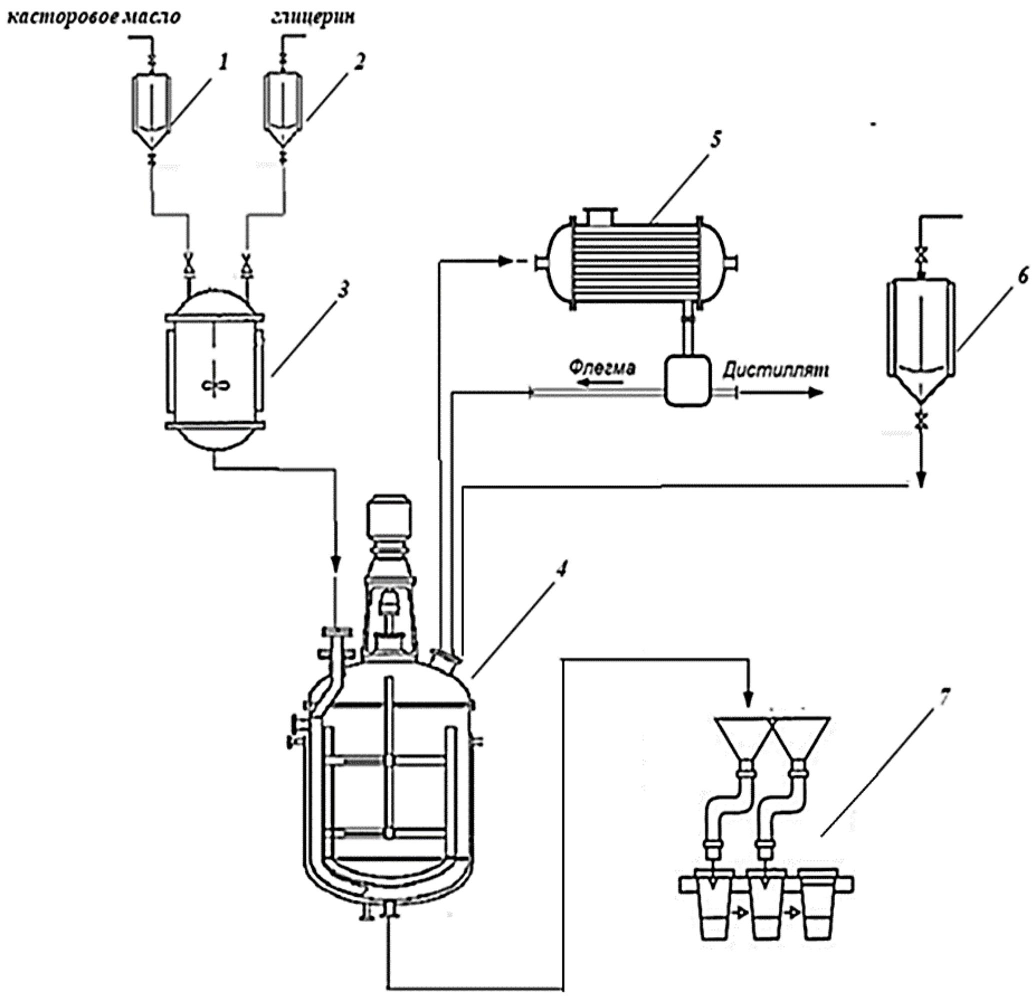
Castor oil is a vegetable oil that is extracted by pressing from castor seeds, and the pressing technology can be either hot or cold. Most often colorless, sometimes has a slight yellow tint, a thick and rather viscous liquid.

The authors of the article obtained a plasticizer for polyvinyl chloride based on castor oil, which was treated with dimethyl terephthalate, resulting in the formation of a complex ester of terephthalic acid with castor oil diglyceride. Below is a flow chart for obtaining a plasticizer based on castor oil (Fig. 1).

Glycerin and castor oil from tanks with dispensers 1 and 2 enter the intensive mixing reactor 3, where the transesterification process takes place at a temperature of 180 to 250^{0}C, then the resulting ester enters the reactor 4, where it is mixed with dimethyl terephthalate from tank 6, after which it enters the separation column 5, where the finished product is separated from the unreacted substances by distillation. They are subsequently recycled.

According to the images of the obtained samples with the MIRA 2 LMU scanning electron microscope, a smoother surface of the sample with the use of a plasticizer synthesized on the basis of castor oil is clearly visible. This may indicate that this composition can be used for rigid PVC products, since high density gives higher rigidity and strength to the composition and products made from it. By replacing the PVC plasticizer dioctyl phthalate with a plasticizer based on castor oil, it was possible to obtain a non-toxic and environmentally friendly PVC composition, which can subsequently be used for the production of medical equipment and children's toys. The optimal parameters for the process of synthesizing a plasticizer based on castor oil were identified, and IR spectra of the PVC composition were obtained using the synthesized plasticizer.

Figure 1.



Technological scheme for obtaining a plasticizer based on castor oil

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