

Thermogravimetric and FTIR studies of chitosan blends

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Abstract

Results of spectrophotometric and thermogravimetric studies of chitosan (CH) blends with polyvinyl alcohol (PVAL), starch (S) and hydroxypropylcellulose (HPC) obtained by casting from solutions in the form of transparent films containing 0–1.0 weight fraction of CH were discussed. Blends containing S are homogeneous only in the case of low-weight fraction of S (to 0.3).

On the basis of results of thermodegradation in dynamic and isothermal conditions, thermal stability of the tested systems was estimated. Thermogravimetric measurements in dynamic conditions were carried out in the temperature range of 100–450 °C at constant heating rate 15 °C/min. From thermogravimetry (TG) and DTG curves the activation energy and characteristic parameters of degradation of the tested blends were determined. The observed growth of activation energy and T_p —temperature of initial weight loss, T_{max} —temperature of maximal rate and C_e —degree of conversion at the end of the measurement (at temperature 450 °C) along with the increase of polymer fraction (HPC and S) in the CH blend provides an evidence of improved thermal stability of the systems tested.

Investigations in isothermal conditions in air at temperature from 100 to 200 °C confirmed appreciable improvement of CH thermal stability in the blends being tested.

Infrared spectroscopic analysis of the blends showed a distinct stabilization of the process of chain scission. In the band at 1080 cm^{-1} associated with absorption in $-\text{C}-\text{O}-\text{C}-$ group during degradation of the blends at temperature 200 °C much smaller decrease due to molecular scission were observed than in the case of pure CH.

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1. Introduction

In view of a growing amount of wastes from man-made fibers, research projects are concentrated now on searching for polymer materials which would be man- and environment-friendly and characterized by a definite lifetime. Their degradation in various environmental conditions leads to a destruction of chains by breaking, splitting of fragments of the main chain or side constituents and release of volatile products.

For many years, chitosan (CH) being a deacetylated form of chitin which occurs in various ecosystems has aroused great interest of researchers. Because of its unique properties [1–5] such as bioactivity or biodegradability [6–8], it finds application in many areas of man's life and health [9–12]. The search for new applications calls for developments in the production methods, investigations of the structure [5,13] and degradability of CH and blends that contain CH [14–19].

The study aims at the estimation of thermal stability of biodegradable blends of CH with polyvinyl alcohol (PVAL), starch (S) and hydroxypropylcellulose (HPC)

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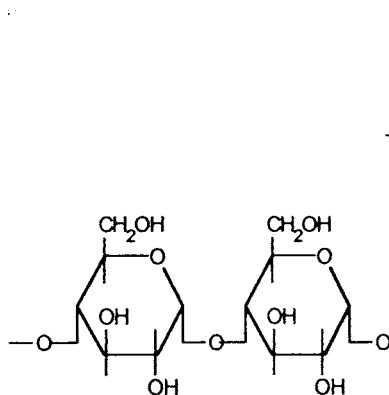
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obtained from a solution in the form of transparent, homogeneous films. To record the process of thermal degradation of CH and its blends, the methods of thermogravimetry (TG) and infrared spectroscopy (FTIR) were used. The analysis of results was used to describe the degradation kinetics of CH and its blends. Important elements of the kinetic model of degradation are the values of activation energy and reaction order.

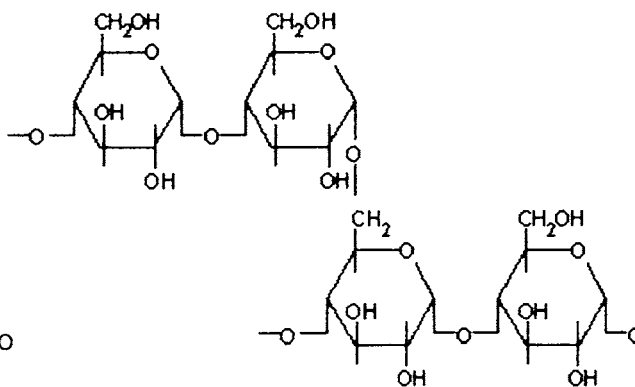
$$DD = \frac{x}{x + y}$$

where x is the number of deacetylated monomeric units, and y is the number of chitin monomeric units.

S, potato starch was a commercial product. It is a recoverable biopolymer composed of amylopectin and amylose



amylose

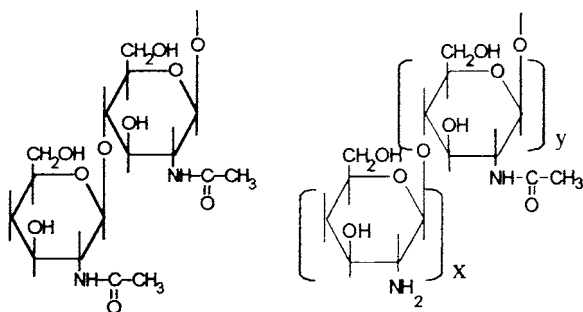


amylopectin

2. Experimental

2.1. Materials used

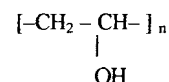
CH (poly-2-aminoglucose) of deacetylation degree $DD = 78\%$ and molecular weight $M = 2.1 \times 10^5$, was produced by the Sea Fishery Institute in Gdynia. It is a biodegradable natural copolymer obtained by chitin modification



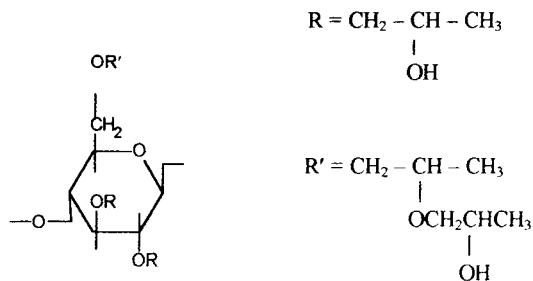
chitin

chitosan

PVAL of molecular weight $M = 7.2 \times 10^4$ (Polskie Odczynniki Chemiczne, Gliwice). It is a synthetic polymer with the structural formula



HPC of molecular weight $M = 1.0 \times 10^5$, produced by SIGMA-ALDRICH, Steinheim.



2.2. Blends preparation

The CH/S, CH/PVAL and CH/HPC blends were obtained in the form of films by mixing water solu-

tions of S, PVAL and HPC with CH solution in 1% acetic acid and casting. The CH/PVAL and CH/HPC blends are transparent homogeneous films in whole composition of 0–1.0 weight fraction of CH. Blends containing S are homogeneous only in a low-weight fraction of S (to 0.3). A morphological structure of CH/S blends of various S content is shown in Fig. 1.

2.3. Measuring methods

2.3.1. TG

Changes which take place during thermal degradation of the investigated polymer systems were observed while performing thermogravimetric measurements. For this purpose a Mettler thermobalance (TGA/SDTA 851e) was used to carry out

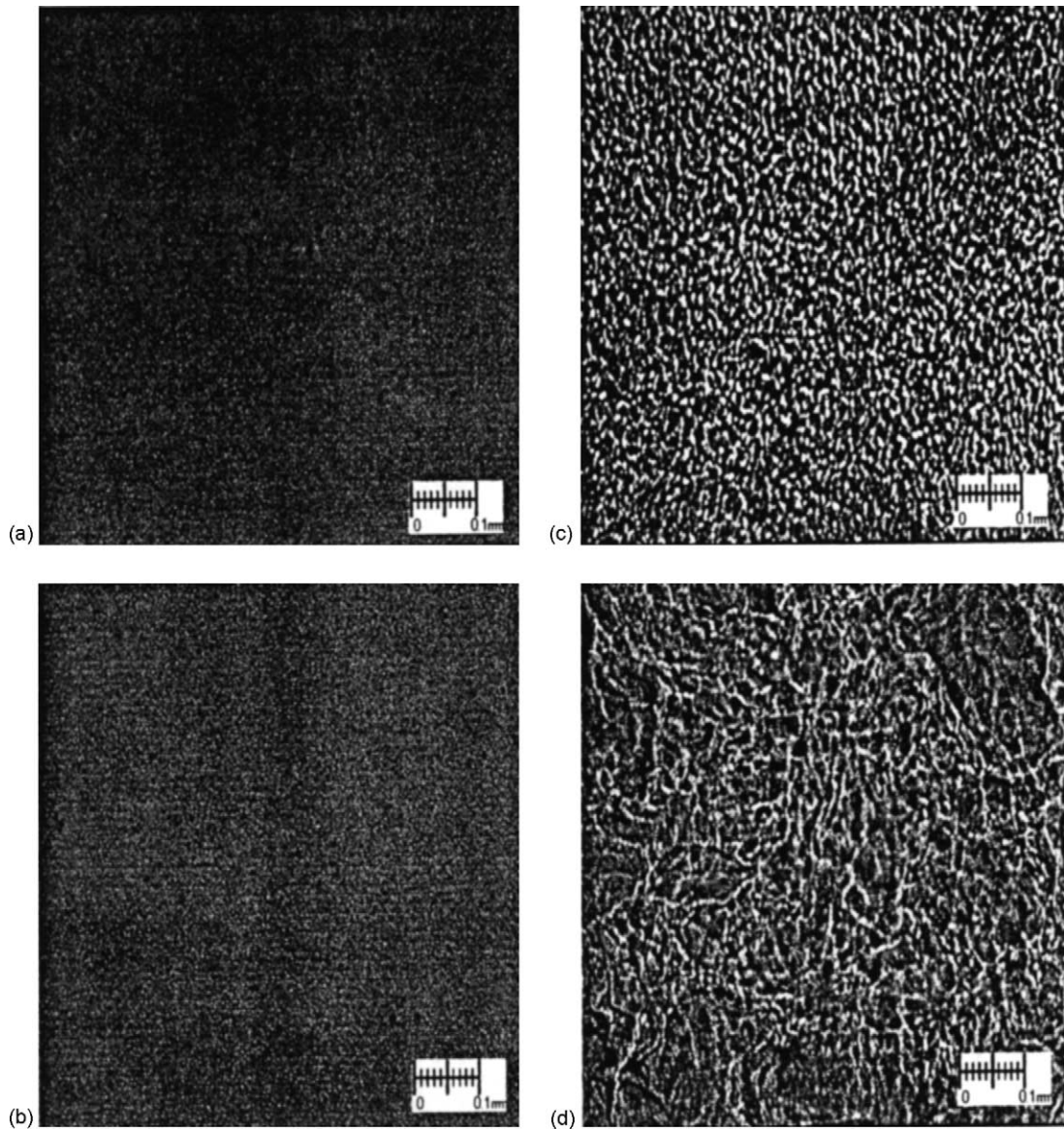


Fig. 1. Micrographs of CH/S blends of various weight fraction w_f of S: (a) 0; (b) 0.2; (c) 0.8; (d) 1.

measurements in the air, at a constant heating rate $\beta = 15^\circ\text{C}/\text{min}$ in the range of temperature from 100 to 450°C .

The CH blends were also subjected to thermodegradation in the air at different temperatures from 100 to 200°C (isothermal TG in a special oven) while analyzing mass loss and structural changes.

2.3.2. FTIR

The information on structural changes which took place during the degradation, was collected in the FTIR analysis using Genesis II spectrophotometer (Mattson). All spectra were recorded at ambient temperature at the resolution of 4 cm^{-1} and 16-times scanning. Films used in the infrared tests were about $10\ \mu\text{m}$ thick. The FTIR analysis was based on the identification of absorption bands concerned with the vibrations of functional groups present in CH, S, HPC, PVAL macromolecules [15,19–21]. The bands wave number (cm^{-1}) were as follows:

1. 3450: OH hydroxyl group.
2. 3360: NH group-stretching vibration.
3. 2920, 2880, 1430, 1320, 1275, 1245: symmetric or asymmetric CH_2 stretching vibration attributed to pyranose ring.
4. 1730: carbonyl group vibration.
5. 1660: C=O in amide group (amide I band).
6. 1560: NH-bending vibration in amide group.
7. 1590: NH_2 in amino group.
8. 1415, 1320: vibrations of OH, CH in the ring.
9. 1380: CH_3 in amide group.
10. 1255: C–O group.
11. 1150–1040: –C–O–C– in glycosidic linkage.
12. 850, 838: CH_3COH group.

3. Results and discussion

3.1. Interactions between components

Formation of homogeneous CH blends with PVAL, S and HPC is a result of strong interactions by hydrogen bonds between the functional groups of the blend components in which amino and amide groups present in CH take part. The analysis of FTIR spectra of the blends enables these interactions to be identified [22,23].

On the basis of the harmonic oscillator model the reduction in force constant Δf can be represented by Eq. (1) [24]

$$\Delta f = f_{\text{nb}} - f_{\text{b}} = \frac{\mu(v_{\text{nb}}^2 - v_{\text{b}}^2)}{4\pi^2} \quad (1)$$

where $\mu = m_1m_2/(m_1 + m_2)$ corresponds to the reduced mass of the oscillator, v the oscillating frequency and f is the force constant. The subscripts b and nb denote bonded and non-bonded oscillators, respectively. The reduction of force constant brought about by some interaction is directly related to the frequency (or wave number) shift of stretching vibrations. Thus, the lower the peak frequency the stronger is the interaction. Also absorbance is dependent on the strength of the interaction.

When analyzing FTIR spectra of CH blends, it was found that there were evident changes of the wave number and absorbance in the bands corresponding to mobility in amino ($1/\lambda = 1585\text{ cm}^{-1}$) and amide ($1/\lambda = 1660\text{ cm}^{-1}$) group. Susceptibility to the formation of intermolecular complexes within both functional groups induces changes in intermolecular vibrations.

Fig. 2 illustrates changes in the wave number and absorbance in the region of amino and amide group vibrations with an increase of CH fraction in the blend. The presence of PVAL or HPC decreases remarkably the bond strength in the amino group band. In connection with this a decrease of the wave number occurs and changes of absorbance are not proportional to changes of the blend composition. Positive deviation from Lambert–Beer's law denotes that the system is less rigid and more susceptible to vibrations. In the case of amide group an increase of the wave number (much lesser changes) and negative deviation (in the case of PVAL and S) from the Lambert–Beer's law caused by molecule rigidity is observed.

3.2. Dynamic TG

Figs. 3–5 show TG and DTG curves obtained for CH/S, CH/PVAL and CH/HPC blends. DTG curves for the CH/S blends are characterized by a single peak corresponding to the maximum degradation rate at temperature T_{max} , which is a result of similar values of the temperatures of both components (Fig. 3). The

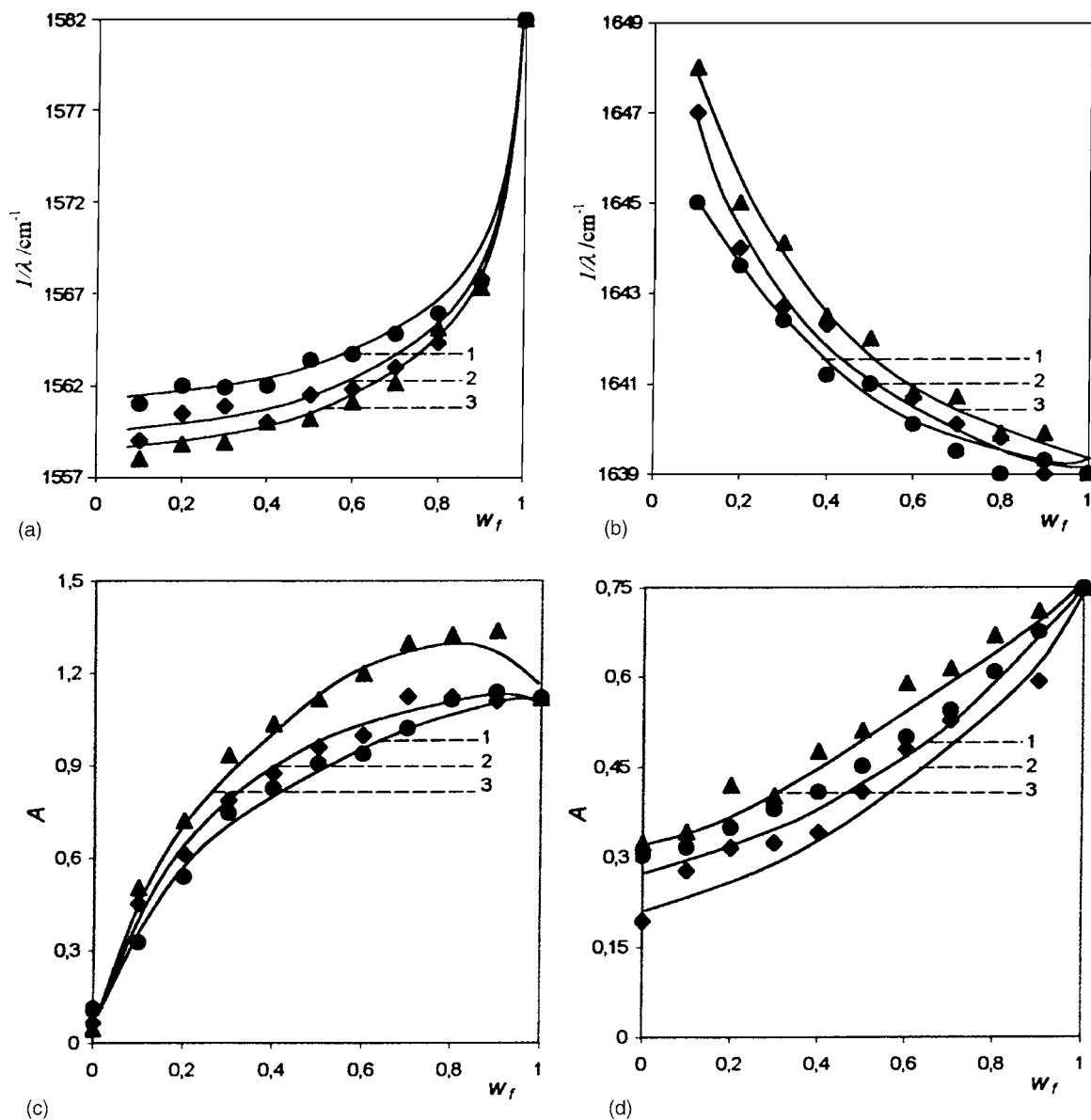


Fig. 2. (a), (b) denotes wave numbers ($1/\lambda$) and (c), (d) denotes absorbance (A) for amine ($1/\lambda = 1590 \text{ cm}^{-1}$ (a, c)) and amide bands ($1/\lambda = 1660 \text{ cm}^{-1}$ (b, d)) in the blends. The curves (1) CH/S, (2) CH/PVAL, and (3) CH/HPC vs. weight fraction of CH w_f is also shown.

other blends: CH/PVA; CH/HPC (Figs. 4 and 5) reveal two stages (two peaks) of fast thermal degradation, characteristic for both components.

On the basis of analysis of thermogravimetric curves some characteristic parameters of blend thermodegradation were determined

- T_p : temperature of the degradation onset was determined on the basis of the deviation of curve TG from the initial run for zero value of the conversion degree C_0 ;
- T_{\max} : temperature of the maximum of degradation rate (from DTG);

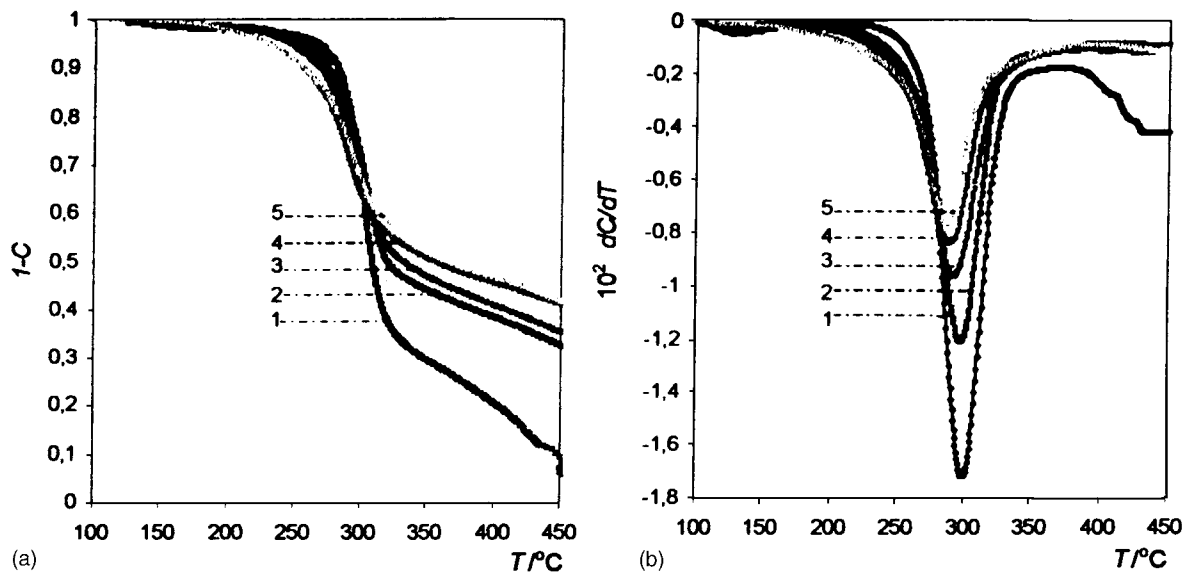


Fig. 3. (a) TG, (b) DTG are the curves obtained for CH/S system. Curves from 1 to 5 represent various weight fractions of S which are as follows: (1) 1; (2) 0.8; (3) 0.6; (4) 0.2; (5) 0.

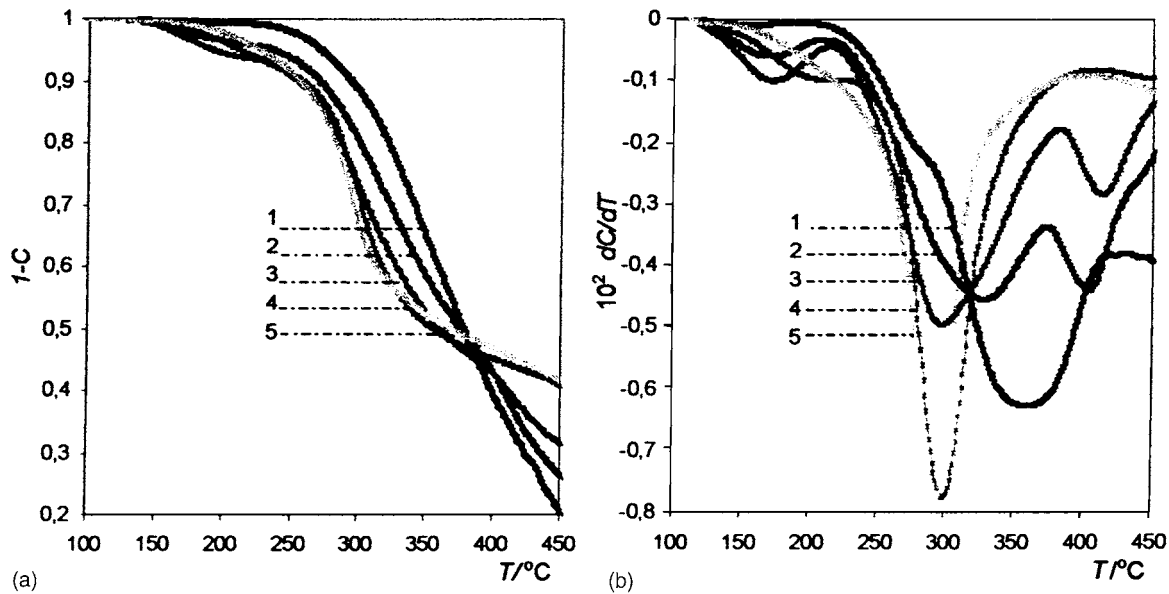


Fig. 4. (a) TG, (b) DTG are the curves obtained for CH/PVAL system. Curves from 1 to 5 represent various weight fractions of PVAL which are as follows: (1) 1; (2) 0.8; (3) 0.6; (4) 0.2; (5) 0.

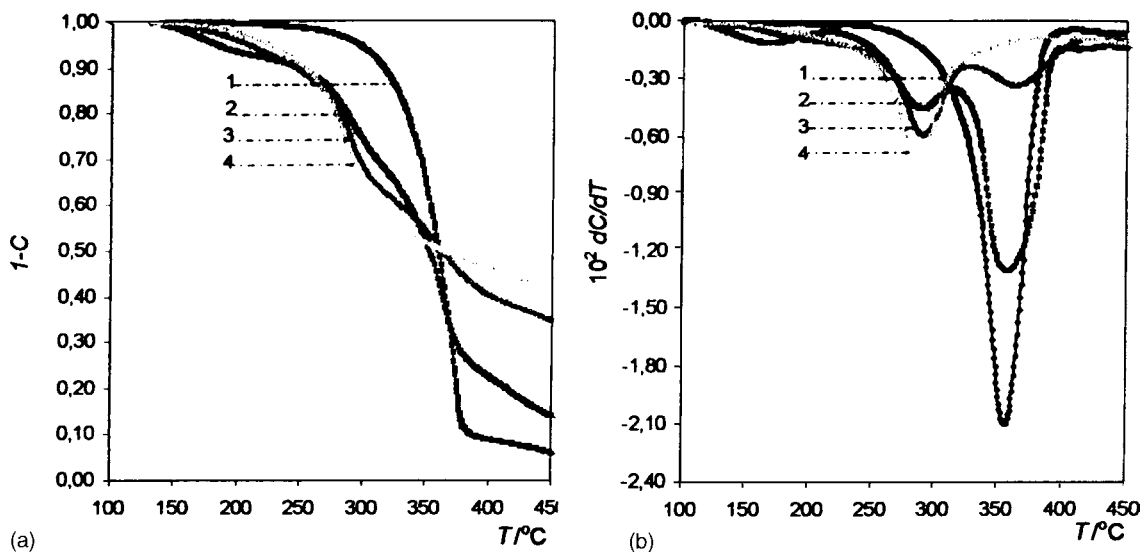


Fig. 5. (a) TG, (b) DTG are the curves obtained for CH/HPC system. Curves from 1 to 5 represent various weight fractions of HPC which are as follows: 1 (1); (2) 0.6; (3) 0.2; (4) 0.

- C_e : degree of conversion at the end of the measurement (at temperature 450 °C).

Fig. 6 shows a relation which enables a comparison of T_p , T_{max} and C_e of tested blends: CH/S; CH/PVAL; CH/HPC. With an increase of polymer fraction in the CH blend an increase of T_p and C_e (approximately linear) is observed. However, temperature T_{max} corresponding to the maximum rate of thermal decomposition shifts towards higher values of the peak representing CH decomposition at lower temperature and S, HPC and PVAL observed at higher temperature. This provides evidence of some improvement of CH stability in the tested blends.

To analyze the thermogravimetric results, Freeman–Carroll’s method [25] was used. Eq. (2) shows the applied relation between $\Delta \log(dC/dT)$, $\Delta \log(1 - C)$ and $\Delta(1/T)$

$$\begin{aligned} \Delta \log \frac{dC}{dt} &= \Delta \log \varphi \frac{dC}{dT} \\ &= n \Delta \log(1 - C) - \frac{E_a}{2.3R} \Delta \left(\frac{1}{T} \right) \end{aligned} \quad (2)$$

where n is the reaction order, E_a the activation energy, φ the heating rate, T the temperature, $1 - C$ the weight loss, C the degree of conversion, dC/dT the rate of conversion, and R is the gas constant.

Using the Freeman–Carroll’s method it should be borne in mind that it does not give precise results at the stage of initiating and completing the reaction ($1 - C < 0.2$ and $1 - C > 0.8$, respectively).

When determining changes in the logarithms of (dC/dT) and $(1 - C)$ close to T_{max} , one obtains from the graph of dependence of $\Delta \log \varphi(dC/dT)/\Delta \log(1 - C)$ on $\Delta(1/T)/\Delta \log(1 - C)$ (which should be a straight line) giving values for E_a and n (from the slope and ordinate, respectively). An example of this dependence is illustrated in Fig. 7a.

Activation energy of the tested systems determined by Freeman–Carroll’s method (near both peaks corresponding to the maximum degradation rate of CH, PVAL and HPC) was compared with the values calculated by Fuoss method [26] which enabled activation energy to be determined from Eq. (3) knowing only the values of $(dC/dT)_{max}$, T_{max} and $(1 - C)_{max}$

$$E_a = nRT_{max}^2 \left(\frac{dC}{dT} \right)_{max} \frac{1}{(1 - C)_{max}} \quad (3)$$

As a reaction order, the values of n found by Freeman–Carroll’s method, were assumed in these calculations.

Figs. 7b and 8 show E_a as a function of weight fraction of CH in the blend with S, HPC and PVAL. The character of changes in the values of E_a determined by

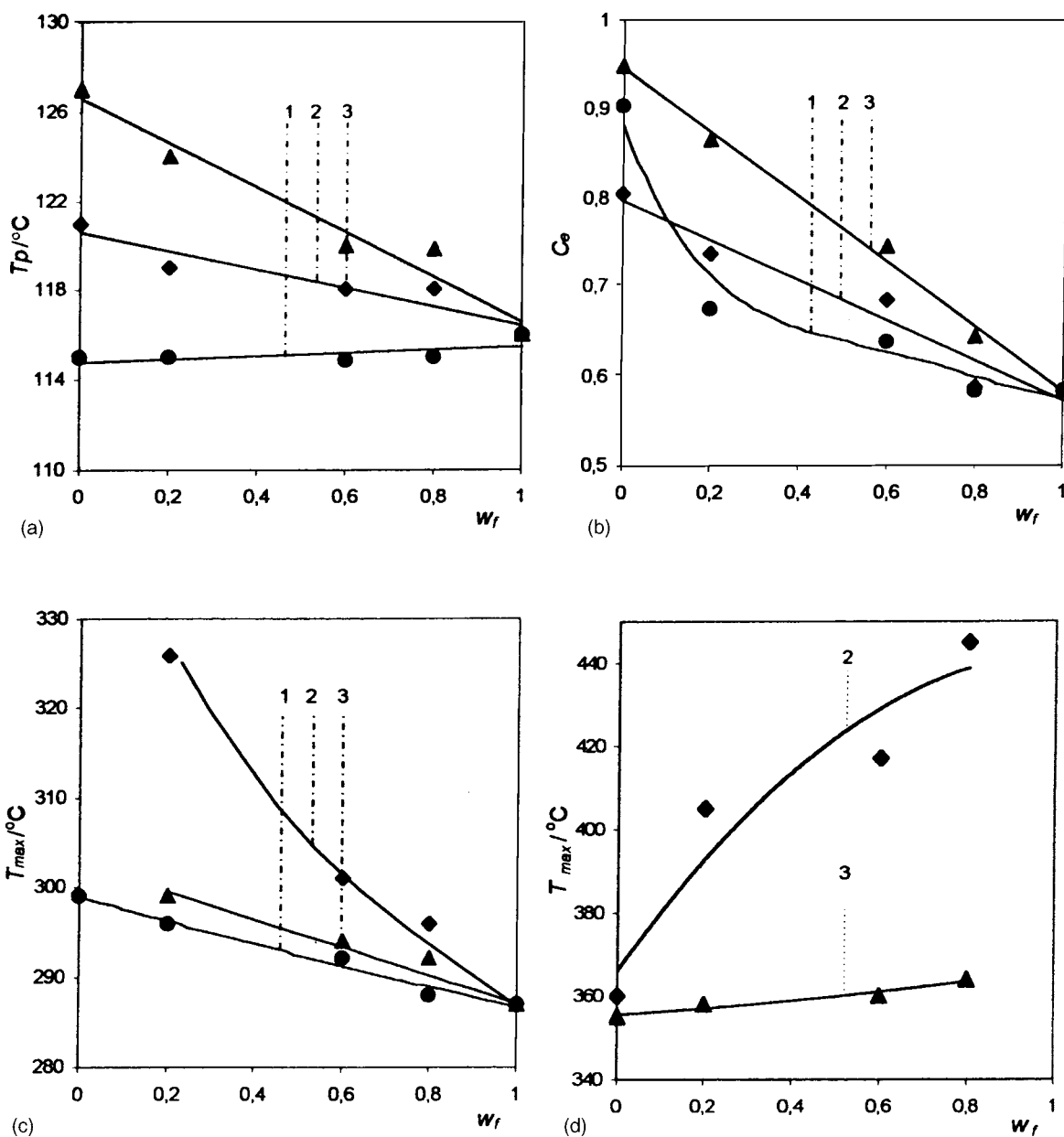


Fig. 6. (a) T_p , (b) C_e , (c) T_{max} (CH) and (d) T_{max} (PVAL, HPC) vs. weight fraction w_f of CH in the blends. The curves denote the following: (1) CH/S; (2) CH/PVAL; (3) CH/HPC.

the two methods as a function of blend composition is similar. Activation energy of pure blend components are as follows:

$$E_a(\text{CH}) = 1.66 \times 10^5 \text{ J/mol} (1.47 \times 10^5 \text{ J/mol}),$$

$$E_a(\text{S}) = 2.4 \times 10^5 \text{ J/mol} (2.25 \times 10^5 \text{ J/mol}),$$

$$E_a(\text{HPC}) = 2.24 \times 10^5 \text{ J/mol} (1.94 \times 10^5 \text{ J/mol}),$$

$$E_a(\text{PVAL}) = 0.89 \times 10^5 \text{ J/mol} (0.86 \times 10^5 \text{ J/mol}).$$

The slightly lower values obtained by the Fuoss method, are given in brackets. The lowest activation energy was observed in PVAL, while the highest one

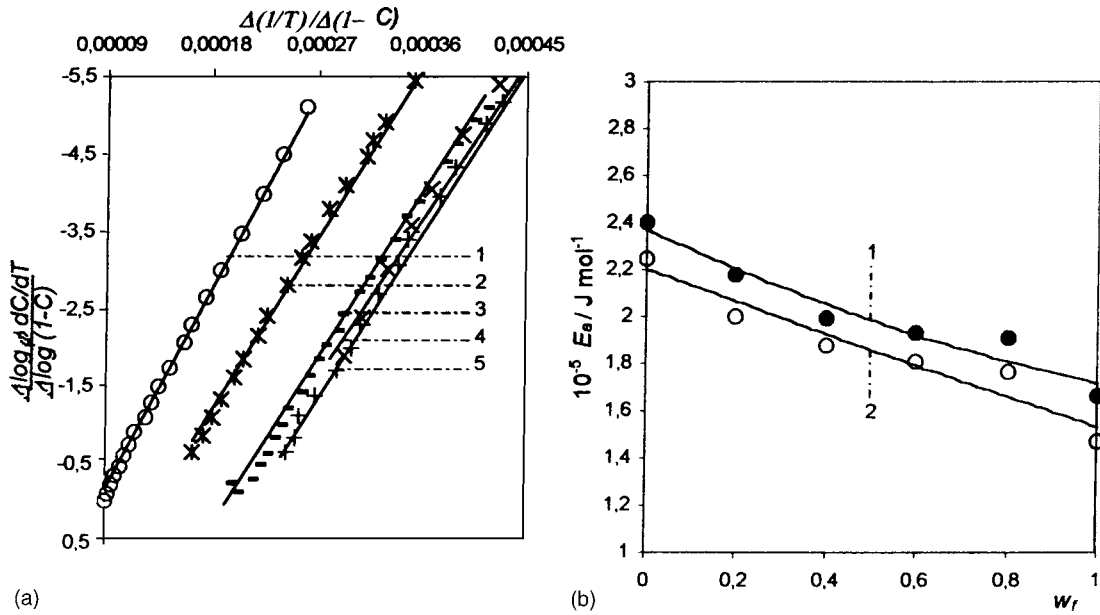


Fig. 7. (a) Plots $\Delta \log \phi(dC/dT)/\Delta \log(1 - C)$ vs. $\Delta(1/T)/\Delta \log(1 - C)$ of the S/CH system. Curves from 1 to 5 represent various weight fraction of S: (1) 1; (2) 0.8; (3) 0.6; (4) 0.2; (5) 0. (b) Activation energy E_a of thermodestruction of the S/CH system obtained by using methods: (1) Freeman–Carroll; (2) Fuoss plotted vs. weight fraction of CH w_f .

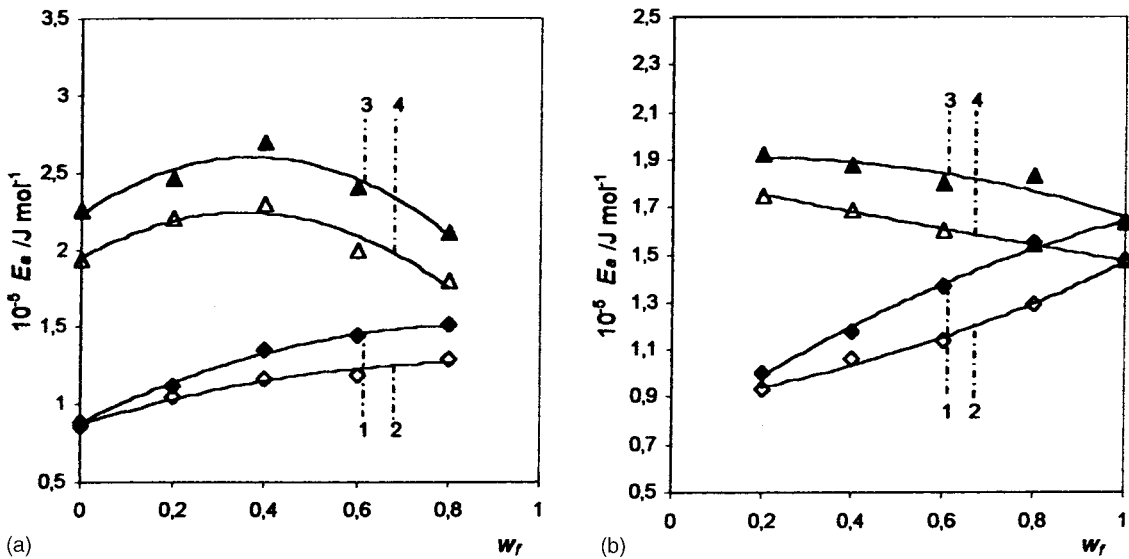


Fig. 8. Activation energy E_a of the thermodestruction of CH blends with PVAL (1, 2) and HPC (3, 4) obtained from methods: Freeman–Carroll (1, 3) and Fuoss (2, 4) vs. weight fraction of CH w_f . (a) PVAL and HPC, and (b) CH components.

in S. When analyzing the dependence of E_a in the blend components on the blend composition, it was found that HPC and S improved CH stability (Figs. 7b and 8b (3, 4)) which was also reflected by the increase of T_{max} (Fig. 6). The presence of CH in the blend has an influence on the increase of E_a in PVAL and HPC (Fig. 8a) up to 40% of its content in the blend.

3.3. Isothermal TG

The isothermal TG was made at $T = 200^\circ\text{C}$ below the weight loss observed initially in the dynamic measurements.

Fig. 9 presents the weight loss of the blends versus time of degradation in air atmosphere at 200°C . After 5 h of degradation, the weight loss of CH sample is

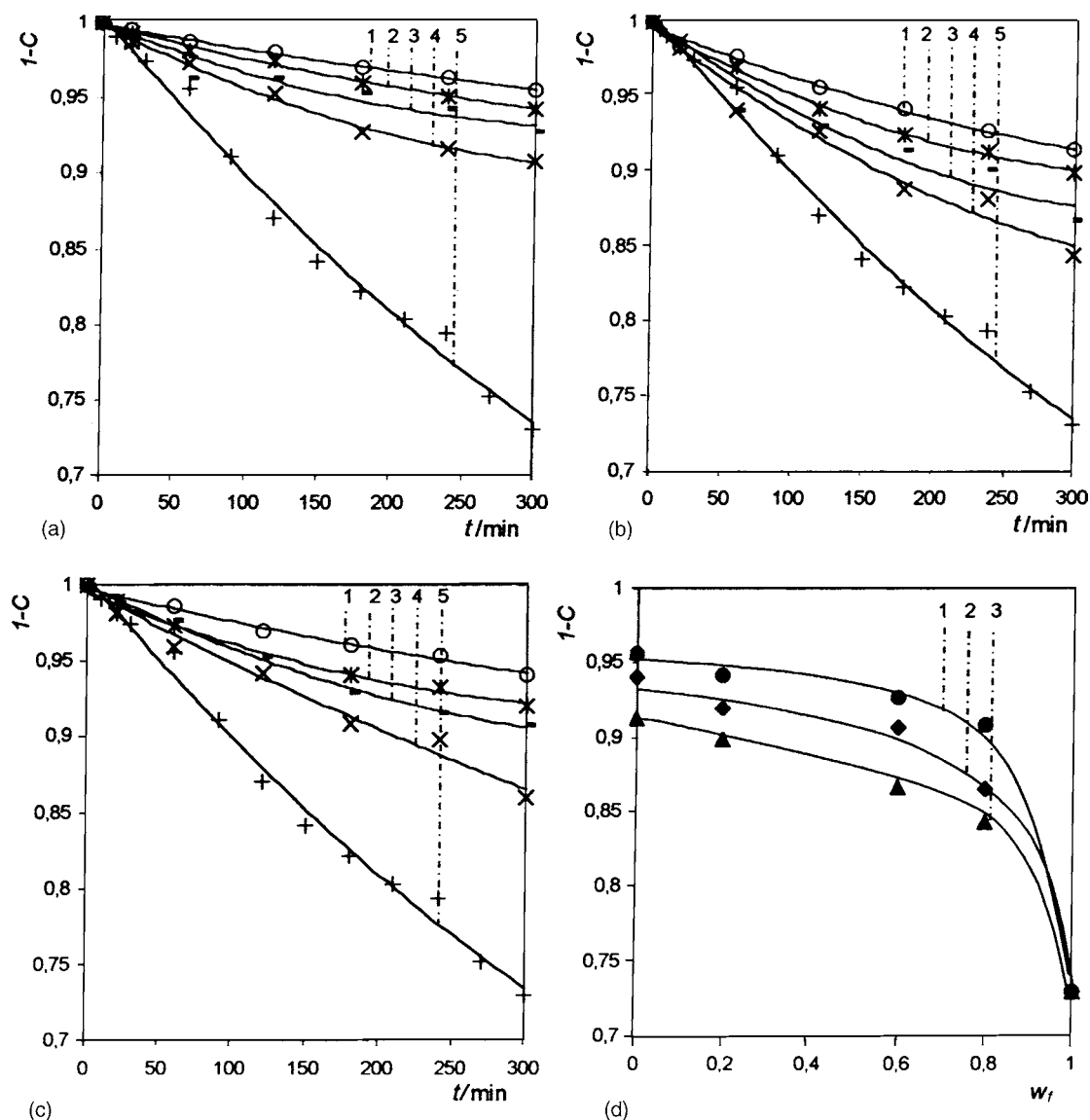


Fig. 9. Weight loss ($1 - C$) of the: (a) CH/S; (b) CH/PVAL; (c) CH/HPC blends of various weight fraction w_f of CH. Curves: (1) 0; (2) 0.2; (3) 0.6; (4) 0.8; (5) 1. (d) Weight loss of the blends: (1) CH/S; (2) CH/PVAL; (3) CH/HPC after 5 h degradation at $T = 200^\circ\text{C}$.

the highest and equal to 27%, in comparison with pure S (4%), HPC (6%) and PVAL (7%). The weight loss versus weight fraction of CH in the blends is plotted in Fig. 9d.

Positive deviation from the linear plot clearly indicates improving thermal stability of CH in the blends in the case of thermal degradation under study.

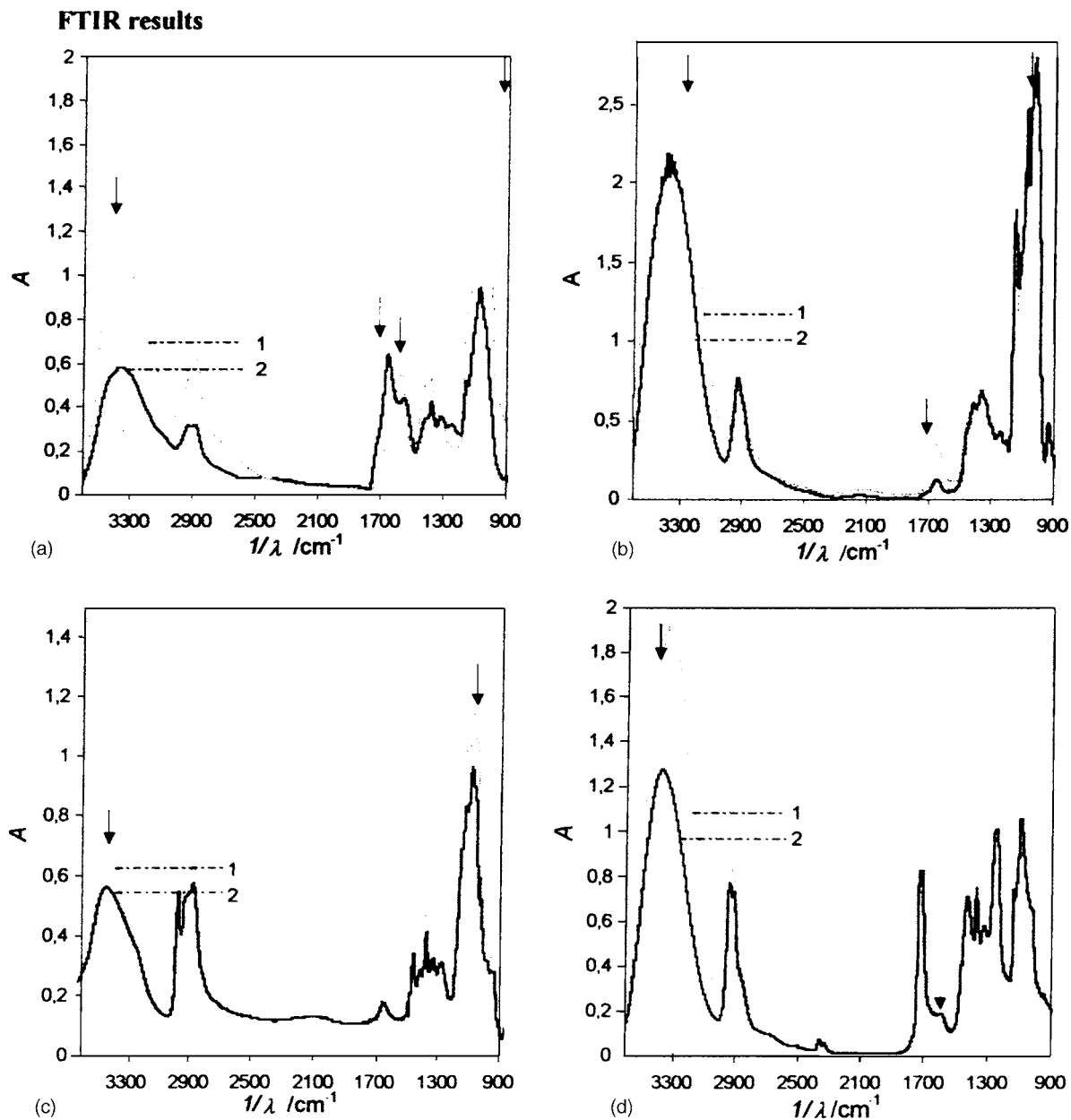


Fig. 10. FTIR spectra of pure components: (a) CH; (b) S; (c) HPC; (d) PVAL. Curves: (1) before thermal degradation; (2) after thermal degradation (5 h at $T = 200^\circ\text{C}$). Arrows show characteristic bands.

3.4. FTIR results

Fig. 10 presents FTIR spectra of pure components before and after thermal degradation at 200 °C in air atmosphere during 5 h. The most pronounced effect

of the thermal destruction of CH on presented spectra is a decrease of band absorbance at 1150–1040 cm^{-1} corresponding to deforming vibrations of $-\text{C}-\text{O}-\text{C}-$ groups. It indicates the molecular chain scission of CH. Changes at 3450 cm^{-1} correspond to the loss of

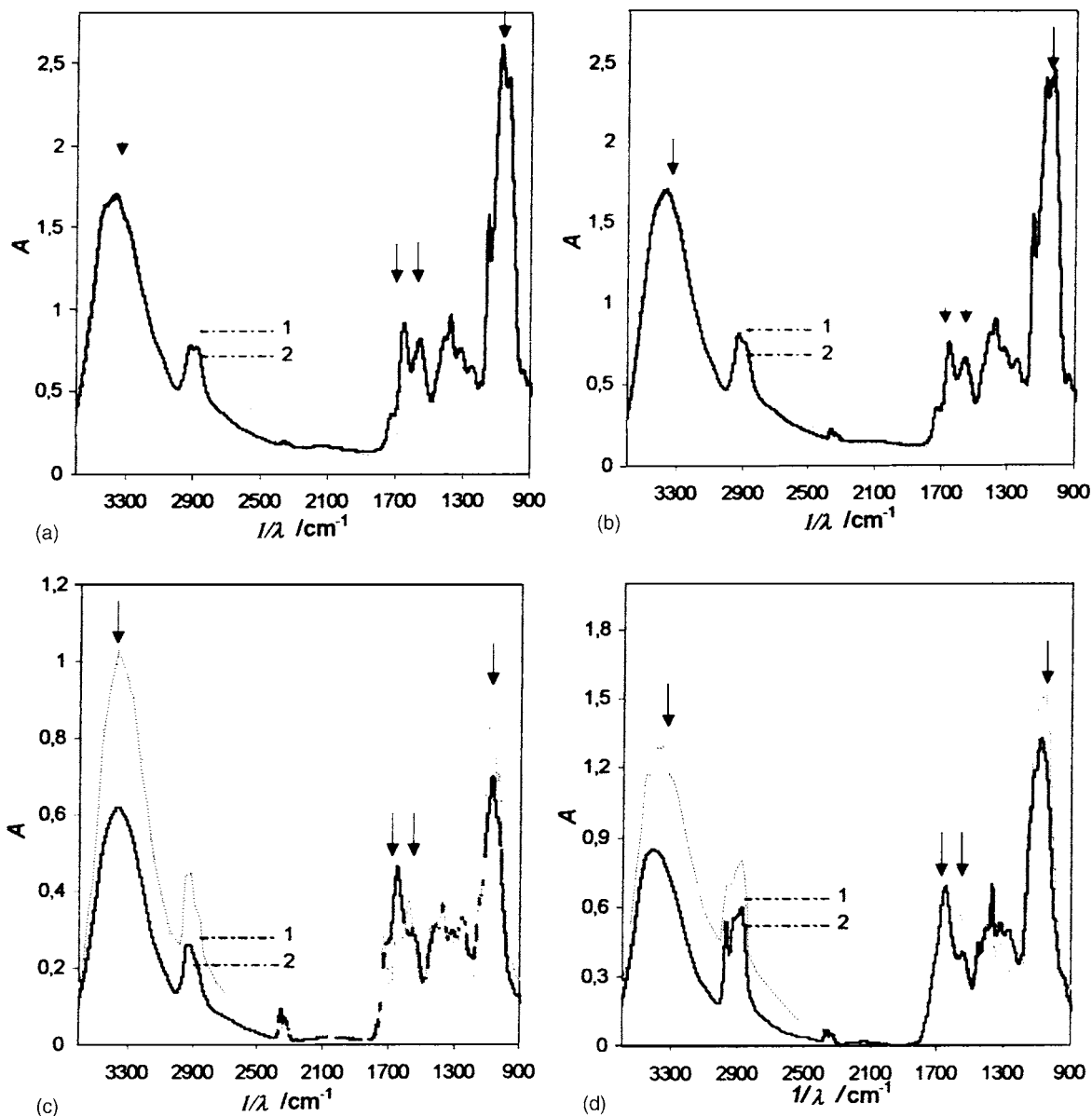


Fig. 11. FTIR spectra of some CH blends with (a) and (b) S, $w_f = 0.6$ and 0.8 , (c) PVAL, $w_f = 0.6$, (d) HPC, $w_f = 0.6$. Here w_f indicates weight fraction of chitosan. Arrows indicate on characteristic bands. Curves: (1) before degradation; (2) after degradation (5 h at $T = 200^\circ\text{C}$).

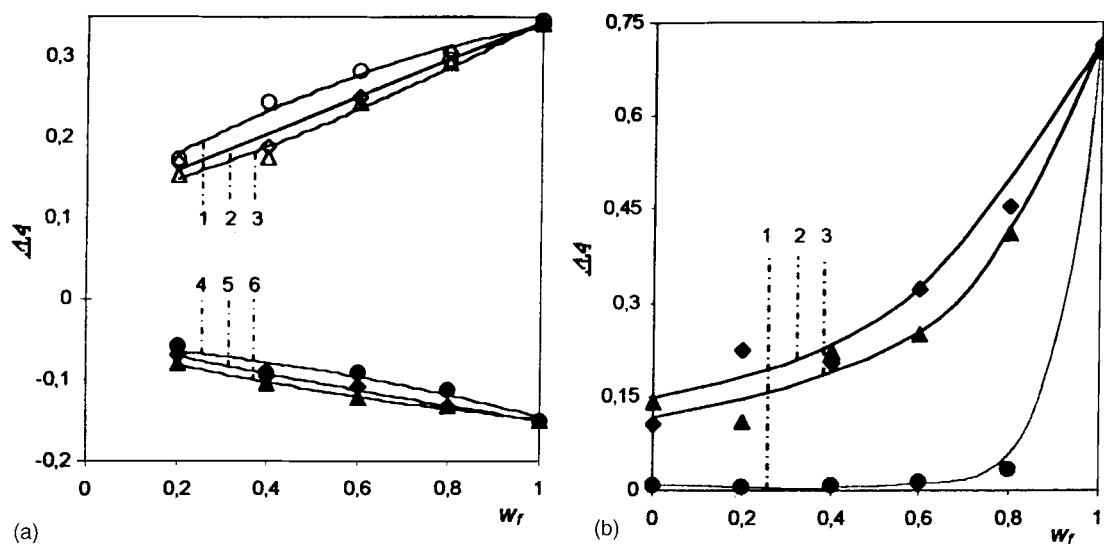


Fig. 12. Effect of degradation on absorbance of the bands present in CH associated with: (a) amide (curves: (1) S; (2) PVAL; (3) HPC) and amine (curves: (4) S; (5) PVAL; (6) HPC) groups vibrations and (b) $-C-O-C-$ group vibration (curves: (1) S; (2) PVAL; (3) HPC). $\Delta A = A - A_0$, where A_0 is the absorbance of sample before degradation, and A is the absorbance after degradation 5 h at 200 °C.

OH stretching vibration and at $1560\text{--}1660\text{ cm}^{-1}$ are associated with amino and amide groups. An increase of band absorbance of amide group at 1655 cm^{-1} ($C=O$) and 1560 cm^{-1} ($-NH-$) with a simultaneous decrease of peak intensity in the band corresponding to the amino group NH_2 at 1590 cm^{-1} is also recorded. It reflects a decrease of deacetylation degree of a CH sample.

Also cross-linking of CH macromolecules can follow the destruction of amino group. In view of a significant chain mobility, destruction of amino group during CH thermodegradation may lead to cross-linking of CH macromolecules. An increase of the gel fraction is observed [14]. During thermodegradation an increase of absorbance was also observed in the band at wave number 1730 cm^{-1} which was caused by carbonyl group which appeared in the CH molecule due to oxidation.

Small changes of the spectra in the case of S and HPC in the region of hydroxyl groups vibrations (destruction of hydrogen bonds) and carbonyl groups vibrations (oxidation) were observed.

Thermal degradation of PVAL in the solid state involves [20] predominantly the elimination of water which is reflected in the loss of OH stretching vibration at 3450 cm^{-1} . It is observed of the formation of

the band at 1655 cm^{-1} associated with appearance of $C=C$ double bonds in the polymer backbone due to molecular chain scission.

Fig. 11 presents FTIR spectra of chosen CH blends. Similar changes of bands absorbance, as in the case of a pure CH sample, were recognized at 3450 , $1560\text{--}1660\text{ cm}^{-1}$ corresponding to a region of amino and amide groups vibrations and at $1040\text{--}1150\text{ cm}^{-1}$ for $-C-O-C-$ groups vibration. Changes of the absorbance at the bands which occurred in the course of degradation found for the blends are shown in Fig. 12.

A decrease of the absorbance in the range of amino bands (at 1590 cm^{-1}) along with increasing absorbance of amide bands at 1660 cm^{-1} is observed to be a linear function of CH weight fraction in the blends (Fig. 12a). However, a very strong decrease of molecular chain scission of CH in the blends corresponding to the change of $-C-O-C-$ band absorbance is clearly seen (Fig. 12b).

4. Conclusions

- Both dynamic and isothermal thermogravimetric analysis of CH and its blends with HPC, PVAL and S revealed improving stability of CH in the blends.

2. With an increase of the amount of S, PVAL and HPC in the blends an increase of T_p and T_{max} is observed. It is most distinct for CH/HPC and CH/PVAL blends. These blends reveal two stages of fast decomposition characteristic of both components. A certain increase of the activation energy of CH degradation calculated on the basis of TG analysis is observed in the case of CH/HPC and CH/S blends.
3. The analysis of FTIR spectra of CH/S, CH/PVAL and CH/HPC blends, indicates a decrease of the number of chain scissions of CH macromolecules inserted in the blends. It corresponds to a slower decrease of absorbance at 1080 cm^{-1} connected with —C—O—C— groups in the glycosidic linkage. Also a rate of CH oxidation (appearance of carbonyl group absorption at 1730 cm^{-1}) is lower.

Acknowledgements

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