Thermal Analysis of the Compounds Obtained by Polymerization Between Inulin Esters And Different Monomers

G. Rusu[*], L. Rusnac[*], G. Bandur[*], I. Manoviciu[*], N. Joly[**], P. Martin[**]

[*] University "Politehnica" Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, Place Victoriei 2, 300006, Timisoara, Romania

[**] Département de Chimie, 1230 rue d'Université, B.p. 819, 62408 Béthune cedex, France ; Fax 33-(0)3-21-63-02-94

Abstract: Inulin was esterified with methacryloyl chloride and palmytoyl chloride in order to transform the polysaccharide into a possible biodegradable plastic. The obtained inulin esters were, further, copolymerized with n–butyl acrylate and 2–ethyl hexyl acrylate. The FT-IR spectroscopy was used to characterize the inulin esters and the obtained copolymers. The glass transition temperature was evaluated using DSC and DMA technique. Furthermore, using DMA the storage and loss modulus was evaluated. Thermogravimetrical studies were carried out on the plastics and the thermal stability of the obtained products was studied. These new modified polysaccharides would have biodegradability properties.

Keywords: inulin, inulin copolymers, FT-IR spectroscopy, glass temperature

1. Introduction

Currently, most polymeric materials are based on non-renewable fossil resources, petrochemicals. Along with the rise in petrochemistry, world annual production has increased from approximately 7 million tons (1960) up to 100 million tons (1990) [1]. An increase in production of plastics as well as in energy and fuel is expected due to growing markets in highly populated countries like China or India. Two aspects must be particularly considered from this background:

· the availability of resources;
· the effect of the products on the environment.

Petrochemical plastics are based on finite resources: optimistic calculations assume an availability of mineral oil for approximately 50 years. But sooner or later, the low-priced and easily available mineral oil will run short entailing a drastic rise in price [1]. Due to the low degradation rates of these materials, their effect on the environment is dramatic. To overcome the disadvantages, recycling and incinerations are the alternatives. Recycling of plastics is not economically feasible in many cases due to deterioration of mechanical properties and excessive cost. Incineration of these materials makes a net contribution to atmospheric CO_2, moreover, plastics currently account for an excess of 20% of the nation's landfills. In addition, many widely used materials are made from noxious or toxic monomers [2]

Renewable resources are an alternative for fossil resources. The development of synthetic polymers using monomers from natural resources provides a new direction to biodegradable polymers from renewable resources [3].

Polysaccharides are the most abundant natural polymers on the planet. In this paper, we present the thermal characteristics of the compounds obtained by copolymerization between inulin esters and some acrylic monomers.

Inulin, often called by the generic name of oligofructose, is a mixture of polysaccharides composed of a chain of fructose units (linked by (2→1) *D*-fructosyl-fructose bonds) with generally a terminal glucose unit (linked by an *D*-glucopyranosoyl bond). Only a small fraction depending essentially on hydrolysis rate does not contain any glucose units at all [4, 5]. The general formula may be depicted as GFn and Fm, with G being a terminal glucose unit, F representing the fructose residue and *n* or *m* characterizing the number of fructose units. [6]

Inulin is mainly found in chicory roots, Jerusalem artichokes and dahlia tubers. Composition depends on the plant source, harvesting date but also on extraction and post extraction process [1]. The various inulin chains can be characterized according to molecular size or degree of polymerization (*DP*); *DP* expressing the total number of residues and being equal to *n*+1 or *m* for the formula GFn and Fm, respectively [5].

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) (Fluka), 2–ethyl hexyl acrylate (EHA) (Fluka). All this materials were used as received.

2.2. The synthesis of the inulin esters

The inulin esters were synthesized as follows: 3 g inulin and 4.52 g DMAP (3 Eg/fructose unit) were dissolved in 20 mL DMAc. In order to graft a double bond, 1.8 mL MCl (1 Eg/fructose unit) was added and the reaction mixture was stirred for 1 hour at room

temperature. In the second step, PCl was added. Three different inulin esters were synthesized, using the same amount of MCl and different amount of PCl (1, 1.5 and 2 Eg/fructose unit) in order to obtain products with different plasticity degrees (Table 1). When the reactions were finished, 60 mL distillate water was added to neutralize the reaction mixture. The isolation of the inulin esters was carried by separation using CCl_4 and water. [7].

TABLE 1. The synthesized inulin esters

Sample	Inulin [g]	MCl [Eg]*	PCl [Eg]*	η [%]
E1	3	1 Eg	1,0 Eg	78,5
E2	3	1 Eg	1,5 Eg	84,5
E3	3	1 Eg	2,0 Eg	88,6

*for every fructose unit
η – reaction yield

2.3. Copolymerization of the inulin mixed esters with different acrylic monomers

0.5 g of inulin ester was dissolved in 1 g acrylic monomer (AB and EHA), and benzoyl peroxide was added as promoter (1% toward the monomers). The reaction mass was stirred at 60ºC for 30 minutes when the solution was introduced in glass tubes and kept at 60ºC until the mass got solid, and the temperature was rise with 10ºC/hour until 100ºC [7]. The obtained copolymers from ester E1 are E1_AB and E1_EHA; from ester E2 are E2_AB and E2_EHA; and from ester E3 are E3_AB and E3_EHA.

2.4. FT-IR spectrometry

To characterize the inulin esters and the copolymerized products FT-IR spectra were recorded in KBr pallets for solid compounds, with FT-IR Jasco 430.

2.5. Differential scanning calorimetry analysis (DSC)

Differential Scanning Calorimetry (DSC) analysis ware performed on DSC 204 equipment (Netzsch) under nitrogen atmosphere and under dynamic conditions (with 5 K/min from -100÷20°C) to determine the glass temperature.

2.6. Thermogravimetry analysis (TG)

Thermogravimetrical analysis (TGA) were performed on TG 209 equipment (Netzsch) under nitrogen atmosphere and under dynamic conditions (5 K/min from 20 to 500°C) in order to evaluated the thermal stability of the products.

2.8. Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis (DMA) was performed on DMA 242 C equipment (Netzsch) in air, as follows: temperature range -100°C ÷ 70°C, heating rate 1 K/min, strain frequencies 0.5, 1, 2, 5 and 10 Hz.

3. Results and Discussion

3.1. The characterization of inulin mixed esters using FT-IR spectrometry

The three synthesized inulin esters were characterized using FT-IR spectroscopy. By comparing the obtained spectra with inulin's spectra it can be concluded that both acid chlorides had reacted with inulin (the decrease in width of the characteristic band of hydroxyl group, the occurrence of a band around 1740 cm^{-1} characteristic of carbonyl ester functions, the appearance of the double bond characteristic band at 1670 cm^{-1} and the intensification on the CH signals around 2920 and 1850 cm^{-1} that pointed out the presence of palmytoyl chains).

Figure 1 presents the FT-IR spectra of the synthesized inulin esters.
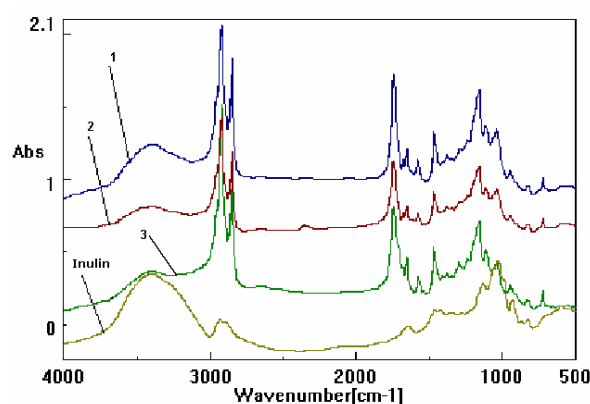

Figure 1. FT-IR spectra for inulin, and inulin esters (1-E1, 2-E2 and 3-E3)

After the copolymerization process the double bond band disappeared, denoting that the copolymerization process took place.

3.2. The characterization of copolymerized products using differential scanning calorimetry analysis (DSC)

By recording spectra with 5 K/min in nitrogen atmosphere between -100 and 20ºC, the glass temperature of the copolymerized polymers was evaluated.

The glass transition is emphasized by the shift of the base line of the DSC curve (figure 2). The glass temperature is considered to be the inflexion temperature.
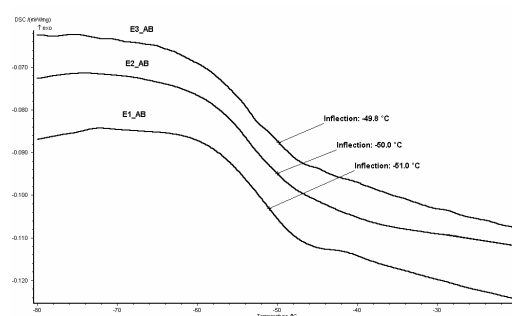

Figure 2. DSC curves for inulin ester copolymerized with AB

The obtained values for the glass transition temperatures are presented in table 2.

TABLE 2. The glass transition temperature for the copolymerized inulin esters

Product	Tg (°C)
E1_AB	-51,0
E2_AB	-50,0
E3_AB	-49,8
E1_EHA	-49,3
E2_EHA	-48,5
E3_EHA	-47,2

It can be noticed (table 2) that the glass transition temperature is increasing as the molecular mass of the inulin ester that was used to obtain the copolymer increases. For the copolymers obtained with EHA the molecular mass is higher and so the transition temperature in higher than for the copolymers obtained with AB.

3.3. The characterization of the copolymerized products using dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) measures the response of a given material to an oscillatory deformation (here in tension–torsion mode) as a function of temperature. DMA results are composed of three parameters: (a) the storage modulus (G'); (b) the loss modulus (G''); and (c) tan δ; the ratio (G''/G'); useful for determining the occurrence of molecular mobility transitions, such as the glass transition temperature (Tg) [8].

The variation of the storage modulus G' and tanδ as function of temperature for different strain frequencies is presented in figure 3 for product E1_AB.
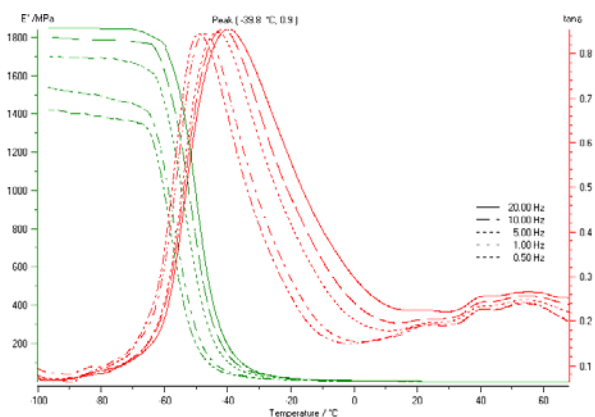

Figure 3. The variation of the storage modulus E' and tanδ as function of temperature for different strain frequencies for E1_AB

The obtained values for the storage modulus, the loss modulus and tan δ are presented in table 3.

It can be noticed that for the same sample, both storage and loss modulus decrease as the strain frequency is increasing. For different samples, it can be seen that the storage and loss modulus are decreasing as the plasticity degree is increasing. For products E1_AB, E2_AB and E3_AB the plasticity degree increases as the substitution degree of the inulin ester that was used for the copolymer synthesis increases. The copolymers obtained with EHA have a higher elasticity due to the higher and longer molecular structure of the co-monomer (EHA) compared with the molecular structure of AB. The glass temperature is considered to be at the maximum value of tanδ. It can be seen (table 3) that the glass transition temperature is decreasing as the molecular weight of the product rises.

TABLE 3. The storage modulus, the loss modulus and tan δ for the copolymerized products

Product	Frequency [Hz]	G' [MPa]	G'' [MPa]	Max tanδ (Tg)
E1_AB	0,5	1352	367	-49,2
	1	1426	390	-47,5
	5	1636	495	-43,4
	10	1766	583	-41,6
	20	1845	671	-39,8
E2_AB	0,5	1221	355	-48,2
	1	1282	362	-46,2
	5	1493	398	-41,5
	10	1612	421	-39,3
	20	1706	437	-37,1
E3_AB	0,5	656	195	-45,6
	1	682	209	-43,9
	5	769	255	-39,8
	10	834	283	-38,0
	20	896	306	-35,2
E1_EHA	0.5	649	113	55.9
	1	675	121	53.7
	5	711	147	47.5
	10	737	163	44.3
	20	787	177	41.1
E2_EHA	0.5	327.2	104.5	55.6
	1	340.6	116.6	53
	5	362.8	121.6	46.6
	10	393	146	43.5
	20	439.7	152	40.6
E3_EHA	0.5	186	53	55.3
	1	200	58	52.1
	5	237	72	46
	10	256	80	43.1
	20	275	87	39.3

Further, the activation energy of the glass transition is evaluated by the graphical representation of the strain frequency versus 1/T, where T is the glass temperature or maximum value of tanδ, and the obtained values are presented in table 4.

TABLE 4. The activation energy for the glass transition of the copolymers

Product	Ea [kJ/mol]
E1_AB	172,25
E2_AB	161,46
E3_AB	152,05
E1_EHA	101,72
E2_EHA	102,44
E3_EHA	103,41

The obtained values are between 100 and 170 kJ/mol.

3.4. The characterization of the copolymers using thermogravimetry analysis (TG)

The thermogravimetric analysis was used to determine the thermal stability of the synthesized copolymers.
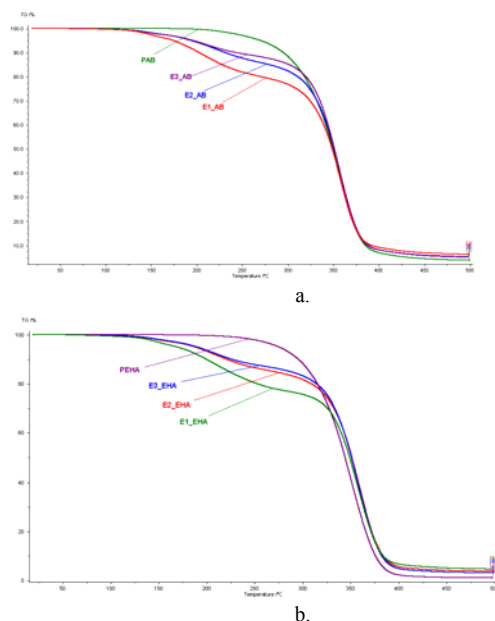

a.

b.

Figure 4. TG curves for the homo-polymers and copolymers obtained with a. AB and b. EHA

Figure 4a presents the TG curves for the copolymers obtained with AB and for the homopolymer – poly(n-butyl acrylate) and figure 4b presents the TG curves for the copolymers obtained with EHA and for the correspondent homopolymer – poly(2-ethyl hexyl acrylate). It can be noticed, that the thermal stability of the copolymers is lower compared to the thermal stability of the correspondent homopolymer. Also, the copolymerized products are degraded in two steps, while the correspondent homopolymers have a one step degradation.

TABLE 5. The weight loss for the synthesized products

Product	Weight loss (%)			
	20-100 °C	20-200 °C	20-300 °C	20-400 °C
PAB	0,10	0,30	11,60	93,04
PEHA	0,07	0,31	11,61	97,85
E1	**1,50**	**19,35**	**70,50**	**92,88**
E1_AB	0,32	9,43	23,14	90,83
E1_EHA	0,53	9,95	24,30	93,35
E2	**1,86**	**20,20**	**75,60**	**96,42**
E2_AB	0,29	7,66	17,58	91,85
E2_EHA	0,26	6,63	18,19	94,43
E3	**2,81**	**20,58**	**80,30**	**98,60**
E3_AB	0,25	5,43	14,76	91,91
E3_EHA	0,09	6,27	16,67	95,17

The thermal stability is better seen from table 5, which presents the weight loss of the inulin esters and their copolymers as well as the weight loss for the correspondent homopolymers.

Comparing the thermal stability of the copolymerized products with the thermal stability of the inulin esters, it can be seen that the copolymers have a better thermal stability.

The thermal stability of the inulin esters is decreasing as the substation degree is increasing. Furthermore, the thermal stability of the copolymerized products is increasing as the molecular weight is decreasing. The weight loss for the copolymerized products, until 100ºC is just under 0.3%, until 200ºC is between 5.4 and 10%, until 300ºC is between 14.7 and 24.3%; at 400ºC the weight loss for all the copolymers are over 90%.

4. Conclusion

The aim of this paper was the thermal characterization of the copolymers obtained using different inulin esters and acrylic monomers. The obtained crosslinked compounds have different plasticity degree due to the different quantities of palmitoyl chloride used to synthesize the inulin esters, and due to the different length of the acrylic co-monomers used in the copolymerization/crosslink process.

This different plasticity degree is pointed out from the DMA data, where the storage and loss modulus are decreasing as the plasticity degree increases. Moreover, the grass transition temperatures evaluated using both DSC and DMA technique show that the glass transition takes place between - 51 and - 47ºC for all the synthesized products.

The thermal stability of the copolymerized products is higher than for the inulin esters. However the homopolymers have a better thermal stability than the crosslinked products. This behaviour is caused by the different chemical structure of the two products: the homopolymers have the esteric bond only as a side group while the copolymers contained in the main chain, so the thermal stability of the formerly is lower.

The importance of these copolymers, obtained by combing a natural polymer (inulin) with a petroleum resource (n-butyl acrylate and 2-ethyl hexyl acrylate) is the key to the biodegradable polymer synthesis. The natural polymer offers an easier degradation, while the synthetic monomers offer quality and functionality. The obtained results justify the future research in this field.

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