Determination of Enthalpy of Formation of the Graft Copolymer of Chitosan with Poly (2-Ethylhexyl Acrylate)

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This is the first study to determine the calorific value of the condensed graft copolymer of chitosan with poly (2-ethylhexyl acrylate) at T = 298.15 K by combustion calorimetry. The empirical data obtained were used to calculate standard enthalpy of combustion and enthalpy of formation of the condensed tested compound at T = 298.15 K. The resulting thermochemical properties were analyzed and compared with the data for previously studied chitosan copolymers and the starter chitosan.

Keywords: Chitosan; Poly (2-Ethylhexyl Acrylate); Enthalpy of Combustion; Enthalpy of Formation.

1. Introduction

A pressing task of today's material science is the creation of biodegradable polymers that can biodegrade to environmentally safe components under suitable conditions [1, 2]. Chitin and its deacetylated derivative, chitosan (CHI) hold a unique position among natural polymers. Chitosan, biocompatible and hypoallergenic, has antimicrobial properties for certain bacteria and molds, is readily degraded by natural factors. Due to multiple natural sources and useful properties, chitosan can be produced on a large scale to create various multi-purpose materials, however, chitosan-based materials have low stress-strain performance [3-6].

Availability of reactive groups in the macromolecule and high complexing ability of chitosan allows to combine it with different biologically active substances and synthetic polymers, such as poly(2-ethylhexyl acrylate) (PEHA) [6]. Due to their stability, transparency, flexibility and relative inexpensiveness, polyacrylates are widely used in the industry for production of plexiglass, films, paints, adhesives, and impregnating solutions for paper, leather, wood, fabrics, etc. [7-9].

Combination of properties of chitosan and poly(2-ethylhexyl acrylate) compositions is promising for creation of a number of new purpose-made products that would combine and enhance properties of both components, allowing to improve chitosan stress-strain performance and create new materials based on compounds with known operational properties [10]. Block and graft copolymers of chitosan with acrylic series compounds can be used as the base for biodegradable film materials, gas-separation membranes and aqueous emulsion paints.

Existing literature contains data on thermodynamic and thermochemical properties of the starting chitosan [11-13] and poly(2-ethylhexyl acrylate) [14]. We [15, 16] have determined thermodynamic properties of chitosan and poly(D,L-lactide) copolymers. There are no thermochemical properties of the chitosan and poly(2-ethylhexyl acrylate) copolymer in the existing literature. Therefore, the purpose of this study is to determine the calorific value and to calculate standard enthalpy of combustion and enthalpy of formation of the condensed graft copolymer of chitosan with poly(2-ethylhexyl acrylate) at T = 298.15 K, and to compare the results with the data for previously studied copolymers of chitosan with poly(D,L-lactide) and the starting chitosan.

2. Experimental

2.1. Properties of the Sample under Study

Synthesis of graft copolymer of chitosan with poly(2-ethylhexyl acrylate) (CHI/PEHA) was performed using chitosan (*Bioprogress, OJSC, Russia*) with MM = 1.2·10^5 and deacetylation degree of 0.82. The CHI molecular mass was determined with an Ubbelohde-type capillary viscometer at room temperature.

Poly(2-ethylhexyl acrylate) (M_w = 1.56·10^6, M_n = 8.75·10^5) was obtained by polymerization of 2-ethylhexyl acrylate in closed glass bulbs at T = 333 K. PEHA molecular mass characteristics were determined by gel permeation chromatography at T = 423 K with tetrahydrofuran (THF) used as an eluent.

Graft polymerization of PEHA on CHI was performed using azobisisobutyronitrile (AIBN) as an initiating agent. Its weighted amount was preliminarily dissolved in the required volume of monomer

with dioxane, then mixed with 3% chitosan solution in 1.5% acetic acid. The process was conducted at T = 333 K for 4 hours with constant stirring. The [PEHA]/[CHI] ratio was changed from 0.1 to 0.26 (mol/base-mol), the [AIBN] initiating agent concentration = 0.01 mol/L, [dioxane] = 2.0 mol/L [10].

Formation of CHI/PEHA graft copolymer was proved by infrared spectroscopy (using a Perkin-Elmer spectrophotometer). The sample infrared spectrum shows a band consistent with fluctuation of PEHA functional groups: 1738 cm^{-1}.

The effectiveness and degree of PEHA grafting on CHI was assessed by extraction of homopolymers from the tetrahydrofuran reaction product in a Soxhlet extractor during 48 hours. The extraction showed the effectiveness of grafting, i.e., the ratio of the monomer quantity in the graft copolymer to the polymerized monomer quantity, of up to 95%.

The molecular mass of grafted PEHA chains was determined by breakdown of the chitosan part of $NaNO_2$ copolymers. The molecular mass distribution of grafted PEHA chains was determined by gel permeation chromatography at T = 313 K using a Shimadzu Prominence LC-20VP liquid chromatograph (M_n = 1.9¨10⁶, M_w = 2.4¨10⁶). A differential refractometer was used as the detector, THF was used as the eluent.

2.2. Measurement Equipment and Techniques

The enthalpy of combustion of the copolymer was determined using an improved B-08MA static bomb calorimeter [17]. The calorimetric system was calibrated using reference K-2 grade benzoic acid ($\Delta_c U$ = −26460.0 J/g by air weighing). The system caloric equivalent is W = 14805 ± 3 J/K with a double standard deviation from the average result of 0.02%. The sample was burned at oxygen pressure of 3×10^6 Pa in melted paraffin wax the presence of which provided a standard temperature rise in the

experiments while creating conditions for complete combustion of the starting sample weight. Gaseous combustion products were analyzed for CO_2 content, the quantity of which was used to calculate the weight of the substance test sample. Combustion completeness was determined by the absence of carbon monoxide in the combustion products by passing the tested gas through special indicator tubes.

3. Results and Discussion

The calorific value of the condensed CHI/PEHA copolymer at T = 298.15 K was calculated as an average result of six experiments. Calculation was performed for the following combustion reaction:

$C_{7.14}H_{12.9}O_{3.77}N_{0.82}$ (s) + 8.48O_2 (g) → 7.14CO_2 (g) + 6.45H_2O (l) + 0.41N_2 (g), (1)
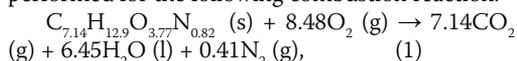
where bracketed letters indicate physical states of the reacting substances: s – solid, g – gas, l – liquid.

Under bomb calorimetry conditions, the calorific value $\Delta_c U$ of the tested copolymer sample was determined, experiment data are provided in Table 1. Standard enthalpy of combustion of the CHI/PEHA sample corresponds to enthalpy of reaction (1) under standard pressure and at temperature T = 298.15 K.

Based on the average value of $\Delta_c U$, molecular mass (M = 170.56 g/mol), with the Washburn correction and the correction for gas mole number variation, standard values of $\Delta_c U°$ and $\Delta_c H°$ were calculated for the condensed copolymer combustion reaction. The obtained experimental values of $\Delta_c H°$ were used to determine the enthalpy of $\Delta_f H°$ formation of the condensed copolymer at T = 298.15 K. The values of standard enthalpy of formation of liquid water (−285.830 ± 0.42 kJ/mol) and carbon dioxide gas (−393.51 ± 0.13 kJ/mol) required for the calculations were taken from the ref-

Table 1

Results of experiments for determination of the calorific value of the condensed CHI/PEHA graft copolymer at T = 298.15 K

m, g	ΔT, K	q_{par}, J	q_{ct}, J	q(HNO_3), J	q_c, J	−$\Delta_c U$, J/g
0,21911	2,56462	32987,5	41,3	4,80	9,83	22570,5
0,22113	2,56893	33002,1	39,5	4,98	10,3	22596,3
0,22955	2,56712	32781,3	47,5	5,27	10,6	22577,8
0,22724	2,57261	32914,1	38,7	5,10	10,1	22617,9
0,22341	2,56107	32833,2	42,2	4,69	10,2	22589,6
0,22691	2,56951	32890,2	38,5	5,39	10,8	22556,5
Average value: (22584.8 ± 17.7) J/g						

Legend: m is the burned substance mass, ΔT is the temperature rise during the experiment adjusted for heat exchange; q_{par}, q_{ct}, q(HNO_3), q_c are corrections for paraffin wax, cotton thread calorific value, energy of formation of the aqueous solution of HNO_3, and incomplete combustion of carbon, respectively; $\Delta_c U$ is the calorific value of the analyzed substance under bomb calorimetry conditions.

Table 2

Standard calorific values, enthalpy of combustion and enthalpy of formation of condensed chitosan copolymers analyzed in this and previous [16] studies at T = 298.15 K

Specimen	Gross formula	$\Delta_c U°$, kJ/mol	$-\Delta_c H°$, kJ/mol	$-\Delta_f H°$, kJ/mol
CHI/PEHA	$C_{7.14}H_{12.9}O_{3.77}N_{0.82}$	3849,6 ± 2,4	3853,0 ± 2,4	800,3 ± 2,4
CHI/PL (18.1 mol%)*	$C_{6.25}H_{10.7}O_{4.12}N_{0.82}$	3187,1 ± 2,3	3187,6 ± 2,3	801,1 ± 2,3
CHI/PL (22.5 mol%)*	$C_{6.23}H_{10.57}O_{4.12}N_{0.78}$	3157,8 ± 2,2	3158,2 ± 2,2	804,0 ± 2,2
CHI/PL (33.2 mol%)*	$C_{6.20}H_{10.2}O_{4.10}N_{0.67}$	3098,5 ± 2,4	3098,9 ± 2,4	798,6 ± 2,4
CHI*	$C_{6.3}H_{11.3}O_{4.15}N$	3291,7 ± 2,5	3292,3 ± 2,5	801,7 ± 2,5

* The data are from Ref. [16].

erence guide [18, 19]. The resulting values are provided in Table 2.

It seemed interesting to compare the values of enthalpy of formation of the CHI/PEHA copolymer with chitosan copolymers with polylactide (CHI/PL) analyzed by us previously [16] (Table 2). We found that the condensed copolymers and starting chitosan compared have the same enthalpy of formation at T = 298.15 K within the measurement accuracy. This may be due to formation of energetically similar conformations of macromolecules of copolymers and absence of intermolecular interaction.

Acknowledgment

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