

APPLICATION OF CAPRATE ALIPHATIC ESTER AS BIO-PLASTICIZER AND BIO-ADDITIVE IN PLASTICS

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Abstract

The aim of the present study is to investigate the application of caprate aliphatic esters as co-plasticizers and biodegradable additives in polyvinyl chloride. i-Bu caprate was used in different proportions. The applicability of a mixture of esters as bio-plasticizers and bio-additives in polyvinyl chloride was studied. The influence of the ester on the glass transition temperature Tg of polyvinyl chloride at the selected ratios was determined by the method of differential-scanning calorimetry. It was found that with increasing its amount Tg of the polymer decreases, i.e. the flexibility of macromolecules increases which is a prerequisite for higher deformability. This supports the conclusion that the ester mixture has a plasticizing effect.

Keywords: keywords, keywords, keywords, keywords, keywords, keywords.

INTRODUCTION

During plasticization, the ability of the polymer to large highly elastic deformations is improved [1]. The addition of plasticizers in polymer composite materials leads to a reduction in energy costs during their processing, the duration of preparation of the mixtures. The participation of plasticizers facilitates the dispersion of the components of the polymer compositions and the formation of the products.

There are major theories explaining the changes in the polymer during plasticization, all of which explain the effect of the plasticizer on the interaction of its molecules with the polymer at the molecular and supramolecular level, which is determined by the compatibility between the polymer and the plasticizer. An indicator of this is the lowering of the glass transition temperature of the polymer T_g , which is largely determined by the chemical composition, the structure of the molecule and the amount of plasticizer [2].

Of the esters of aliphatic acids, stearates and oleates are the most widely used, especially for compositions with plasticity at low temperatures. The search for possibilities to replace the classic plasticizers with non-toxic and biodegradable products leads to researching the possibilities of using aliphatic esters of higher fatty acids or esters of mono-, di- and polysaccharides. [3, 4]

Glycerol, sorbitol and urea have been found to be used as hydrophilic plasticizers in biodegradable starch films. [5, 6]

A similar study was conducted to determine the influence of sucrose and invert sugar on the mechanical properties, hydrophilicity of starch films. The mechanical properties of sucrose, oleic acid, sorbitol and mannitol as plasticizers for gelatin films were investigated. [7-10]

Yin and co-authors investigated the application of three glucose esters, in comparison with glucose pentaacetate and sucrooctaacetate, as bioplasticizers for polyvinyl chloride. [9]

The purpose of the study is to investigate the influence of *i*-Bu caprate when incorporated into polyvinyl chloride polymers to evaluate the possibilities of its application as a plasticizer.

MATERIALS AND METHODS Preparing the samples

For the purposes of the experiment, commercial polyvinyl chloride was used, without dyes, stabilizers and fillers. *i*-Bu caprate obtained by the method described by Vasilev and co-authors [11] was used as a polyvinyl chloride plasticizer. The experimental studies were carried out with samples in the form of

polymer films prepared by solution casting in tetrahydrofuran. The weighed amount of polyvinyl chloride is placed in a beaker and 100 cm³ of tetrahydrofuran is added to it. The mixture is heated in a water bath at 40°C until the complete dissolution of the polyvinyl chloride, after which the selected plasticizer is added. The resulting solution was homogenized for 2 h, then poured into a Petri dish and left at room temperature until the solvent completely evaporated. The film was dried at room temperature in a vacuum dryer. [9]

Investigation of the plasticizing effect differential scanning calorimetry

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 cm^{3}/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 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 Tg 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

RESULTS AND DISCUSSION

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.

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The results of the DSC analysis of the studied samples are presented in Table 1 and Fig. 1.

Table 1. Ig data depending on the content of <i>i</i> -Bu caprate	
Content of <i>i</i> -Bu caprate in the	The glass transition
studied sample, %	temperature (Tg), °C
0	80.5
10	75.8
20	68.1
40	56.7
60	53.5

Table 1 To data depending on the content of i Ba

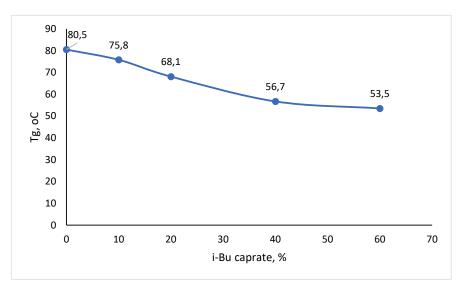


Fig. IV.13. Variation of Tg depending on the content of i-Bu caprate in the sample

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 *i*-Bu caprate and PVC. The glass transition temperatures of the studied samples depending on the content of *i*-Bu caprate are presented in *Fig. 1*. There is a significant decrease in Tg with increasing content of *i*-Bu caprate, which is a confirmation of its plasticizing effect on PVC. As the content of *i*-Bu caprate increases, a sharp decrease in the glass transition temperature is observed, and at 40 and 60% the difference in Tg is minimal.

CONCLUSION

The applicability of sonochemistry synthesized *i*-Bu caprate as a bio-plasticizer and/or biodegradable filler in polyvinyl chloride mixtures was investigated. Using the DSC method, the effect of ester on the glass transition temperature of PVC at contents of 0-60% was determined. It was found that as its amount increases, the Tg of the polymer decreases, i.e. the flexibility of macromolecules increases, which is a prerequisite for higher deformability.

The results obtained at this stage of the research show that sonochemistry synthesized *i*-Bu caprate is applicable as a bio-plasticizer and/or biodegradable filler in polyvinyl chloride mixtures in contents up to 40%. Further research is needed to establish the mechanism of action of the ester at higher concentrations, with a view to expanding its application.

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REFERENCE

- [1]. George Wypych, Handbook of plasticizers, ChemTec Publishing, 2004
- [2]. Wilkes, Ch., Ch. Daniels, J. Summers, PVC Handbook, ISBN 3-446-22714-8
- [3]. Tishkova, J., V. Ch.-Bagdassarian, T. Georgieva, Migration of primary aromatic amines from polyamide kitchenware, Bulgarian journal of public health, Vol.7 (1), 2015, 87-98
- [4]. Baker, I., R. Willing, D. Furlong, F. Grieser, C. Drummond, Sugar Fatty Acid Ester Surfactants: Biodegradation Pathways, Journal of Surfactants and Detergents, Vol. 3, No. 1, 2000, 13-27
- [5]. Galdeano MC, Grossmann MVE, Mali S, Bello-Perez LA, Garcia MA, Zamudio-Flores PB. Effects of production process and plasticizers on stability of films and sheets of oat starch. Mater Sci Eng C 2009, 29 (2), 492-8.
- [6]. Galdeano MC, Mali S, G. MVE, Yamashita F, García MA. Effects of plasticizers on the properties of oat starch films. Mater Sci Eng C 2009, 29 (2) 532-8
- [7]. Veiga-Santos P, Oliveira LM, Cereda MP, Scamparini ARP. Sucrose and inverted sugar as plasticizer. Effect on cassava starch–gelatin film mechanical properties, hydrophilicity and water activity. Food Chem 2007, 103(2):255–62.
- [8]. Yang X Cao N, Fu Y. Effects of various plasticizers on mechanical and water vapor barrier properties of gelatin films. Food Hydrocol 2009;23(3):729–35.
- [9]. Yin, B., N. Atsenggari, Xi Yang, M. Hakkarainen, Glucose esters as biobased PVC plasticizers, European Polymer Journal 58 (2014) 34–40.
- [10]. Jia P., et al. al. Properties of polyvinyl chloride incorporated with a novel soybean oil based secondary plasticizer containing a flame retardant group, Journal of Applied Polymer Science, 2015.
- [11]. Vassilev, D., N. Petkova, P. Denev, Application of sonochemistry for the synthesis of capric