Degradable Polymers with Inulin Content

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Abstract: Polysaccharide based plastic materials were obtained using modified inulin with methcryloyl and palmitoyl chlorides. These esters were copolymerised with *n*-butyl acrylate and 2-ethyl hexyl acrylate. The hardness of the obtained samples was evaluated using the Hőppler equipment. Moreover, the chemical stability of the samples in acid and basic medium was evaluated.

Keywords: inulin, inulin mixed ester, polymers hardness, and chemical stability

1. Introduction

The main reasons for the continues increase in the demand of the commodity plastics are as follows:

- Plastics are low density solids, which makes it possible to produce lightweight objects
- Plastics have low thermal and electric conductivities, hence they are widely used for insulation purposes
- Plastics are easily moulded into desired shapes
- Plastics usually exhibit high corrosion resistance and low degradation rates and are highly durable materials
- Plastics are low cost – materials

All these advantages make the plastic materials to be used in almost every field of the every day life. [1].

Figure 1 illustrates plastics consumption in Western Europe by product [2], confirming that plastics are versatile materials which can be found in a wide rage of products.
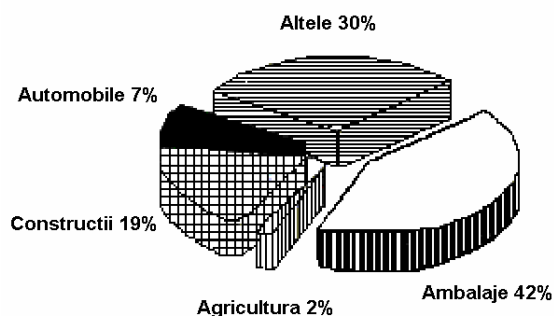

Figure 1. Plastics consumption by sector in Western Europe [2]

As their lifecycle ends the plastic materials are polluting by accumulation due to their low degradation rates.

In this paper inulin was promoted as degradable polymer. Inulin is a polydisperse polysaccharide consisting mainly of β-(2→1) fructosyl fructose units (F_m) with normally, but not necessarily, a glucopyranose unit at the reducing end (GF_n) [3,4]. It is also known that the fructose molecules in the GF_n form are all present in the furanose form. Only in the F_m forms, the ending and reducing fructose is in the pyranose form [5].

The degree of substitution varies from 2 to 150 depending mainly of the plant, the weather condition and the physiological age of the plant.

Inulin was chemically modified in two steps: first three inulin esters were obtained that were, in the second step copolymerised with different acrylic monomers in order to obtain materials with specific properties that could replace some of the synthetic polymers [6].

In this paper the hardness and the chemical stability of the modified inulin samples were studied.

2. Experimental

2.1. Materials

Chicory inulin (Aldrich, average degree of polymerization n=10), *N,N*–dimethylacetamide (DMAc) (Merck), *N,N*-dimethyl-4-aminopyridine (DMAP) (Merck), methacryloyl chloride (MCl), (Fluka), palmitoyl chloride (PCl) (Merck), carbon tetrachloride (Merck), *n*-butyl acrylate (AB), 2-ethyl hexil acrylate (EHA) (Merk), benzoyl peroxide (POB) (Merk). All this materials were used as received.

2.2. Ester Synthesis

The inulin esters were synthesized as previously described [6]: 2 g inulin and DMAP (3 Eg/fructose unit) were dissolved in 20 mL DMAc. MCl (1 Eg/fructose unit) was added and the reaction mixture was stirred for 1 hour at room temperature when PCl (1, 1.5 and 2 Eg/fructose unit) was added. The inulin esters were purified using distillate water and carbon tetrachloride.

TABLE 1. The synthesized inulin esters

	Inulin [g]	MCl [mL]	PCl [mL]
E1	2	1.2	3.8
E2	2	1.2	5.6
E3	2	1.2	7.5

2.3. Inulin based copolymers synthesis

The obtained inulin esters were further copolymerised with two different acrylic monomers, using POB as initiator, as previous described [6] and the schematic illustration of the copolymerisation process is presented in the following scheme (figure 2).
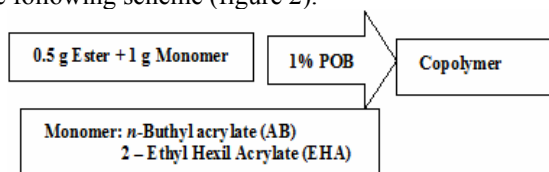
Figure 2. Schematic illustration of the inulin ester copolymerisation

2.4. Hardness determination

In order to determine the hardness of the synthesized samples the Hőppler equipment was used, with the following equation:

$$F_K = \frac{4G}{\pi \cdot T^2} \quad (1)$$

Where:

F_K is the hardness [kg/cm^2], G the loading [kg], T the penetration depth [cm].

2.5. Chemical stability determination

In order to determine the chemical stability, the copolymerized samples were held in acid (pH~3) and basic (pH~10) medium for 40 days. After 10, 20 and 40 days samples were taken and the effects on the thermal stability on the samples was studied. The thermal analyses were carried out with a dynamic heating program (from 20 to 500°C with 10 K/min, under N$_2$ atmosphera) using TG 209 Netzsch equipment.

3. Results and discussion

3.1. Hardness determination

For the copolymerised inulin esters with AB and EHA the hardness was evaluated. Table 2 presents the obtained values. It can be seen that the hardness is decreasing as the plasticity degree is increasing.

The plasticity degree is increasing in two ways: with the increase of the palmitoyl rest content of the inulin ester, and with the chain length of the co-monomer molecule (EHA with respect of AB). From the hardness values it can be seen that copolymers with AB have the highest hardness

values comparing to the copolymers with EHA. Also, the copolymers obtained with E1 have the highest hardness.

TABLE 2. The hardness of the synthesized samples

Sample	Hardness [kg/cm^2]
E1_AB	6,46
E2_AB	5,95
E3_AB	4,59
PAB	1,37
E1_EHA	4,53
E2_EHA	3,98
E3_EHA	3,53
PEHA	1,26

3.2. Chemical stability determination

In order to ensure the acid and basic medium acetic acid (pH~3) and NaOH (pH~10) solutions were used. Samples at 10, 20 and 40 days respectively were taken and thermograms were recorded. By plotting the weight loss (for example at 200°C) versus time that the acid or basic medium acted (figure 3) three strait lines were obtained. By extrapolating we can theoretically evaluate the necessary period of time in which the samples is totally degraded.
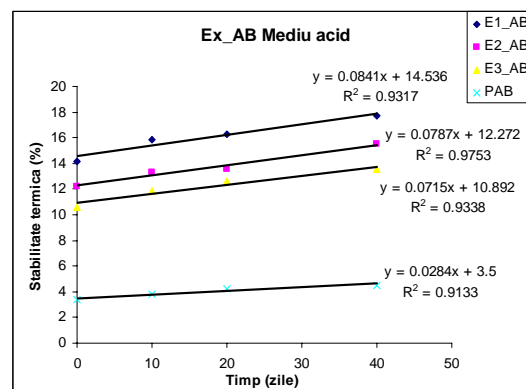

Figure 3. Chemical stability in acid medium for the copolymers obtaied from inulin esters and AB

TABLE 3. Theoretical period of time needed for the total degradation of the samples

Sample	Degradation time	
	Acid medium	Basic medium
E1_AB	2.8	2.4
E2_AB	3.0	2.6
E3_AB	3.4	2.9
PAB	9.4	8.7
E1_EHA	2.4	2.2
E2_EHA	2.6	2.4
E3_EHA	2.8	2.7
PEHA	8.8	6.4

Table 3 presents the theoretical period of time needed for the total degradation of the samples. It can be seen that in acid medium the degradation takes place faster comparing to the degradation in the basic medium. This behaviour is due to the fact that the ester band is highly unstable in acid medium and suffers hydrolytic processes producing higher degradation rates of the samples.

The degradation rates for the copolymers obtained with EHA are lower comparing to the copolymers with AB because these have a much compact structure – the comonomer's chain is shorter and less ramified comparing to the EHA chain.

4. Conclusions

By chemically modifying a natural polysaccharide, inulin, a new type of plastic materials was obtained. This class of products was proven to have lower degradable rates. The theoretically needed period to the total degradation is between 2 to 3 years for the inulin based copolymers, while for the homopolymers is between 6 to 8 years.

Moreover, the hardness of these materials is higher comparing to the homopolymers.

These results are promising for the future research in this area.

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