



# Thermal studies on the starch-g-copolymers prepared from two terpene acrylate monomers under oxidative conditions

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Received: 4 September 2018 / Accepted: 19 January 2019 / Published online: 22 February 2019  
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## Abstract

The simultaneous thermal studies (TG/DTG/DSC) coupled with the FTIR analysis of the gaseous decomposition products created under oxidative heating of starch-g-poly(neryl acrylate) and starch-g-poly(geranyl acrylate) copolymers have been presented. To these studies, the copolymers with the following grafting percents ( $G$ ) were selected: starch-g-poly(neryl acrylate) copolymers:  $36.6 \pm 0.3\%$ ,  $40.3 \pm 0.4\%$ ,  $42.8 \pm 0.4\%$  and starch-g-poly(geranyl acrylate) copolymers:  $28.9 \pm 0.2\%$ ,  $32.4 \pm 0.6\%$ ,  $35.6 \pm 0.4\%$ . The performed tests proved that the thermal resistance of the copolymers was strongly dependent on their  $G$  values, despite a small difference in the  $G$  values between the samples. The slight increase (ca. 6.2–6.7%) in the  $G$  value caused the significant drop of the thermal stability of all the studied materials. The TG/DTG/DSC studies confirmed at least three-stage decomposition mechanism of the copolymers where simultaneous pyrolysis, oxidation, dehydration and decarboxylation processes took place. The TG/FTIR analyses showed the emission of various structure fragments; among them, one can mention the creation of some organic fragments such as aldehyde, acid, alkene, alkane, furan fragments,  $\text{CH}_4$  and inorganic species ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{O}$ ) as a result of the oxidative decomposition processes of the studied copolymers. In addition, the conducted studies demonstrated similar decomposition course and mechanism for both types of the copolymers, regardless of the monomer type used to the graft process.

**Keywords** Potato starch · Starch-g-copolymers · Geranyl acrylate · Neryl acrylate · TG/FTIR

## Introduction

The synthesis and the properties of starch graft copolymers obtained using various structure vinyl and meth(acryl) monomers have been extensively studied. Chemical modification of starch under the graft copolymerization processes allows achieving a large variety of novel, more environmentally-friendly materials with improved or modified properties than a raw starch which can be practically employed as plastics, stabilizers, compatibilizers, excipients for a drug delivery system, flocculants, heavy metal ion removal, waste water treatment, etc. Several examples which, however, do not exhaust the bibliographical references regarding the preparation of the starch

graft copolymers are highlighted below. Çankaya has reported the preparation of the graft copolymers obtained from starch methacrylate and *N*-cyclohexyl acrylamide or methyl methacrylate which may be applied for fabrication of optoelectronic devices [1]. Meshram et al. [2] have described the starch graft copolymers synthesized from the mixture of monomers such as styrene/methyl methacrylate or styrene/butyl acrylate suitable textiles application. Several authors have presented the synthesis and the properties of starch-g-polyacrylonitrile copolymers [3–9]. The studies on the starch-g-poly(methyl methacrylate) are widely described [10–15]. Also, the properties of starch-g-poly(vinyl acetate) are presented [16–19]. Starch/lactic acid graft copolymers [20–22], maleated thermoplastic starch-g-poly(lactic acid) [23], esterified maleic anhydride starch-g-poly(lactic acid) [24], hydroxyethyl starch-grafted-poly(lactide) [25], starch-g-poly(vinyl alcohol) [26], starch-g-poly(*n*-vinylimidazole) [27], carboxymethyl starch-g-poly(*N*-vinylimidazole) [28, 29] copolymers have been precisely studied. In addition, the copolymers received

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from potato starch and aromatic type meth(acrylate) monomers [30–36] and more, environmentally-friendly starch-g-poly(citronellyl acrylate) [37] and starch-g-poly(citronellyl methacrylate) copolymers [38, 39] under the free radical copolymerization have been presented.

One of the most important properties of any new, received materials are the thermal stability because it determines the application of the novel materials in the appropriate section of an industry. Generally, the thermal stability and the decomposition course of various origins materials are tested by the thermogravimetric analysis. This method permits the evaluation of initial decomposition temperatures, the maximum decomposition temperatures, the mass losses in each decomposition stage, residual mass, the amount of the residue, etc. It is a simple and fast method in order to verify the thermal properties of the studied compounds. This method is often connected with the spectroscopic methods which make it possible to specify the type of the volatiles emitted under decomposition of the heated compounds and thus their potential decomposition mechanism [40–47].

The present paper describes the oxidative thermal properties and the decomposition course of starch-g-copolymers prepared from two terpene acrylate monomers obtained from two geometric isomers of terpene alcohol: *cis*-3,7-dimethyl-2,6-octadien-1-ol (nerol) and *trans*-3,7-dimethyl-2,6-octadien-1-ol (geraniol) which are evaluated using the TG/DTG/DSC/FTIR-coupled method. The effect of the grafting percent and the structure of the copolymers on their thermal resistance, decomposition course and decomposition mechanism was specified.

## Experimental

### Materials

Starch-g-copolymers were prepared from potato starch and two terpene acrylate monomers under the graft copolymerization process applying the “grafting from” method. Terpene acrylate monomers were obtained from two geometric isomers of naturally occurring terpene alcohol: geraniol and nerol according to the method described in Refs. [33, 34, 38]. Potato starch (purity 97%) was extracted and purified from potato flour produced by Melvit S.A., Poland, according to the procedure described elsewhere [48]. It was composed of amylopectin (83%) and amylose (17%) which was determined by the technique described in Ref. [49]. To the thermal studies, the materials prepared during the listed below graft reaction conditions were selected, Table 1. Their structures were affirmed by the spectroscopic methods.

**Table 1** The grafting percent (%G) and grafting efficiency (%GE) of the selected materials

Copolymer no/starch to monomer ratios	GE/%	G/%
Geranyl acrylate		
Copolymer 1/1:0.25	72.5 ± 0.6	28.9 ± 0.2
Copolymer 2/1:0.75	76.9 ± 0.7	32.4 ± 0.6
Copolymer 3/1:1	79.0 ± 0.6	35.6 ± 0.4
Neryl acrylate		
Copolymer 4/1:0.25	94.4 ± 0.8	36.6 ± 0.3
Copolymer 5/1:1	90.2 ± 0.6	40.3 ± 0.4
Copolymer 6/1:1.5	90.7 ± 0.8	42.8 ± 0.4

The graft reaction conditions: starch-g-poly(geranyl acrylate) copolymers: the reaction temperature of 70 °C, the reaction time of 210 min, initiator (potassium persulfate) concentration of 2.5 mass%, rpm 300

Starch-g-poly(neryl acrylate) copolymers: the reaction temperature of 70 °C, the reaction time of 180 min, initiator (potassium persulfate) concentration of 2.0 mass%, rpm 300

Starch-g-poly(geranyl acrylate) copolymers: FTIR (KBr disk,  $\text{cm}^{-1}$ ): 3315 ( $\nu$  OH), 3010 ( $\nu$  =C–H), 2950 ( $\nu$  C–H), 2915 ( $\nu$  C–H), 2845 ( $\nu$  C–H), 1730 ( $\nu$  C=O), 1630 (moisture), 1437 ( $\delta$  C–H), 1375 ( $\delta$  C–H), 1147 ( $\nu$  C–O), 1051 ( $\nu$  C–O), 1008 ( $\nu$  C–O), 925 ( $\nu$  C–O), 835 ( $\gamma$  =CH), 760 ( $\gamma$  =CH);  $^{13}\text{C}$  CP/MAS NMR (75 MHz,  $\delta$  ppm): 174.1 (C=O), 141.5 (=C), 135.7 (=C), 122.5 (=CH), 117.5 (=CH), 100.7 (CH–O), 93.8 (CH–O), 80.2 (CH–O), 72.3 (C–O), 61.1 (CH<sub>2</sub>–O), 38.3–28.7 (CH<sub>2</sub>), 25.2 (CH<sub>3</sub>), 23.6 (C–CH<sub>2</sub>), 17.7 (CH<sub>3</sub>).

Starch-g-poly(neryl acrylate) copolymers: FTIR (KBr disk,  $\text{cm}^{-1}$ ): 3310 ( $\nu$  OH), 3010 ( $\nu$  =C–H), 2947 ( $\nu$  C–H), 2912 ( $\nu$  C–H), 2846 ( $\nu$  C–H), 1729 ( $\nu$  C=O), 1630 (moisture), 1435 ( $\delta$  C–H), 1371 ( $\delta$  C–H), 1147 ( $\nu$  C–O), 1053 ( $\nu$  C–O), 1008 ( $\nu$  C–O), 924 ( $\nu$  C–O), 835 ( $\gamma$  =CH), 758 ( $\gamma$  =CH);  $^{13}\text{C}$  CP/MAS NMR (75 MHz,  $\delta$  ppm): 174.3 (C=O), 141.6 (=C), 135.9 (=C), 122.6 (=CH), 117.2 (=CH), 100.6 (CH–O), 93.8 (CH–O), 80.5 (CH–O), 72.4 (C–O), 61.2 (CH<sub>2</sub>–O), 38.4–28.6 (CH<sub>2</sub>), 25.3 (CH<sub>3</sub>), 23.5 (C–CH<sub>2</sub>), 17.6 (CH<sub>3</sub>).

### Methods

The FTIR spectra of the prepared materials in the wavenumber region from 600 to 4000  $\text{cm}^{-1}$  and 4  $\text{cm}^{-1}$  resolution using KBr disk technique and the absorption mode on a FTIR Tensor 27, Bruker spectrometer, were gathered.

The  $^{13}\text{C}$  CP/MAS NMR spectra of the copolymers at the resonance frequency of 75.5 MHz on a Bruker Avance 300 MSL apparatus were collected.

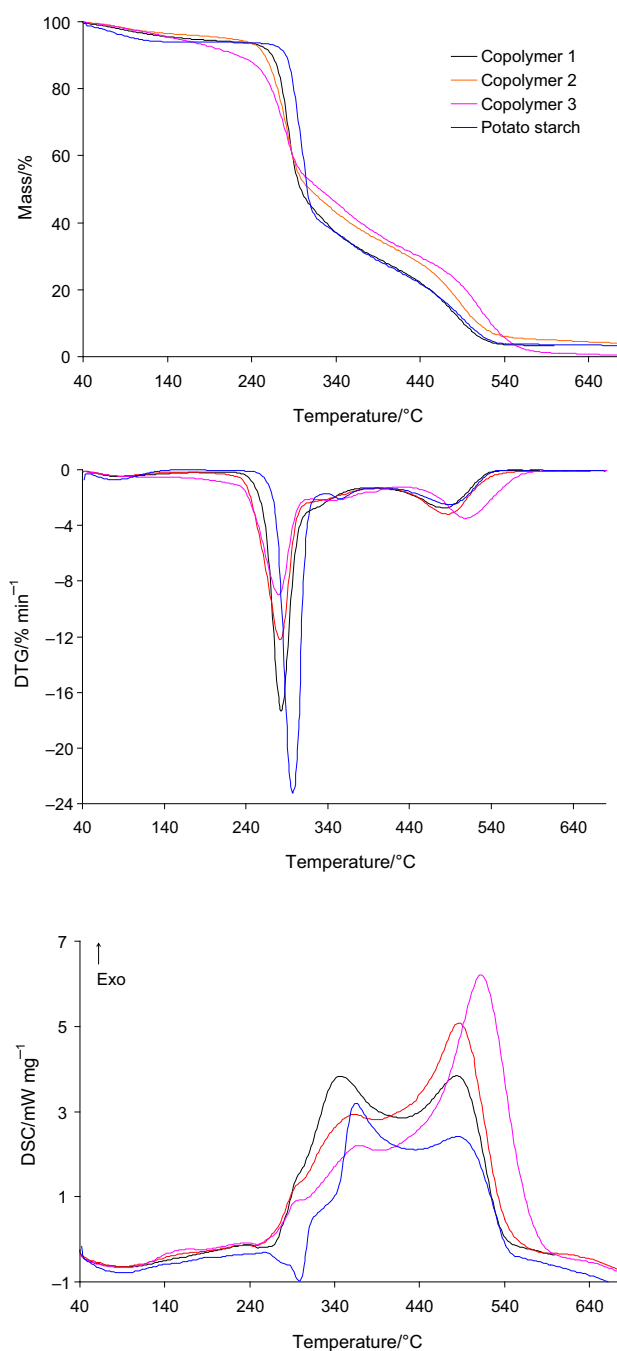
The thermal studies (TG–DTG–DSC) of the obtained starch-g-copolymers on a STA 449 Jupiter F1 Netzsch (Germany) apparatus have been made. The analyses in open Al<sub>2</sub>O<sub>3</sub> crucibles using sample mass ca. 10 mg under synthetic air atmosphere (flow rate 100 mL min<sup>-1</sup>) and at temperatures between 40 and 700 °C have been performed. The heating rate was 10 °C min<sup>-1</sup>. Each experiment was repeated three times. The TG–DSC instrument was calibrated with standard weights according to the manufacturer proceedings (temperature and sensitivity calibrations) and checked with calcium oxalate monohydrate. The Netzsch Proteus Thermal Analysis (version 5.2.) software was used to analyze the data.

The identification of the type of gaseous products emitted under the heating of the copolymers by a FTIR spectrometer Bruker TGA 585 (Germany) coupled with a STA instrument has been made. The FTIR spectra for the volatiles at the wave range of 600–4000 cm<sup>-1</sup> and 4 cm<sup>-1</sup> resolution were gathered.

## Results and discussion

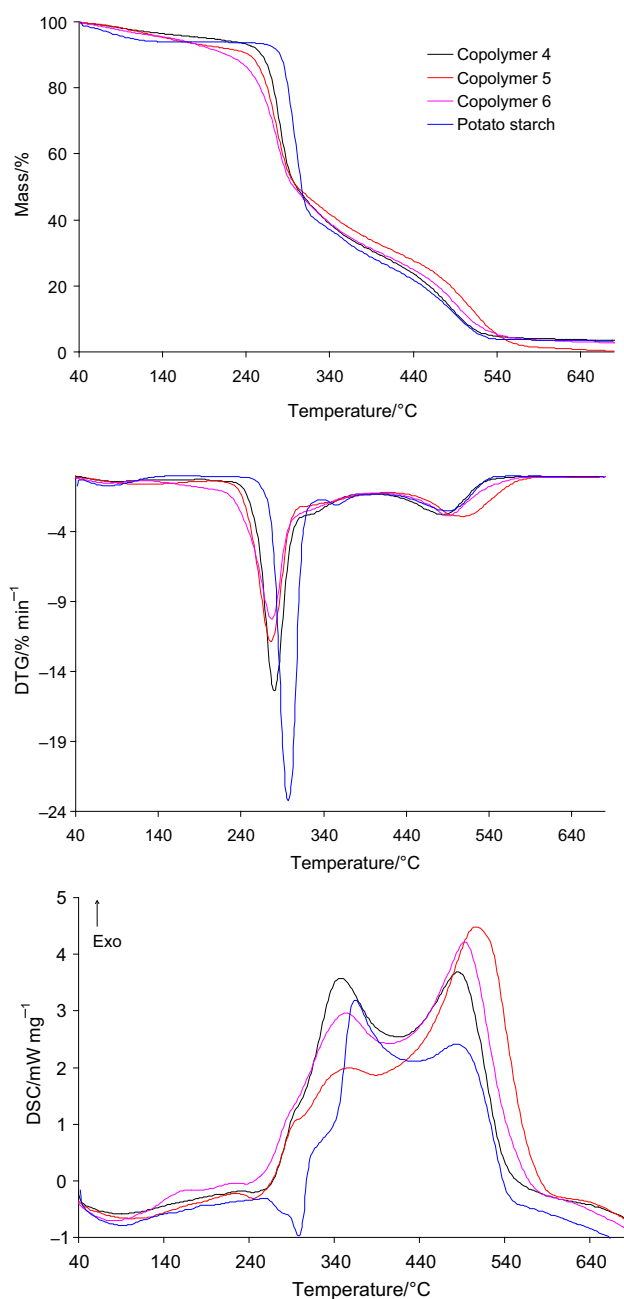
The course of the TG/DTG/DSC curves is presented in Figs. 1 and 2. However, the data read from the thermal curves are placed in Table 2. As it is well seen, similar course of the thermal curves for both types of starch-g-copolymers is observed. Generally, on the TG/DTG curves, four ranges of the mass loss are clearly indicated. First range of the mass loss with a mass loss below 8%, from 40 °C to ca. 150 °C with  $T_{\max 0}$  from 77 to 110 °C is appeared. On the DSC curves, only one endothermic signal is visible at this temperature range. This low-temperature signal as it is confirmed based on the gaseous FTIR spectra, as shown in Figs. 3 and 4, is due to the evaporation of the moisture from the studied materials. On the gaseous FTIR spectra, only the absorption bands characteristic for water vapor at the range of 1400–1800 cm<sup>-1</sup> and 3500–3900 cm<sup>-1</sup> are observed.

The heating of the copolymers above 200 °C in oxidative conditions causes their decomposition. For all the studied materials, the first decomposition stage composed of at least two steps at the temperature range between ca. 200 °C and ca. 420 °C and with  $T_{\max 1}$  from 277 to 283 °C is detected. The mass loss in this stage is comparable for all the studied materials and amounts from 62.2 to 66.3%. Moreover, as the %G increases, the copolymers are characterized by a less thermal stability as it is confirmed by their initial decomposition temperatures marked as 5% of the mass loss (IDT). For starch-g-poly(geranyl acrylate) copolymers, the initial decomposition temperatures for growing the %G are as follows: 266 °C, 250 °C and 231 °C. However, for starch-g-poly(neryl acrylate)



**Fig. 1** TG/DTG/DSC curves for starch-g-poly(geranyl acrylate) copolymers

copolymers, the corresponding IDT values are 256 °C, 248 °C and 210 °C, respectively. The differences in the %G are not dramatically high, but there are influenced considerably on the thermal resistance of the obtained materials. As it is visible, enhancement the %G values only ca. 6% causes the significant drop of IDT values. In the case of starch-g-poly(geranyl acrylate), the IDT values are ca. 35 °C lower for the %G which amounts to ca. 35.6% than those observed for the %G ca. 28.9%. On the contrary,



**Fig. 2** TG/DTG/DSC curves for starch-g-poly(neryl acrylate) copolymers

the IDT values are ca. 46 °C lower for starch-g-poly(neryl acrylate) copolymers with the %G which equals ca. 42% than those for the %G amounting to ca. 36.6%. Moreover, taking into account the values of the IDT, one can see that copolymers prepared from *trans* terpene acrylate isomer are characterized by higher thermal stability than those obtained from *cis* terpene acrylate isomer. It may be due to higher energy needed in order to decompose the bonds in the structure of the copolymers obtained from *trans* monomer as compared to the energy required to break the

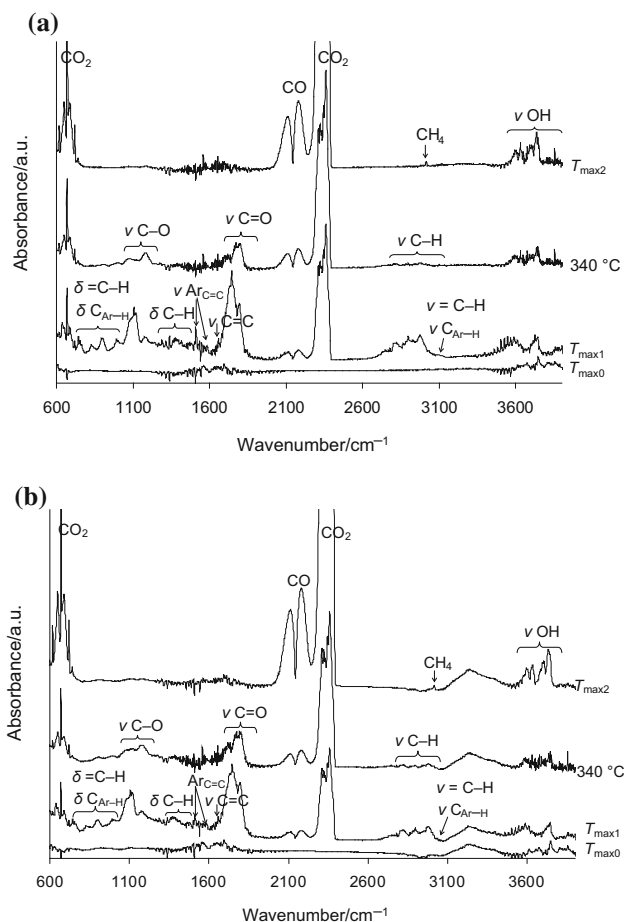
bonds in the structure of the copolymers prepared from *cis* monomer. Moreover, the IDT values for the copolymers are lower as compared to these values obtained for unmodified potato starch (ca. 280 °C). This can be because of higher energy is needed in order to break the glycosidic bonds in starch macromolecule than the bonds in the copolymer structure. What is interesting is that depending on the %G values, the differences in the rate of the decomposition of the copolymers are shown. The rate of the decomposition increases as the %G values of the copolymers decrease, as shown in Figs. 1 and 2. It means that the copolymers with lower %G values and unmodified potato starch decompose faster than these copolymers characterized by higher %G values. As it is well seen, the DSC curves show only exothermic signals at this temperature range. It may be the evidence of some chemical processes of the volatiles and residues with oxygen which lead to obtain different structure gaseous fragments. According to the gaseous FTIR spectra collected at  $T_{\max 1}$ , the emission of some organic fragments such as aldehyde, acid, alkene, alkane and furan fragments as a result of the oxidative decomposition of the copolymers is confirmed, as shown in Figs. 3 and 4. On the FTIR spectra, one can notice the absorption bands characteristic for the following vibrations: the stretching vibrations of OH (above  $3500\text{ cm}^{-1}$ ), the stretching vibrations of  $=\text{C}-\text{H}$  and  $\text{C}_{\text{Ar}}-\text{H}$  ( $3072\text{ cm}^{-1}$ ), the stretching vibrations of  $\text{C}-\text{H}$  ( $2720\text{--}2990\text{ cm}^{-1}$ ), the stretching vibrations of  $\text{C}=\text{O}$  ( $1722\text{--}1790\text{ cm}^{-1}$ ), the stretching vibrations of  $\text{C}=\text{C}$  ( $1656\text{--}1660\text{ cm}^{-1}$ ), the stretching vibrations of  $\text{C}=\text{C}_{\text{Ar}}$  ( $1500\text{ cm}^{-1}$  and  $1565\text{ cm}^{-1}$ ), the deformation vibrations of  $\text{C}-\text{H}$  ( $1350\text{--}1450\text{ cm}^{-1}$ ), the stretching vibrations of  $\text{C}-\text{O}$  ( $1074\text{--}1220\text{ cm}^{-1}$ ), the out-of-plane deformation vibrations of  $=\text{C}-\text{H}$  and  $\text{C}_{\text{Ar}}-\text{H}$  ( $720\text{--}982\text{ cm}^{-1}$ ). In addition to the above vibrations, the emission of  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is confirmed based on the presence of their characteristic bands.

However, the gaseous FTIR spectra gathered at the temperature (ca. 340 °C), where a small shoulder on the DTG curves is noticed, indicate on the emission of different structure volatile fragments than those created at  $T_{\max 1}$ . One can see the following characteristic absorption bands at wavelengths of approx.  $2720\text{ cm}^{-1}$  (the stretching vibrations of  $\text{C}-\text{H}$  in aldehyde groups),  $2777\text{--}2952\text{ cm}^{-1}$  (the stretching vibrations of  $\text{C}-\text{H}$ ), three non-well separated bands at  $1695\text{ cm}^{-1}$ ,  $1756\text{ cm}^{-1}$  and  $1790\text{ cm}^{-1}$  (the stretching vibrations of  $\text{C}=\text{O}$ ),  $1357\text{ cm}^{-1}$  (the deformation vibrations of  $\text{C}-\text{H}$ ),  $1072\text{--}1170\text{ cm}^{-1}$  (the stretching vibrations of  $\text{C}-\text{O}$ ), and  $809\text{--}983\text{ cm}^{-1}$  (the out-of-plane deformation vibrations of  $=\text{C}-\text{H}$ ). It indicates on the emission of aldehyde, alkane and alkene fragments under oxidative conditions as a result of the decomposition processes of poly(geranyl acrylate) and poly(neryl acrylate)

**Table 2** The data received from the thermal curves

Sample	$T_{\max 0}/^{\circ}\text{C}$	$\Delta_{m0}/\%$	$T_{\max 1}/^{\circ}\text{C}$	$\Delta_{m1}/\%$	$T_{\max 2}/^{\circ}\text{C}$	$\Delta_{m2}/\%$	rm/%
Copolymer 1	92	5.8	283	65.2	483	25.7	3.3
Copolymer 2	88	4.3	282	62.4	487	28.5	4.8
Copolymer 3	94	6.0	280	62.8	509	30.1	1.1
Copolymer 4	91	4.8	280	65.1	484	26.0	4.1
Copolymer 5	110	7.5	277	62.2	508	29.1	1.2
Copolymer 6	77	4.0	278	66.3	490	26.2	3.5
Potato starch	79	6.1	297/356	67.1	492	23.3	3.5

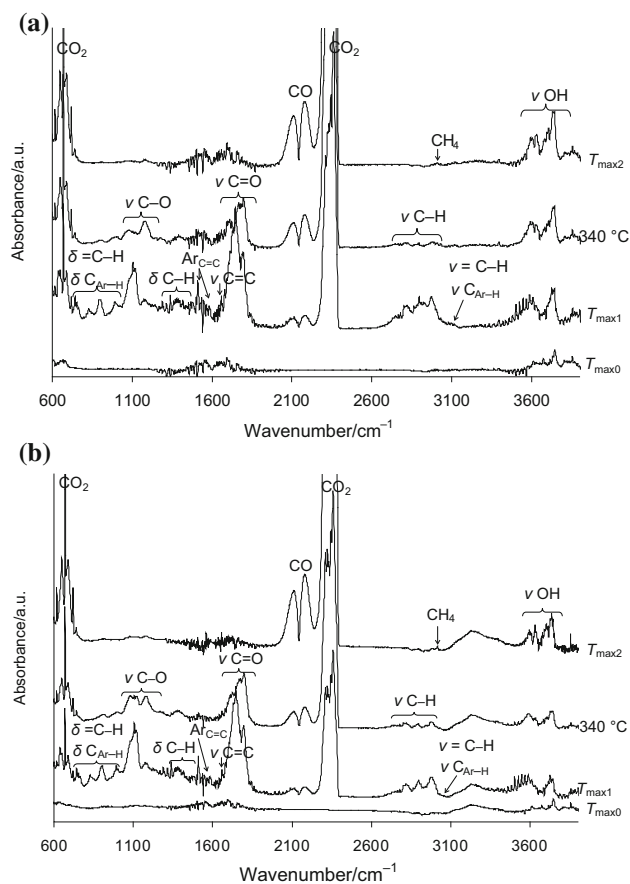
rm residual mass at 640 °C



**Fig. 3** The gaseous FTIR spectra collected under oxidative decomposition of starch-g-poly(geranyl acrylate) copolymers: **a** copolymer 1, **b** copolymer 3

chains. In addition, a high emission of  $\text{CO}_2$  (the bands at  $670\text{ cm}^{-1}$  and at  $2330\text{--}2365\text{ cm}^{-1}$ ),  $\text{CO}$  (the bands at  $2000\text{--}2200\text{ cm}^{-1}$ ) and  $\text{H}_2\text{O}$  (the bands above  $3500\text{ cm}^{-1}$ ) confirms the oxidation and decarboxylation processes of the intermediate decomposition gaseous fragments, as shown in Figs. 3 and 4.

The second decomposition stage spreads from the temperature ca.  $400\text{--}610\text{ }^{\circ}\text{C}$ . This decomposition stage is



**Fig. 4** The gaseous FTIR spectra collected under oxidative decomposition of starch-g-poly(neryl acrylate) copolymers: **a** copolymer 4, **b** copolymer 6

described by one, symmetrical DTG signal which happens at  $T_{\max 2}$   $483\text{--}509\text{ }^{\circ}\text{C}$ . The position of this signal depends on the copolymer type and its %G. The mass loss in this stage is comparable for all the studied materials and hesitates from 25.7 to 30.1%. If one have a look at the DSC curves, one can see only exothermic signals within this decomposition stage. It could be an indication on further reactions of the volatile fragments and/or residues with oxygen at higher temperatures. It causes almost full decomposition of the studied materials; only minor amount

of carbon residues is indicated (1.1–4.8%). As main gaseous products CO<sub>2</sub>, CO and H<sub>2</sub>O are created as it is confirmed from the gaseous FTIR spectra. The results indicate on a complex decomposition mechanism of the studied materials and prove that regardless of the type of monomer (*cis* or *trans*), the decomposition course and decomposition mechanism are similar.

## Conclusions

In this paper, the studies on the thermal oxidative resistance and oxidative decomposition mechanism of two types of the copolymers prepared under the graft reaction of potato starch and monomers synthesized from two geometric isomers of naturally occurring terpene alcohols (nerol—*cis* isomer and geraniol—*trans* isomer) and methacryloyl chloride have been presented. The thermal properties have been determined using the TG/DTG/DSC method. The oxidative decomposition mechanism has been evaluated involving the TG/FTIR-coupled method. The copolymers with the following grafting percent values (*G*) were selected to the above experiments: starch-g-poly(neryl acrylate) copolymers 36.6 ± 0.3%, 40.3 ± 0.4%, 42.8 ± 0.4% and starch-g-poly(geranyl acrylate) copolymers: 28.9 ± 0.2%, 32.4 ± 0.6%, 35.6 ± 0.4%, respectively. The conducted tests led to the following observations and results:

- The differences in the *G* values between the samples were little; however, the growth of the *G* values caused the substantial fall of the oxidative thermal stability of the copolymers. The thermal stability for starch-g-poly(neryl acrylate) copolymers decreased by 46 °C for the copolymer with the *G* value equal to 42.8 ± 0.4% as compared with the thermal stability of the copolymer with the *G* value equal to 36.6 ± 0.3%. Meanwhile, the oxidative thermal resistance for starch-g-poly(geranyl acrylate) copolymer with the *G* equal to 35.6 ± 0.4% was ca. 35 °C lower than this observed for the copolymer with the *G* equal to 28.9 ± 0.2%;
- Generally, all the studied copolymers decomposed at least three stages under oxidative conditions;
- The first decomposition stage composed of at least two steps happened between ca. 200 and ca. 420 °C. The mass loss in this stage was significant (62.2–66.3%), and it was connected with the emission of aldehyde, acid, alkene, alkane, furan fragments, CO<sub>2</sub>, CO, and H<sub>2</sub>O as a results of the simultaneous pyrolysis, oxidation, dehydration and decarboxylation processes of potato starch, poly(neryl acrylate) and poly(geranyl acrylate) chains;

- The second decomposition stage was observed at the temperature range of ca. 400–ca. 610 °C and the mass loss from 25.7 to 30.1%. Mainly, the creation of inorganic species such as CO<sub>2</sub>, CO, H<sub>2</sub>O and very small amounts of CH<sub>4</sub> was emitted which was due to the oxidation processes of the formed volatiles and residues.

It is therefore concluded that starch-g-poly(neryl acrylate) copolymers were less thermally stable materials under the heating in the presence of air atmosphere than starch-g-poly(geranyl acrylate) copolymers. However, their thermal decomposition course and decomposition mechanism were almost similar.

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