

SONOCHEMICAL SYNTHESIS OF FATTY ACIDS ESTERS FOR PLASTIC'S BIO-ADDITIVES WITH PLASTICIZING EFFECT

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Abstract

Plasticizers are additives that increase the plasticity of polymers by increasing the flexibility of macromolecules. The selection of substances with a similar function is carried out in accordance with criteria that include requirements for non-toxicity, good miscibility, low migration ability, low volatility, etc. The plasticizers most used in plastics processing, for example polyvinyl chloride (PVC), are esters of carboxylic acids with linear or branched aliphatic alcohols of moderate chain length. In organic synthesis, research related to the application of ultrasound in the synthesis of esters is promising - the goals set are to reduce reaction time, increase yields, use safe raw materials, and reduce energy consumption. Its influence on the esterification process in the preparation of aliphatic and sucrose esters with short- and medium-chain fatty acids has not been sufficiently studied. The aim of the present study is to apply ultrasound in the esterification of stearic acid with fatty alcohols. The resulting esters are to be used as potential plasticizer additives in plastics, and the possibility of application in polyvinyl chloride has been investigated.

Keywords: sonochemical synthesis, fatty acids ester, bio-additive, plasticizer

INTRODUCTION

Plasticizers are additives that increase the plasticity of polymers by increasing the flexibility of macromolecules. The selection of substances with a similar function is carried out in accordance with criteria that include requirements for non-toxicity, good miscibility, low migration ability, low volatility, etc. The plasticizers most used in plastics processing, for example polyvinyl chloride (PVC), are esters of carboxylic acids with linear or branched aliphatic alcohols of moderate chain length. [1-3]

Among the plasticizers used in the processing of plastics, the most important are phthalates (esters of phthalic acid with fatty alcohols). They have excellent compatibility with many polymers but are among the suspected causes of health problems in humans. Their acute toxicity is very low, but sub chronic and chronic effects are significant, both of phthalates and their metabolites. This necessitates the

search for safer and at the same time suitable plasticizers for plastics. [4-6]

The industrial synthesis of esters is based on the chemical esterification of fatty acids with alcohol in the presence of inorganic catalysts at high temperatures. These chemical processes are equilibrium and therefore slow, non-selective, energy consuming and low productivity. Several industrial technologies generate waste that poses a risk of environmental pollution. In this regard, the research activity in recent years has been aimed at the search for new technological solutions to intensify the processes. For reactions taking place in solution, the use of ultrasound is effective. Ultrasound has been found to affect the rate of chemical reactions in solution through the phenomenon of cavitation and the generation of microbubbles. This process can be characterized by the formation, growth, and implosive collapse of gas bubbles in the solution. During their

disintegration, because of cavitation, extremely high pressure and temperature are generated inside the microbubble. This unique energy is a means of interaction of substances in solution. [7-9]

In organic synthesis, research related to the application of ultrasound in the synthesis of esters is promising - the goals set are to reduce reaction time, increase yields, use safe raw materials, and reduce energy consumption. Its influence on the esterification process in the preparation of aliphatic and sucrose esters with short- and medium-chain fatty acids has not been sufficiently studied. [10-15]

The aim of the present study is to apply ultrasound in the esterification of stearic acid with fatty alcohols. The resulting esters are to be used as potential plasticizer additives in plastics, and the possibility of application in polyvinyl chloride has been investigated.

EXPERIMENT

1. Ultrasonic synthesis of aliphatic esters of stearic acid

In a 50 cm³ flask 2 mmol of the used alcohol (n-butanol, i-propanol) are added conc. H₂SO₄ as a catalyst, then the weighed amount of 4 mmol stearic acid was added. The flask was connected to a water-cooled reflux condenser and placed in a Dimoff A-2/2 ultrasonic bath (100 W, 44 kHz). It is treated with ultrasound for 15 min at room temperature. After completion of the reaction, the reaction mixture was cooled intensively with the addition of 100 cm³ of ice-cold distilled water and neutralization with 10% Na₂CO₃ was carried out. A triple extraction with 20 cm³ each is carried out diethyl ether. The extracts were combined and dried over anhydrous Na₂SO₄. After filtration, the ether and alcohol are evaporated under vacuum. The residue was separated, and the yield of the ester was determined.

2. Investigation of the applicability of the obtained ester as a plasticizer

Commercial polyvinyl chloride, without dyes, stabilizers, and fillers (EMKA[®]) was

used for the purposes of the experiment. As a plasticizer of polyvinyl chloride, the synthesized ester was used in a concentration of 10, 20, 30, 40%. The experimental studies were carried out with samples in the form of polymer films prepared by casting from a solution in tetrahydrofuran according to the following method: the amount of polyvinylchloride weighed on an analytical balance was placed in a beaker and 100 cm³ was added to it tetrahydrofuran. The mixture is heated in a water bath at 40° C until the polyvinyl chloride is completely dissolved, after which the weighed amount of ester is added. The obtained solution was homogenized for 2 h, after which it was poured into a petri dish and left at room temperature until the complete evaporation of the solvent. The film was dried at room temperature in a vacuum dryer.

The thermal properties of the obtained films were investigated by differential scanning calorimetry (DSC). The measurements were carried out on a scanning calorimeter DSC 204 F1 Phoenix (NETZSCH Gerätebau GmbH) in an argon environment, with a heat flow rate of 20 cm³/min at the following temperature regimes:

- Heating from 20°C to 200°C at a rate of 10 K/min (first scan);
- Isothermal mode at 200°C for 3 min.
- Cooling in liquid nitrogen from 200 ° C to -50 ° C, with a cooling rate of no more than 10 K/ min.
- Isothermal mode at -50 ° C for 5 min;
- Heating from -50 ° C to 200 ° C at a rate of 10 K/ min (second scan);

The weight of a single sample of each sample is 2.5-4.2 g. The glass transition temperature *T*_g was determined in the second scan as the inflection point of the thermogram. Processing was performed with specialized PROTEUS software for DSC 204 F1.

3. Identification and characterization of the obtained esters

Fourier transform IR spectroscopy. The spectra were recorded on a spectrometer Nicolet Avatar (Thermo Scientific, USA) in

a tablet KBr, in the interval 4000-500 cm^{-1} . The NMR spectra (^1H and ^{13}C) of the synthesized esters were recorded on a Bruker spectrometer (500 MHz) in a solution of CDCl_3 and standard tetramethylsilane (TMS).

RESULTS AND DISCUSSION

The esters obtained by US esterification aliphatic esters of stearic acid were characterized by IR-FT spectroscopy. In the spectra of the synthesized esters, several areas characteristic of the esters stand out. In the region 600-1500 cm^{-1} are the absorption bands of bonds with the hydrocarbon chain. The intense and narrow band in the spectrum at 1743 cm^{-1} due to valence vibrations ($\nu\text{C}=\text{O}$) of the carbonyl group in the ester is very clearly visible. The valence vibrations of the C-H bond are manifested in a band of medium intensity, which is observed in the region of 2930 cm^{-1} . In the case of esters, a band appears at about 2850 cm^{-1} corresponding to $\nu\text{C}-\text{H}_{\text{as}}$ (CH_2). In addition to them, bands characteristic for C-O-C from the ester group appear - 1270, 1223 cm^{-1} .

In the ^1H NMR spectra of the synthesized esters, resonance signals are observed - methylene protons are registered in the spectrum at 1.29-2.31 ppm, and the resonance signals for CH_2 protons connected to the C=O group are observed at 2,28-2.31 ppm. In the ^{13}C NMR spectra, resonance signals for the carbonyl carbon atom were observed at 172.83-174.36 ppm. Esterification reaction was successfully carried out.

The plasticization of polymers is based on increasing the flexibility of macromolecules and supramolecular structures, under the action of the plasticizer, which depends on its compatibility with the polymer. The parameter related to the change in flexibility of the structural elements that can be used to evaluate the compatibility and the plasticizing effect is the glass transition temperature.

The thermal properties of PVC films containing different amounts of esters as a

plasticizer were investigated by DSC to determine the glass transition temperature T_g .

The glass transition temperature was determined in the second scan as the inflection point of the thermogram. The processing was done with PROTEUS specialized software for DSC 204 F1. The results of the DSC analysis of the studied samples are presented in *Table 1*.

Table 1. T_g data depending on ester content.

Ester content in the sample, %	T_g , °C n-butyl stearate	T_g , °C i-propyl stearate
0	80.5	80.5
10	72.1	73.2
20	64.6	65.3
30	62.3	61.9
40	58.4	59.1

The obtained results show the presence of only one inflection point (one glass transition temperature) in the thermograms of the studied films, which indicates good miscibility between esters and PVC. The glass transition temperatures of the tested samples depending on the ester content show that there is a significant decrease in T_g with increasing ester content, which is a confirmation of its plasticizing effect on PVC. As the ester content increases, a sharp decrease in the glass transition temperature is observed.

CONCLUSION

To meet the ever-increasing requirements for plasticizing PVC in terms of environmental friendliness and safety, traditional plasticizers can be replaced with safer ones, thus expanding the application range of PVC and its products.

Due to the established reduction of the glass transition temperature in the studied samples with different content of esters in the PVC, we can consider that they have a plasticizing effect and would find use even as additives with plasticizing properties - as a main or co-plasticizing agent in plastics.

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