

Microwave Synthesis of Inulin Acetate as Potential Bio-Based Additive for Poly(Vinyl Chloride)

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ABSTRACT: The paper presents the findings of an experimental study on the microwave synthesis (MW) of inulin acetate and its possible application as bio-additive in poly(vinyl chloride) (PVC). The obtained inulin acetate has been identified and characterized by spectroscopic methods. Advantages of the MW compared with the conventional synthesis were defined. In order to evaluate possible application of the product as bio-based additive for polymers, effect of the inulin ester on PVC behavior and characteristics has been investigated by differential scanning calorimetry (DSC) and deformation upon extension. Experimental results show that in concentration range up to 30.0 wt. % the inulin ester influences positively the properties of PVC causing effect similar to plasticizing one. At concentration over 30 wt.% the ester shows more specific behavior, which will be further investigated. Conclusions about potential application of MW synthesized inulin acetate as bio-based additive for PVC have been drawn.

KEYWORDS: Inulin esters, microwave-assisted, esterification, poly(vinyl chloride), bio-based additive, tensile properties

INTRODUCTION

Poly(vinyl chloride) is a rigid-chain polymer that forms the basis of materials with wide application. Its production, processing and application, however, generate problems directly affecting human health and the environment. Some of them are related to the generation of toxic chlorine-containing compounds throughout the PVC lifecycle - from polymer synthesis to waste disposal of PVC products. The use of special additives-plasticizers that facilitate processing and increase its plasticity - poses a serious problem-in recent years almost 90% of the plasticizer products produced worldwide are intended for PVC [1]. The most widely used plasticizers and additives for PVC are low-molecular compounds such as phthalates, trimellitate, citrates, sebacates and adipates. Since they are not chemically bonded to the polymer and have a low molecular weight, plasticizers have a tendency towards migration from the inside to the surface of the product. A number of conventional plasticizers used, such as phthalates have a proven toxicity and harmful effects on human health and the environment [2]. One of the research approaches is related to the reduction of plasticizer migration - for example, PVC chemical crosslinking or the blending of PVC with polymeric plasticizers [3]. Another approach is the use of phthalate replacement compounds which combine low toxicity with plasticizing

efficiency close to that of phthalates-for example di-(2-ethylhexyl) terephthalate, diisononyl cyclohexane-1,2-dicarboxylate; Dibenzates; Acetylated monoglycerides of fully hydrogenated castor oil; isosorbide diesters, etc. [4]. Studies on replacement of classical plasticizers with biodegradable compounds resulting from the processing or modification of natural biodegradable raw materials in accordance with the principles of "green chemistry" have been developing rapidly [5-7]. There has been a significant interest in vegetable oil esters - soybean oil [8], canola oil, castor oil [9], linseed oil or tall oil [10], palm oil or mixtures thereof [11-13] and etc.

Over the recent years, the focus is on carbohydrate esters as "green" PVC plasticizers. Renewable oligoesterisosorbide has been synthesized and successfully applied as plasticizer with good plasticizing efficiency for PVC [14]. Carbohydrate esters and polyols esters were successfully applied as plasticizers to cellulose esters, PVC and polylactide [15, 16]. Large potential as "green" PVC plasticizers indicated synthesized by Yin et al. glucose hexanoate esters and sucrooctaacetate [17].

The disadvantages of conventional methods of esterification and environmental problems they pose have been well known. The number of studies conducted resulted in the development of environmentally friendly technologies based on the principles of "green chemistry". MW as promising "green technology" for modification of polysaccharides was successfully applied also [18-21]. The advantages of microwave-assisted chemistry include high efficiency, improvement of reproducibility of the chemical process, reduction of the unwanted side

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reactions and increase in the purity of the final products. The combination of MW activation and solvent-free conditions in organic synthesis provides clean chemical processes characterized by enhanced reaction rates, higher yields and enhanced ease of manipulation [20].

Inulin is a natural, biocompatible and biodegradable polysaccharide consisting of linear chains of β -(2 $\rightarrow$ 1) linked fructose units. It exhibits many hydroxyl functional groups that make inulin versatile and easy to functionalize, especially by esterification. The application of the inulin derivatives, and especially its esters, is constantly expanding. The amphiphilic inulin based copolymer was reported to be used for systemic anticancer drug delivery [18].

Application of inulin acetates as encapsulating agent of lipophilic material (as α -tocopherol), drug carrier, antimicrobial agents or vaccine adjuvant constantly increased [22-28].

Until now acetylation of inulin was performed in solvent media consisted of toxic solvents as pyridine and N,N-dimethylformamide for long reaction time under heating or at room temperature [22-25].

Patil and Babu [29] demonstrated efficient acetylation of mono- and disaccharides by microwave irradiation without solvent only with catalysts. Recently, Petkova et al. successfully obtained inulin acetates with antimicrobial potential by conventional acetylation only with catalyst in good yields [27].

The aims of this study were:

- to synthesize inulin acetates by microwave-assisted esterification process when acetic anhydride is in the role of a solvent, to identify and characterize the obtained inulin esters;
- to study the effect of the synthesized product on behavior and strength characteristics of PVC related to its possible application as bio-based additive partly replacing or supporting the plasticizing effect of conventionally used PVC plasticizers.

2 MATERIALS AND METHODS

2.1 Materials

Long-chain chicory inulin Raftiline HPX (Beneo, Orafi, Belgium) with degree of polymerization (DP) 22 was used for esterification. Acetic anhydride (Sigma-Aldrich, USA) was used as acetylating agent. Anhydrous sodium acetate (Merck, Germany) was used as catalyst for the esterification process. Ethanol (Merck, Germany) was used for inulin acetate recrystallization. Polyvinylchloride amorphous (EMKA Ltd., Bulgaria) was used to study the possible

application of synthesized ester as plasticizer. The polymer was used as obtained by the supplier. Tetrahydrofuran (THF) (Merck, Germany) was used as a solvent for preparing of PVC samples.

2.2 Methods

2.2.1 Synthesis of inulin acetates

The microwave-assisted esterification of inulin was performed in a round-bottom flask connected with reflux in a microwave system (Daewoo KOR, MW output power 700 W and 2450 MHz) for 60 s. Eight grams chicory inulin (DP=22) was esterified with 48 ml acetic anhydride in the presence of 4.8 g anhydrous CH_3COONa as catalysts by the above mention conditions. The molar ratio between reactants inulin: Acetic anhydride: Anhydrous CH_3COONa was 1:10:1. Then, the mixture was poured into a 200 ml water-ice mixture, stirred vigorously and left for 24 h at -18°C . Precipitation in excess of cold water was performed. The obtained white solid was filtered and washed again with cold water. The obtained final product was identified as inulin acetates with melting point $79-82^\circ\text{C}$ and characterized by FTIR, ^1H and ^{13}C NMR spectroscopy. FTIR (1745 cm^{-1} , 1370 cm^{-1} and 1220 cm^{-1}). ^1H NMR (500 MHz, CDCl_3) δ 7.28 (s, 8H), 5.78–5.52 (m, 63H), 5.52–5.34 (m, 68H), 5.15 (d, $J=44.9\text{ Hz}$, 9H), 5.01 (dd, $J=129.6, 34.5\text{ Hz}$, 18H), 4.39 (d, $J=8.7\text{ Hz}$, 64H), 4.36–4.09 (m, 160H), 3.94–3.68 (m, 118H), 3.68–3.59 (m, 8H), 2.38–2.03 (m, 628H), 2.03–1.63 (m, 32H). ^{13}C NMR (126 MHz; CDCl_3): δ 170.67, 170.09, 169.78, 103.73, 77.69, 77.30, 77.05, 76.79, 75.81, 75.51, 63.84, 62.69, 20.79, 20.66 and 20.43 ppm.

2.2.2 Identification of esters

FTIR spectroscopy. The infrared spectra were recorded on a Nicolet FTIR Avatar Nicolet (Thermo Science, USA) spectrometer using KBr pellets with 132 scan and the absorption was reported in wavenumbers (cm^{-1}) in the range of $4000-400\text{ cm}^{-1}$. Degree of acetylation of inulin acetates was calculated by relative intensity of IR bands at 1745 cm^{-1} divided to $\text{C=O}/1020\text{ cm}^{-1}\text{C-O}$. This is the ratio between C=O stretching and C-O stretching vibration of the polysaccharide backbone [24].

^{13}C NMR spectroscopy. ^{13}C NMR spectra were recorded on a Bruker Advance III spectrometer (Bruker, Switzerland, 500 MHz) using CDCl_3 as a solvent. All chemical shifts were reported in ppm with reference to TMS.

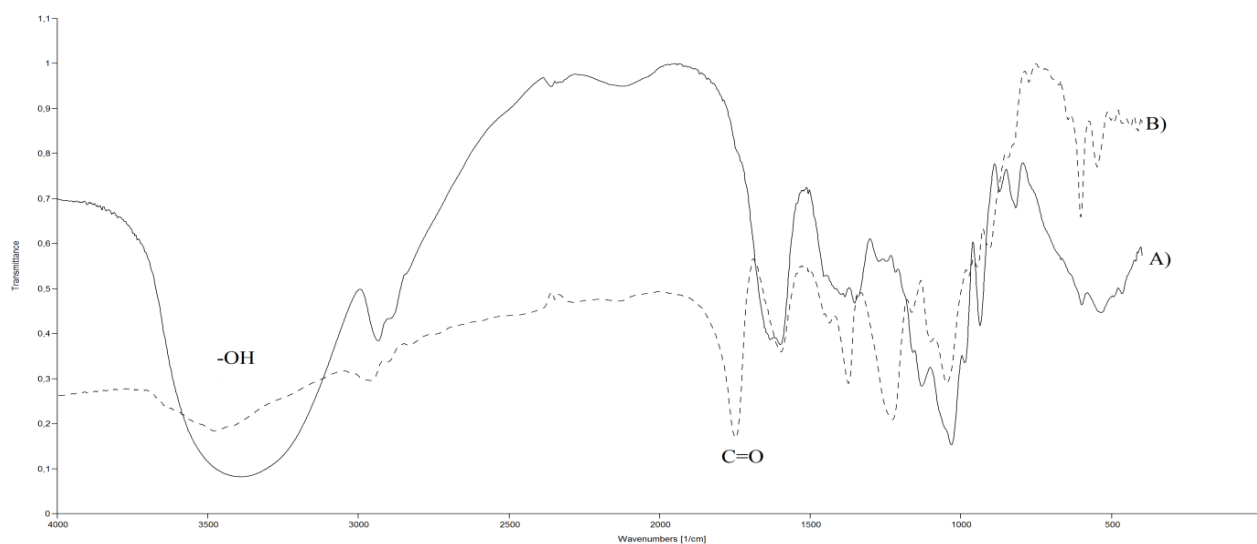


Figure 1 FTIR spectra of inulin (A) and inulin acetates (B).

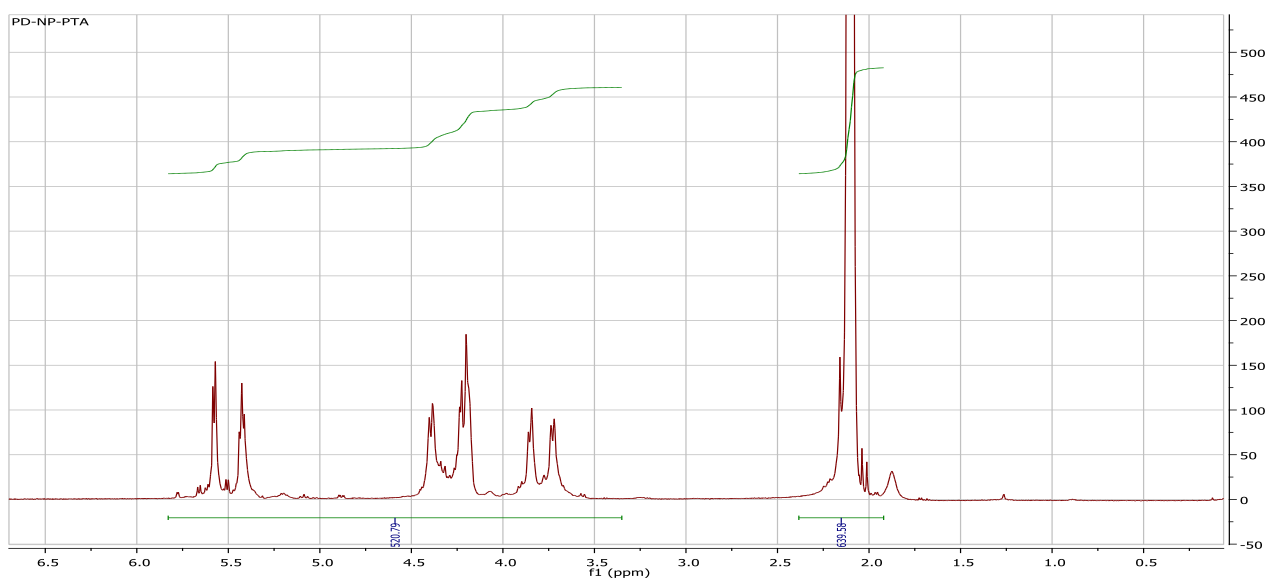


Figure 2 ^1H NMR spectrum of inulin acetate obtained after microwave synthesis.

Table 1 Characteristics of conventional and MW-assisted syntheses of inulin acetate.

Sample	Conditions	Yield, %	Degree of acetylation
Long-chain inulin acetate conventional synthesis [33]	60 min under reflux	78	2.9
Long-chain inulin acetate microwave synthesis	1 min MW	62	2.5

Table 2 DSC analyses of PVC containing inulin acetate.

Inulin acetate content, %	Glass transition temperature T_g , °C	Specific heat capacity, ΔC_p , J/g×K
0.0	80.5±0.1	0,273±0.001
10.0	53.5±0.1	0,357±0.001
20.0	60.7±0.1	0,660±0.001
30.0	56.4±0.1	0,947±0.001
40.0	55.5±0.1	0,529±0.001

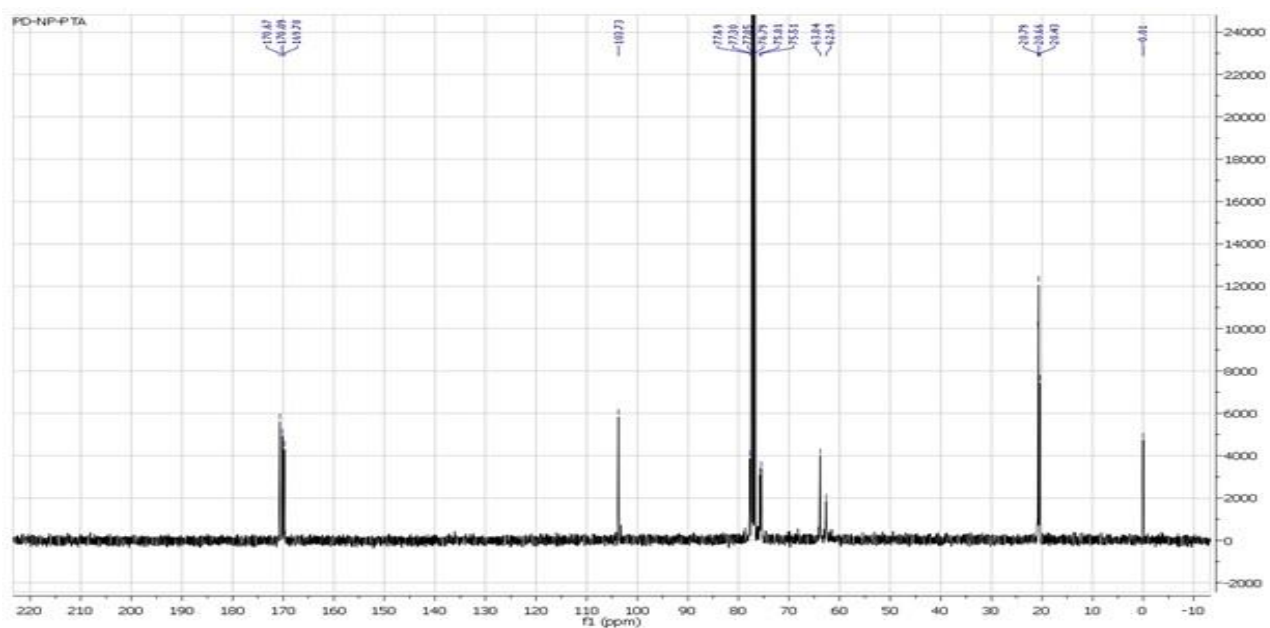


Figure 3 ^{13}C NMR spectrum of inulin acetates (DA=2.5).

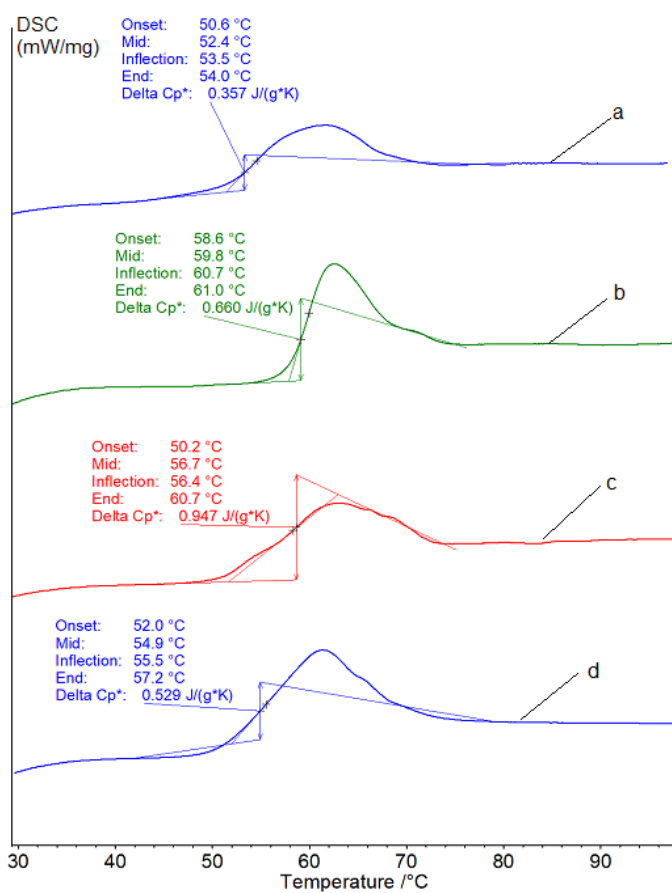


Figure 4 DSC diagrams of PVC/inulin acetate blends: a) 10% inulin acetate; b) 20% inulin acetate; c) 30% inulin acetate; d) 40% inulin acetate.

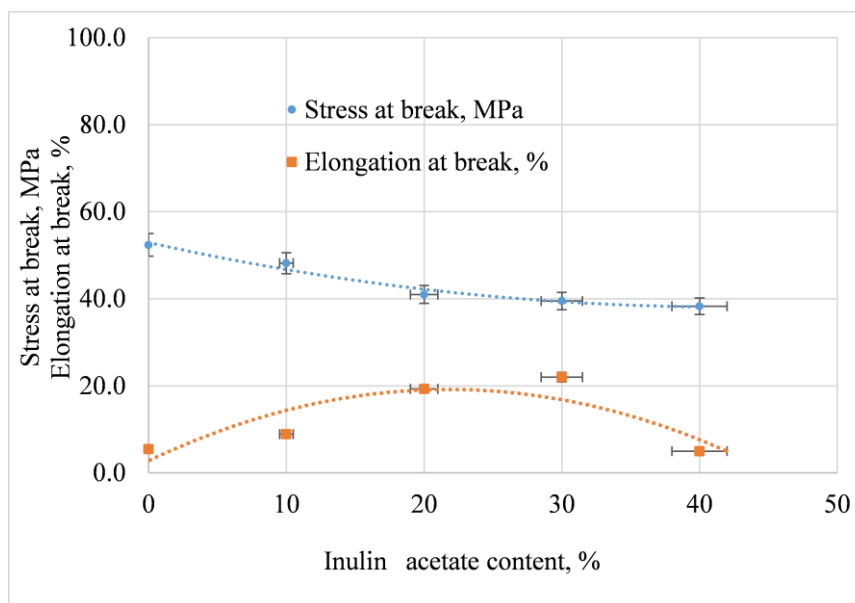


Figure 5 Mechanical properties of PVC containing inulin acetate

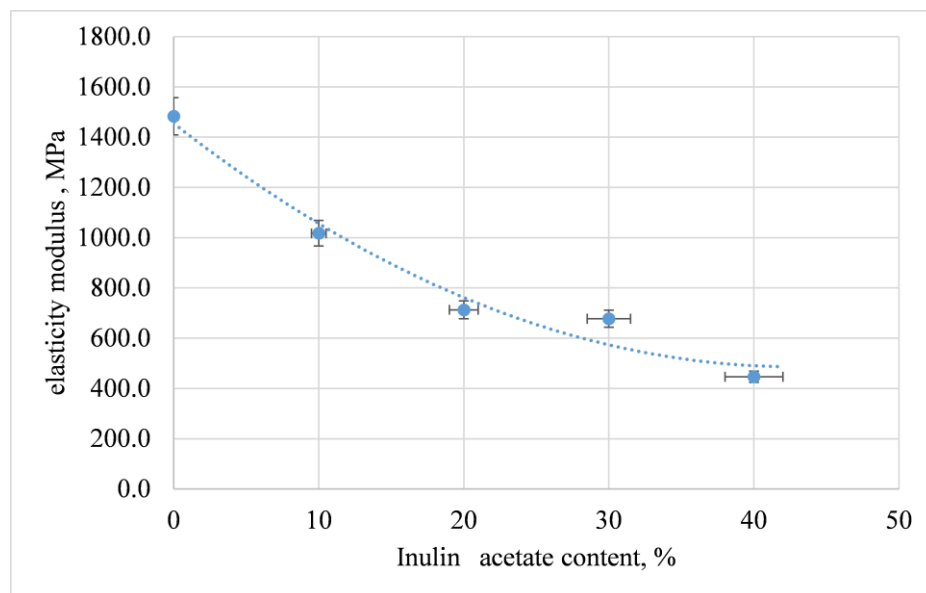


Figure 6 Elasticity modulus of PVC containing inulin acetate.

2.2.3 Evaluation of inulin acetates effect on PVC properties

Samples preparation. Thin PVC films (thickness 0.18-0.28 mm) containing 0 wt. %, 10 wt. %, 20 wt. %, 30 wt. % and 40 wt. % of inulin acetates were used to prepare the experimental samples. The specified amount of PVC was dissolved in 100 cm³ THF in water bath at 40°C until the complete dissolution of the polymer. Then the above mentioned amount of inulin acetate was added and the mixture was stirred for 2 h until complete homogenization. The resulted solution

was poured into a glass Petri dish and dried at room temperature in a vacuum oven for 7 days [17].

Determination of glass transition temperature T_g . The glass transition temperature T_g of the PVC-films was determined by differential scanning calorimetry, by 204 F1 Phoenix (NETZSCH Gerätebau GmbH) calorimeter, using Al pans (2,5-4,2 g of sample), at heating/cooling rate of 10 K/min, in the following consequence: heating from 20°C to 200°C (first scan); cooling in liquid nitrogen from 200°C to -50°C; second heating from -50°C to 200°C (second scan). The

measurements were carried out in argon at a flow rate of 20 cm³/min. The value of *T_g* for each sample was determined in the second scan as the inflection point on the thermogram, by PROTEUS software.

Tensile testing. The tensile tests were conducted by Lloyd LS1 apparatus (Lloyd Instruments, AMETEK, Inc.), equipped with pneumatic grips and NEXYGEN Plus Materials Testing Software, with crosshead speed 100 mm/min to determine the tensile strength, elastic modulus and the elongation at break of each sample. Nine to twelve rectangular specimens of size 5×100 mm and thickness 0.18-0.28 mm were tested and the average value was calculated for each PVC-film.

3 RESULTS AND DISCUSSION

3.1 Identification of Inulin Acetate

The appearance of new functional groups in inulin chain was confirmed by infrared spectroscopy (Figure 1). Inulin acetate showed strong new bands at 1745 cm⁻¹ attributed to stretching vibration of C=O groups from ester, 1370 cm⁻¹ bending of C-H (from CH₃ group) and 1220 cm⁻¹ due to stretching vibration of C-O from ester group. These three typical bands were due to ester bonds of acetyl residues to the inulin chains. The strong bands at 3335 cm⁻¹ typical for the stretching vibrations of OH groups decreased significantly in the inulin acetate spectra. The presence of bands at 817 cm⁻¹ in both spectra proved that resulting ester contained β-D-fructose residues linked 2→1 glycoside bonds.

¹H NMR spectrum of inulin acetate showed shifts typical for COCH₃ that appeared appears at ~2.00 ppm (Figure 2). The efficiency of acetylation reaction performed under microwave irradiation was evaluated by degree of acetylation (DA). The degree of acetylation of inulin acetate was estimated from its ¹H-NMR spectrum by using relative change in the ratio of integrals of resonance peaks at ~2 ppm corresponding to methyl protons of acetate (acetylation), and these at 3.5-5.5 ppm corresponding to protons of fructose skeleton (native inulin) respectively (Figure 2). The number of acetyl groups per fructose unit for the microwave-synthesized inulin acetate was calculated to be 2.5. The degree of acetylation was from 2.5 to 2.9 so the ester was characterized as highly acetylated. These results are close to these ones reported by other authors [22, 28]. The structure of inulin acetates was additionally confirmed by the ¹³C NMR spectrum (Figure 3). Three chemical shifts characteristic for acetyl carbonyl was clearly appeared at δ 170.15. All the methyl carbons from the acetyl residue appeared at δ 20.5 (3×COCH₃). Carbon atoms of the inulin moiety were found in the range of 62.66~103.73 ppm.

Compared to the conventional synthesis it could be concluded, that the MW irradiation intensifies the reaction of esterification in absence of solvent, resulting in 62% yield for only 1 min, without affecting the chemical content and structure of the obtained products (Table 1).

3.2 Evaluation of Inulin Acetate Effect on PVC Properties

3.2.1 Differential scanning calorimetry analyses

The results of the DSC analysis of PVC containing inulin acetate show that the ester influences the behavior of the polymer, whereas its content increases while the glass transition temperature lowers (Table 2, Figure 4). According to the existing theories on the plasticizing mechanism, the function of the polymer additives called “plasticizers” is to reduce the interaction between the polymer chains, thereby increasing the free volume in the polymer, which in turn is a prerequisite for increasing their flexibility [30]. In this case, the quantitative measurer of the action of the plasticizer is the lowering of the glass transition temperature of the polymer. As the presence of inulin acetate results in decrease of *T_g* from approximately 81°C in pure PVC to approx. 56°C in ester content of 30%, it could be supposed that it increases flexibility of structural elements of the polymer and that way exhibits similar to the plasticizing effect on PVC.

3.2.2 Mechanical Properties of PVC/inulin acetate blends

It is known that the increased flexibility of structural elements of the polymer affects its deformation behavior and its strength characteristics. When it is a result of the activity of specific additive (plasticizer), the extent and nature of this influence are functions of the quantity and chemical structure of the additive, and are usually estimated under tensile load [30].

The results of the tensile tests on PVC films containing inulin acetate show that the ester content increases to 30 wt.%, while the elasticity modulus decreases nearly twice starting from 1483 MPa for pure PVC. The breaking stress also decreases starting from 52.3 MPa for pure PVC with increase of the additive content up to 30 wt. %. At the same time the relative elongation at break increases with increasing of the ester content - at 20 wt. % it is up to 4 times higher than the one of the pure PVC (Figures 5 and 6).

These results also allow conclusion that in concentration up to 30 wt. % the inulin ester affects positively the properties of PVC causing similar to the plasticizing effect.

When inulin acetate content is over 30 wt. %, certain characteristics in PVC/inulin acetate system are reported, such as the increase of breaking stress, and the relative elongation expectedly decreases. Although the downward trend for the modulus is maintained, its alteration with increase of acetate content is relatively feebly marked.

That is, with inulin acetate content over 30 wt. %, certain positive effect on the strength properties of the polymer appears.

It is known that the effectiveness of the additives acting as plastic plasticizer depends on the size and polarity of its molecule-the ability of the small molecule of the plasticizer to penetrate the amorphous regions and to weaken interaction between macromolecules is in the basis of the mechanism of plasticizing. In comparison to the conventional plasticizers for PVC, such as phthalates which are low-molecular compounds, molecules of inulin acetate are considerably larger-apart from being long-chain polysaccharides, they also contain a substituent as a result of acetylation. At low contents, ester exhibits effect similar to plasticizing probably due to the ability of its molecules to occupy the free volume between macromolecules of the polymer, predominantly in amorphous regions. At higher contents, however, most probably due to the close contact with PVC macromolecules, molecular chains of inulin acetate "intertwine with them", thus reducing their flexibility - the result is increase in the stress and decrease of the relative elongation upon breaking of the. Similar behavior has been observed in some bio-additives based on palm oil and used as co-plasticizers for PVC [31]. In this case, however, modular increase is also observed which allows the authors to draw a conclusion about the increasing effects of the test compounds.

With a view of the above, the influence of ester on PVC behavior in contents over 30 wt. % is also of interest. This, however, shall be subject of further in-depth studies. In case similar "increasing" mechanism of action of inulin acetate is confirmed, it could successfully be applied as bio-based additive in a combination with or replacing a part of conventional PVC plasticizers, while contributing to the improvement of strength properties of the polymer.

CONCLUSIONS

The inulin was successfully esterified by microwave irradiation. Microwave impact dramatically accelerated the synthesis without affecting the chemical structure of the obtained products.

The application of the MW-synthesized inulin acetate as PVC bio-additive has been examined. It has been

found out that the increase of its quantity results in decrease of polymer T_g , i.e. flexibility of macromolecules increases which is a prerequisite for higher deformability. It is proved by studies on the influence of ester over PVC behavior under tensile load. Contents of inulin acetate of up to 30 wt. % have been found out to reduce the tension and to increase the relative elongation upon breaking, and to reduce the modulus. More specific behavior of the polymer has been observed in ester contents of over 30 wt. %, namely increase of the stress and decrease of the relative elongation at brake along with insignificant alteration of the modulus. The results obtained at this stage of the study allow for a conclusion that MW synthesized inulin acetate could be potentially applied as bio-additive for PVC in contents of up to 30 wt. %. Additional experiments should be held to clarify the mechanism of the ester influence at higher contents in order to enlarge its application.

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