Thermal Properties of Copolymers Based on Sugar

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Abstract: Carbohydrate based polymers have emerged as exciting topics of the polymer research, due to a worldwide focus on sustainable materials. The biodegradable polymers are indispensable in the modern society and their importance is continuously growing. We report here the characterization of a new class of biodegradable copolymers derived from monosaccharides. The glycomonomers 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene-α-glucofuranose (ADAG), and 1-*O*-acryloyl-2,3:5,6-di-*O*-isopropylidene-α-mannofuranose (ADAM), were co-polymerized with some acrylates and methacrylates, using as initiators benzoyl peroxide and lauroyl peroxide. The resulting copolymers were characterized by FT-IR, and the thermal stability of the copolymers was investigated using TG analysis, allowing a kinetic study of the degradation.

Keywords: carbohydrate, glycopolymers, biodegradable polymers, thermal analysis, activation energy

1. Introduction

In recent years, there has been increasing concern about land filling non-degradable materials such as plastics. The main reasons for the continue 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, since 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 all fields of the every day life [1]. The great majority of the plastic materials are derived from petroleum, which is a finite source (the most optimistic evaluations are foreseeing that the depletion of petroleum reserves will happen in about 50 years from now on) [2].

As a result, sooner or later, a dramatic increase in the price of petroleum will be recorded, and its effect will be a series of processes that today are considered very expensive to become extremely attractive. As a result of the facts mentioned above, the best would be to obtain a production of polymers based on agricultural products, because of the following two characteristics of this raw material: regeneration and biodegradation. Since the beginning of the 1980's a reassessment of the regenerating raw materials has been noticed. The interest was determined on one hand because of the limited resources of petroleum and the expensive possibilities of coal conversion and on the other hand because of the availability and insufficient utilization of the vegetal resources [3].

The utilization of some natural raw materials for obtaining the polymers is not a new idea : oils (as they are or "boiled") were the basis for dyes used for painting [4]. Further were developed the synthetic resins modified with oil, used for a long time period in the industry of varnishes and dyes.

In the present times, the basic raw materials used for polymers have expanded by including the sugars. The study of carbohydrates began in the late nineteenth century with the work of Emil Fischer. Carbohydrate ring structure was elucidated in the 1930's by Haworth and colleagues [5]. There has been a worldwide realization that nature derived mono-, di-, oligo- and polysaccharides can provide us the raw materials needed for the production of numerous industrial consumer goods [6].

In this paper we report the characterization of a new class of biodegradable copolymers derived from monosaccharides.

Two glycomonomers: 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene-α-glucofuranose (ADAG) and 1-*O*-acryloyl-2,3:5,6-di-*O*-isopropylidene-α-mannofuranose (ADAM) were co-polymerized with some acrylates and methacrylates, and were characterized by FT-IR, and thermal analysis.

2. Experimental

2.1. Materials

Glucose, mannose, cyclohexane, chloroform, ethyl acetate, hexane, butyl acrylate (AB), 2-ethylhexyl acrylate (EHA), 2-hydroxypropyl methacrylate (HPMA), benzoyl peroxide (POB) and lauroyl peroxide (POL) were purchased (bought) from Merck. Sulfuric acid and acetone were purchased from Carlo Erba, sodium bicarbonate from Chemapol, acryloyl chloride from Aldrich, sodium hydroxide and sodium sulfate from Acros Organics.

2.2. Glycomonomers synthesis and their copolymerization

Diacetoneglucose (DAG) and diacetonemannose (DAM) are the key intermediary in the synthesis of the glycopolymer and their were obtained according to the literature [7, 8].

These intermediaries were further reacted with acryloyl chloride (AC), in acetone (Scheme 1, Scheme 2), according to [9]:
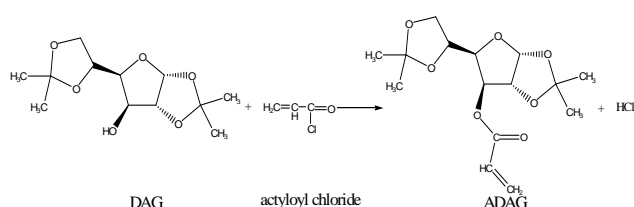
Scheme 1. The synthesis of 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene-α-glucofuranose (ADAG)
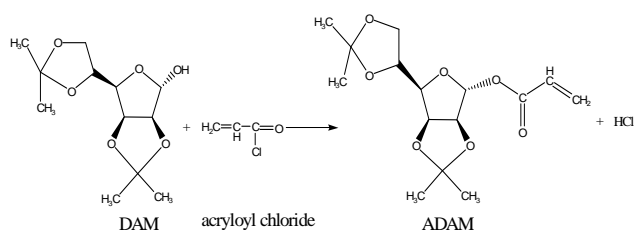
Scheme 2. The synthesis of 1-*O*-acryloyl-2,3:5,6-di-*O*-isopropylidene-α-mannofuranose (ADAM)

The glycomonomers, 3-*O*-acryloyl-1,2:5,6-di-*O*-isopropylidene-α-glucofuranose (ADAG), and 1-*O*-acryloyl-2,3:5,6-di-*O*-isopropylidene-α-mannofuranose (ADAM) were characterized using FT-IR and RMN spectroscopy (^{1}H-NMR and ^{13}C-NMR) analysis presented in a previous paper [10].

The copolymerization procedure of these glycomonomers, with AB, 2-EHA respectively 2-HPMA (molar ratio 1:2): the glycomonomer was dissolved in the co-monomer, then the initiator - benzoyl peroxide (POB) or lauroyl peroxide (POL) - was added (1% wt. from the mixture), and the mixture was stirred until the peroxide was dissolved.

2.3. IR spectroscopy

The FT-IR spectra were recorded on a Jasco FT/IR-410 spectrometer. The IR analyses were done using KBr pellets for solid samples and ATR DIAMANT cellule.

2.4. Thermogravimetric analyses

Thermogravimetrical analysis (TGA) were performed on TG 209 equipment (Netzsch) under nitrogen atmosphere and under dynamic conditions (with 2.5, 5, 7.5, 10 and 12.5°C/min from 20 to 500°C) in order to obtain the activation energy for the degradation processes and to study the thermal stability of the obtained products.

3. Results and Discussion

From the FT-IR spectra of the glycomonomers, ADAG and the ADAM, comparatively to FT-IR spectra of DAG and DAM, results that the absorption bands specific to OH groups were no longer present in the spectrum, while the intense absorption bands characteristic to the C=O and C=C groups appeared. The absorption bands characteristic to esters can also be identified [10, 11].

Figure 1 presents the IR spectra of copolymerized products starting from 3-O-acryloyl-1,2:5,6-di-O-isopropylidene-α-glucofuranose (ADAG) monomer. It can be observed that the double bond spectral band that appeared in the case of the glycomonomer is missing from the glycopolymer spectrum. This denotes that no unreacted monomer remained and the crosslinking process took place. Further, in figure 2 the IR sectra of 1-O-acryloyl-2,3:5,6-di-O-isopropylidene-α-mannofuranose (ADAM) co-polymerized with butyl acrylate (AB) and the homo-polymer – poly(n-butyl acrylate) is presented. With the increase of the molar ratios, the absorbtion bands characteristic to poly(n-butyl acrylate) are more intense. The same behavior has been also seen for the other copolymerized glycomonomers.
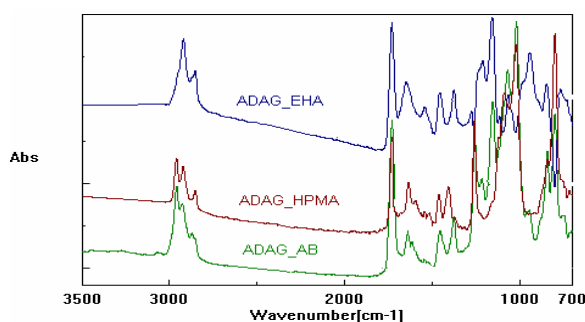

Figure 1. The FTIR spectra for copolymers of ADAG containing AB, EHA and HPMA (POB)
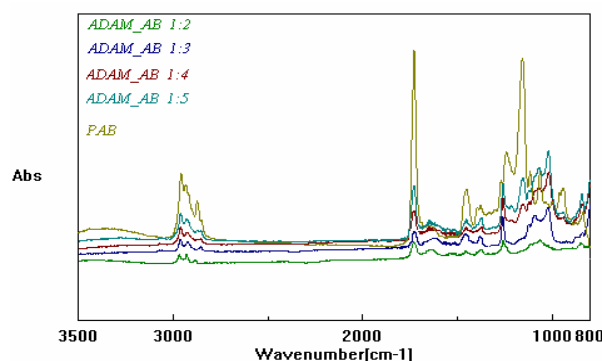

Figure 2. The FTIR spectra of ADAM copolymerized with AB (POB) at different molar ratios (1:2, 1:3, 1:4, 1:5) and homo-polymer AB

Table 1 presents the values of the wavenumbers for the IR spectral absorption of characteristic groups. We can see that in the case of the esters, as well as for the copolymers, the values of the signals suffer slight modifications.

101

TABLE 1. Wavenumber values for IR absorption of characteristic groups

Compund	CH$_2$			COO	C=C	OH
DAG	2984	2943	2902	-	-	3422
DAM	2980	2948	2898	-	-	3430
ADAG	2985	2945	2904	1730	1629	-
ADAM	2983	2950	2901	1731	1630	-
ADAG-AB	2959	2928	2872	1729	-	-
ADAG-EHA	2930	2957	2859	1730	-	-
ADAG-HPMA	2961	2920	2851	1734	-	-
ADAM-AB	2959	2928	2872	1730	-	-
ADAM-EHA	2930	2957	2859	1730	-	-
ADAM-HPMA	2960	2926	2856	1734	-	-

Copolymerization of ADAG and respectively ADAM with the mentioned acrylates and methacrylates (AB, 2-EHMA, 2-EHA and 2-HPMA) gives transparent polymers with different degrees of elasticity.

In order to determine the thermal stability of the copolymerized products, we performed thermogravimetrical analysis under nitrogen atmosphere and under dynamic conditions with 5°C/min heating rate, at temperatures ranging between 20 and 500˚C.

Figure 3 presents the TG curves for the copolymers obtained with AB at different molar ratios and for the homo-polymer – poly(n-butyl acrylate). It can be noticed that the thermal stability of the copolymers is lower compared to the thermal stability of the homo-polymer. The copolymerized product is degraded in two steps, while the correspondent homo-polymer is degraded in one step.

Figure 4 presents the TG curves for the copolymers of ADAM obtained with AB, EHA and HPMA and for the glycomonomer-1-O-acryloyl-2,3:5,6-di-O-isopropylidene-α-mannofuranose (ADAM).

Comparing the thermal stability of the copolymerized products with the thermal stability of the glicomonomers, it can be seen that the copolymers have better thermal stability.
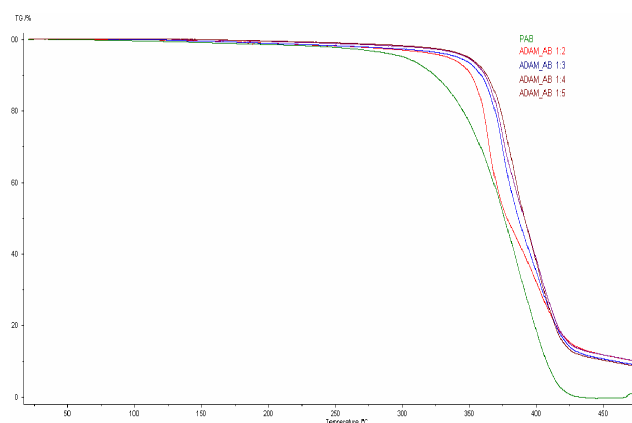
Figure 3. The thermograms of ADAM copolymerized with AB (POB) at different molar ratios (1:2, 1:3, 1:4, 1:5) and homo-polymer AB
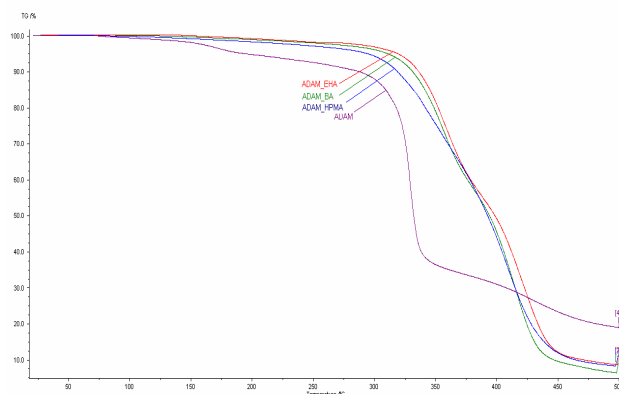
Figure 4. The thermograms of ADAM copolymers containing AB, EHA and HPMA (POB)

The thermal stability is better seen from table 2 and table 3 where the mass loss of copolymers, as well as the mass loss for the homo-polymers, are presented.

TABLE 2. The weight losses of ADAM copolymerized with AB (POB) at different molar ratios (1:2, 1:3, 1:4, 1:5) and homo-polymer AB

Sample	Weight loss (%)							
	20 - 100ºC		20 - 200ºC		20 - 300ºC		20 - 400ºC	
	POB	POL	POB	POL	POB	POL	POB	POL
AB	0.00	0.22	1.4	0.32	4.8	0.8	81.2	57.2
ADAM_AB 1:2	0.00	0.07	0.8	0.61	3.0	2.6	64.0	60.6
ADAM_AB 1:3	0.04	0.07	0.8	0.61	4.3	2.7	66.0	62.2
ADAM_AB 1:4	0.04	0.07	0.8	0.61	4.5	3.8	70.1	62.2
ADAM_AB 1:5	0.13	0.19	0.9	1.37	5.2	4.5	68.2	63.1

TABLE 3. The weight losses of copolymers and the glycomonomer

Sample	Weight loss (%)							
	20 - 100ºC		20 - 200ºC		20 - 300ºC		20 - 400ºC	
	POB	POL	POB	POL	POB	POL	POB	POL
ADAG	1.19		3.9		6.54		67.13	
ADAM	0.62		5.23		12.02		69.03	
ADAG_AB	0.17	0.26	1.12	1.53	3.03	3.39	67.83	67.28
ADAG_EHA	0.01	0.04	0.64	0.49	2.03	1.63	68.95	71.22
ADAG_HPMA	0.70	0.91	2.58	3.63	6.37	9.17	66.95	69.94
ADAM_AB	0.04	0.07	1.08	0.61	4.58	2.77	68.64	62.26
ADAM_EHA	0.21	0.20	0.33	0.46	2.10	3.40	60.25	63.15
ADAM_HPMA	0.35	0.57	2.06	2.67	9.36	10.79	68.20	77.16

102

Once more, the Kissinger method was employed to determine the activation energy for the degradation processes. From the diagram of the plots $\ln \beta/T_i$ versus $1/T_i$ (T_i – inflexion temperature) the activation energy was determined (Table 4.) [12].

TABLE 4. Activation energies of the copolymers calculated via Kissinger method

Sample	Ea [kJ/mol]			
	First step		Second step	
	POB	POB	POB	POL
ADAG_AB	155.821	155.821	183.664	189.218
ADAG_EHA	157.603	157.603	175.895	182.534
ADAG_HPMA	131.281	131.281	174.385	176.730
ADAM_AB	152.320	152.320	175.039	177.460
ADAM_EHA	153.534	153.534	175.807	178.019
ADAM_HPMA	91.320	91.320	174.186	174.319

Table 5 summarizes the activation energies, calculated using the Kissinger method, for copolymerization of ADAM with AB at different molar ratios. It can be observed that the activation energy increases along the increase of the acrylate quantity and the activation energy has bigger values for the second step of thermal decomposing.

TABLE 5. The activation energies for the copolymerization of ADAM with BA at different molar ratios

Sample	Ea [kJ/mol]			
	First step		Second step	
	POB	POB	POB	POL
ADAM_AB 1:2	152.320	151.921	175.807	167.460
ADAM_AB 1:3	151.971	151.173	184.296	209.637
ADAM_AB 1:4	121.143	146.351	177.445	179.166
ADAM_AB 1:5	118.482	138.960	179.482	196.218

4. Conclusions

Thermal properties of the copolymers obtained using different glycomonomers and different acrylate and methacrylate monomers have been investigated.

The thermal stability of the copolymerized products was higher than for the glycomonomers. However, the homopolymers showed better thermal stability than the crosslinked products, and the copolymerized products were degraded in two steps, while the correspondent homopolymer was degraded in one single step.

This behavior can be explained by the different chemical structure of the two products: the homopolymers contained the esteric bond only in a side group whereas the copolymers contained it in the main chain, so the thermal stability of the formerly was lower.

The structure of glycopolymers were confirmed by IR spectra. The double bond band from glycomonomer is missing from glycopolymer spectrum; this denotes that there is no unreacted monomer and that the crosslinking process took place. The activation energies for these copolymerization processes were calculated using Kissinger method. The results indicate that the activation energies increase with the increase of the molar ratios. Thus, the greater the molar ratio of the BA the harder the polymerization process occurs.

The importance of these copolymers is the key to the biodegradable polymer synthesis. The biodegradable polymers are indispensable in the modern society and their importance is continuously growing.

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