TG/DSC studies of modified 1–vinyl-2-pyrrolidone–divinylbenzene copolymers

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Abstract In this paper, the synthesis and characterization of porous copolymers of 1-vinyl-2-pyrrolidone with divinylbenzene are presented. They were obtained by suspension polymerization as pure polymers or composite materials with different inorganic fillers. The influence of the type of filler on the textural and thermal properties was investigated in detail. It was found that the value of the porous surface area and the degree of double bonds' conversion of composites are much lower than in the case of pure copolymers. Thermal properties of the obtained materials were investigated by the means of thermogravimetry and differential scanning calorimetry.

Keywords Thermal properties · Thermogravimetry · Differential scanning calorimetry · Fillers · Porous copolymers · 1-Vinyl-2-pyrrolidone

Introduction

Highly cross-linked, macroporous polymers in the form of microspheres possess many distinctive properties and versatile utilization. They are widely used as effective starting materials and specific sorbents [1–9]. The structure and properties of these polymers are of paramount importance for their applications [10–12]. In recent years, an introduction of inorganic nanoparticles into polymer materials as a simple way to modify the properties of pure polymers

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has been a common practise [13–16]. Quite a large variety of inorganic particle can be incorporated into polymer matrix; however, two classes have been found to offer reinforcing effects: carbon blacks and high-structure silica [17]. This process allows obtaining new specific nano-composites. They exhibit new thermal, mechanical and rheological properties. Interesting effects were observed in relation to glass transition temperature, crystallization kinetics and Young modules of various types of polymers. Thermal stability and glass transition are affected by the type of nanofiller [18–21]. Loading inorganic particles into polymer matrix may also influence the swelling process of the composite material.

In this paper, we present the synthesis and properties of non-filled and modified porous copolymer of 1-vinyl-2-pyrrolidone–divinylbenzene. In the synthesis of the modified copolymers, the following fillers were used:

- high dispersed fumed silica (SI) (specific surface area 330 $m^2\ g^{-1}$, average pore diameter 95 Å) with the methylsilyl group in the surface layer (content of grafted $-CH_3$ groups 0.21 mmol g^{-1});
- MCM-41 silica, mesoporous molecular sieve of high pore uniformity (average pore diameter 40 Å) and highly developed porous structure (specific surface area 1,012 $m^2\ g^{-1}$);
- carbon black(C) (specific surface area 386 $m^2\ g^{-1}$, average pore diameter 49 Å).

The question therefore arose of how these fillers influence the physico-chemical properties of polymeric materials. Thermal properties of the non-filled and modified copolymers were studied by means of TG and DSC. Additionally, textural characterization was carried out on the basis of the low-temperature nitrogen adsorption on the studied copolymers.
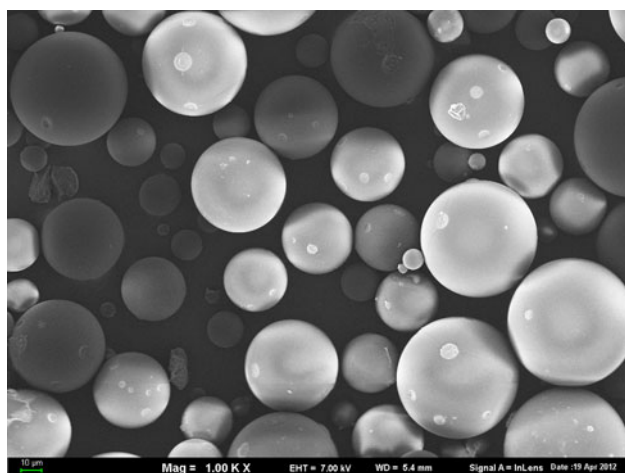
Fig. 1 SEM microphotograph of VP–DVB/MCM material

Experimental

Preparation of copolymers

Chemicals

Divinylbenzene (DVB), Merck (Darmstadt, Germany), and 1-vinyl-2-pyrrolidone (VP), Fluka (Buchs, Switerland), were washed with 5 % aqueous sodium hydroxide in order to remove inhibitors. Poly(vinyl alcohol) and α,α′-azoisobisbutyronitrile from Fluka (Buchs, Switerland) were used without purification. Toluene, *n*-dodecane, acetone and methanol (reagent grade) were from POCh (Gliwice, Poland).

Preparation of porous microspheres All porous microspheres were obtained by suspension polymerization using an equivalent mole fraction of monomers. For copolymerization with 1-vinyl-2-pyrrolidone, divinylbenzene was
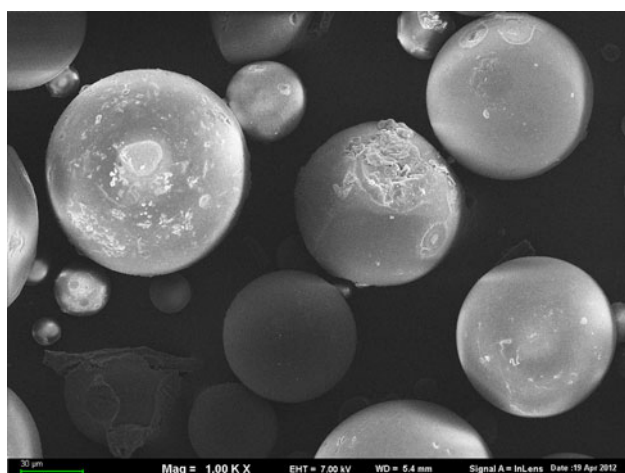

Fig. 2 SEM microphotograph of VP–DVB/C material

Table 1 Elemental analysis of the copolymers

Copolymer	Wt%			Mole ratio of VP to DVB in the copolymer
	C	H	N	
VP–DVB	87.54	8.25	1.75	0.30:1
VP–DVB/SI	86.35	8.01	1.97	0.34:1
VP–DVB/MCM	85.26	8.04	2.71	0.46:1
VP–DVB/C	87.97	8.21	1.56	0.27:1

used as a cross-linking agent. The process of copolymerization proceeded in the following way: 195 mL of distilled water and 6.5 g of poly(vinyl alcohol) were stirred for 6 h at 80 °C in the three-necked flask fitted with a stirrer, water condenser and thermometer. Then, the solution containing 15 g of monomers and 0.075 g of α,α-azoisobisbutyronitrile in 22.5 mL of toluene was prepared. Next, 1.5 g of filler (high dispersed fumed silica, MCM-41 or carbon black) was added. The polymerization mixture was added whilst stirring the aqueous medium. Copolymerization was performed for 20 h at 80 °C. Porous beads (the diameter range 50–250 μm) formed in this process were filtered off, washed with hot water and extracted in a Soxhlet apparatus with acetone, toluene and methanol. The purified beads were separated into fractions by the sieving.

Preparation of block copolymers In the second type of experiment, a series of block copolymers with the increasing concentration of carbon fillers were synthesized. The concentration of the filler was changed from 1 to 8.5 % of the total mass of monomers.

Methods of analysis Textural characterization of the copolymers was carried out by the low-temperature nitrogen adsorption–desorption method. Nitrogen adsorption–desorption measurements were taken at 77 K using a volumetric adsorption analyser ASAP 2405 (Micrometrics
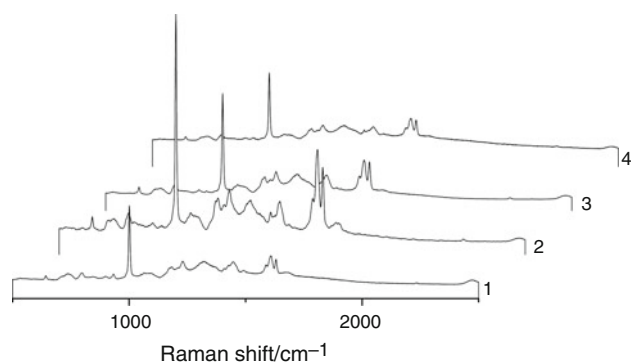

Fig. 3 Raman spectra of the VP–DVB/C (*1*); VP–DVB/MCM (*2*); VP–DVB/Si (*3*); VP–DVB (*4*)

Table 2 Parameters of the porous structure of the studied copolymers

Copolymer	Specific surface area S_{BET}/m² g^{-1}	Pore volume V/cm³ g^{-1}	PSD$_{max}$/Å
VP–DVB	790	1.40	60
VP–DVB/SI	399	0.42	70
VP–DVB/MCM	220	1.16	51
VP–DVB/C	568	0.96	66

Inc., USA). The measurements of the surface properties of the copolymers were preceded by outgassing of the samples at 140 °C for 2 h. The specific surface areas of the investigated samples were calculated by the Brunauer–Emmet–Teller (BET) method for the adsorption data in the range of a relative pressure p/p_o 0.05–0.25. The total pore volume was estimated from a single point adsorption at a relative pressure of 0.985. The pore size distributions (PSD) were obtained from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) procedure [22].

The maximum of PSD was defined as the pore diameter in contrast to the average pore diameter calculated as $D_p = 4V_p/S_{BET}$ (on assumption of a cylindrical shape of pores).

Swellability coefficients (B) were determined by equilibrium swelling in acetone, toluene, tetrahydrofuran and methanol using the centrifugation method. B is expressed as [23]

$$B = \frac{V_s - V_d}{V_d} \times 100\%$$

where V_s is the volume of the swollen microspheres (mL); V_d is the volume of dry microspheres (mL).

Attenuated total reflection (ATR) spectra were recorded using infrared Fourier transform spectroscopy on a spectrometer TENSOR 27 produced by Brucker, Germany, equipped with a diamond crystal. The spectra were recorded in the spectral range of 600–4,000 cm^{-1} with 16 scans per spectrum at a resolution of 4 cm^{-1}. The Raman spectra of polymer samples were recorded using a RENISHAW Raman Microscope (Renishaw, UK) equipped with microscope optical functions. The excited laser line was 785 nm. Elemental analysis of the obtained microspheres was carried out using the Perkin Elmer CHN 2400 apparatus.

Table 3 Swellability coefficients of the copolymers under study

Copolymer	Swellability coefficients B/%			
	Acetone	Methanol	Toluene	Terahydrofuran
VP–DVB	40	50	85	20
VP–DVB/SI	60	80	40	60
VP–DVB/MCM	180	90	220	100
VP–DVB/C	10	90	85	10
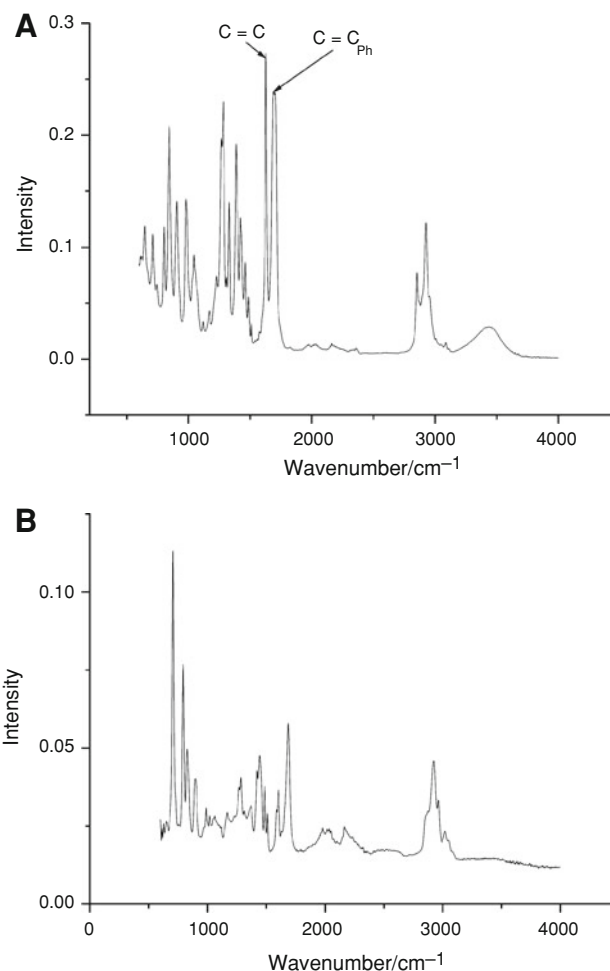
Fig. 4 **a** ATR spectrum of the monomers used for synthesis; **b** ATR spectrum of the VP–DVB copolymer

The surface of the obtained beads was also examined using an atomic force microscope (AFM), AFM Nanoscope III (Digital Instruments, USA), operating in the contact mode. Additionally, the microspheres were imaged using a LEO 1430 VP numerical scanning electron microscope (Germany) with a countershaft and an energy dispersive X-ray detector.

The thermal properties of the synthesized composites were evaluated on the basis of TG and DSC measurements performed using the STA449, F1 Jupiter analyser from Netzsch (Selb, Germany). The procedure was as follows: About 10 mg of the sample was placed in the TG pan and heated in helium or in air atmosphere at a rate of 10 K min^{-1} up to 1,000 °C.

Results and discussion

Porous copolymers of 1-vinyl-2-pyrrolidone–divinylbenzene used in this study were obtained by suspension copolymerization in the form of regular microspheres

Table 4 Degrees of double bond conversion

	VP–DVB	VP–DVB/Si	VP–DVB/MCM	VP–DVB/C
DC/%	86	74	78	69

(Figs. 1, 2). In the synthesis, an equivalent mole number of functional monomer and cross-linker was used and three different fillers—high dispersed fumed silica, MCM-41 and carbon black—were incorporated into polymer network. Table 1 presents the results of elemental analysis of the copolymers under study. They indicate that compared with the starting polymerization mixture, a lower amount of VP was incorporated in the copolymer networks. The molar ratio of VP to divinylbenzene was calculated on the basis of nitrogen content in the polymer. As the nitrogen occurs only in the functional monomer, it was possible to evaluate the molar ratio of VP to the cross-linker. In the initial system, the ratio was 1:1; in the obtained products, it fluctuated from 1:0.27 to 1:0.46 depending on the used filler. The lowest quantity of nitrogen was found in the VP–DVB/C copolymer. Only about a quarter of the initial amount of VP was built into this copolymer. Generally, the preparation of cross-linked VP copolymers is difficult to carry out. This is caused by the fact that radical copolymerizations involving 1-vinyl-2-pyrrolidone are usually characterized by a low value of reactivity ratios r_{VP}. In most cases, they approximately equal zero. It is worth noticing that the presence of polar filler promotes the incorporation of VP into polymer network. The presence of VP in copolymers was confirmed by Raman spectroscopy. Peaks at $1,650–1,660$ cm^{-1} corresponding to pyrrolidone structure units are visible on the Raman spectra (Fig. 3). Their intensities differ depending on the used filler and are in accordance with the elemental analysis.
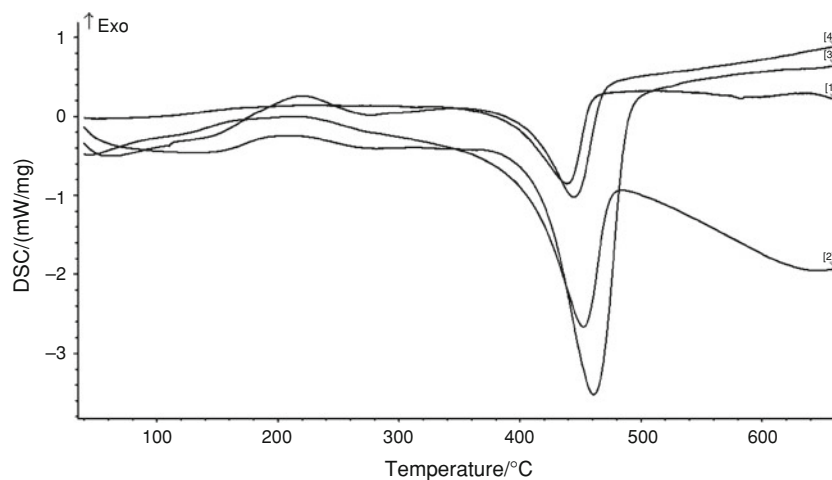
The presence of inorganic fillers in the polymerization mixture also significantly influences the process of porous structure formation. Table 2 presents the parameters of porous structure of the copolymers under study. Copolymer VP–DVB possesses the highest value of specific surface area (790 m^2 g^{-1}) and pore volume (1.40 cm^3 g^{-1}). An addition of the fillers diminishes these parameters. It is especially visible in the case of the VP–DVB/MCM copolymer. Despite the fact that MCM-41 has a well-developed porous structure itself, the specific surface area of the VP–DVB/MCM composite is much lower (220 m^2 g^{-1} compared with $1,012$ m^2 g^{-1} of pure MCM-41 and 790 m^2 g^{-1} of VP–DVB copolymer). This effect could be explained by the fact that during synthesis, the phase separation occurs very early in the system with MCM-41. Therefore, the nuclei of polymers in formation could capture preferably monomers from the local solution and consequently increase their size and the sizes of pores formed between them. As a consequence, the value of the porous structure is quite low, whereas the pore volume is considerable (1.16 cm^3 g^{-1}). Two other fillers also influence the formation of the porous structure; however, the changes are not so spectacular.

The differences in internal structures created during the polymerization with various fillers are also reflected by the ability to swell. Table 3 presents the swellability coefficients of copolymers in acetone, methanol, toluene and tetrahydrofuran. One can observe that the highest swellability coefficients possess the VP–DVB/MCM material, whereas the VP–DVB/C swells less than pure VP–DVB copolymer.

Degree of conversion

Conversion of double bonds in the microspheres synthesized with the use of multifunctional cross-linkers is rarely

Fig. 5 The DSC curves of VP–DVB/C (*1*); VP–DVB/Si (*2*); VP–DVB/MCM (*3*); VP–DVB (*4*) determined in helium

Fig. 6 TG curves of VP–DVB (*1*); VP–DVB/C (*2*); VP–DVB/Si (*3*); VP–DVB/MCM (*4*) determined in helium
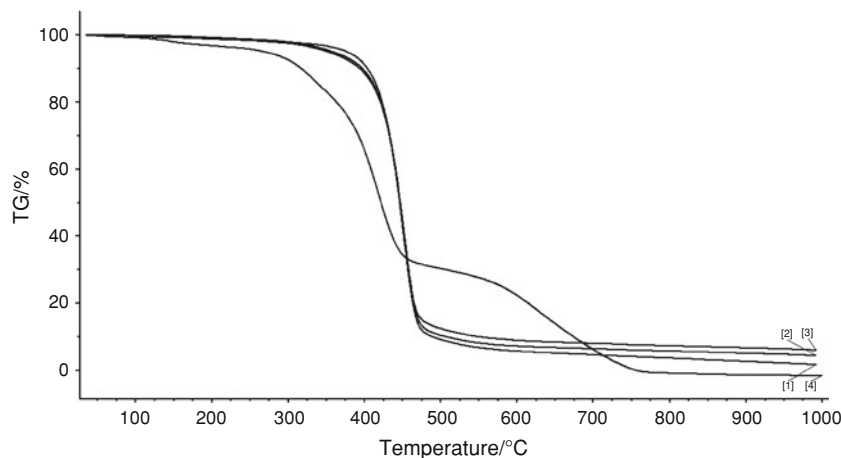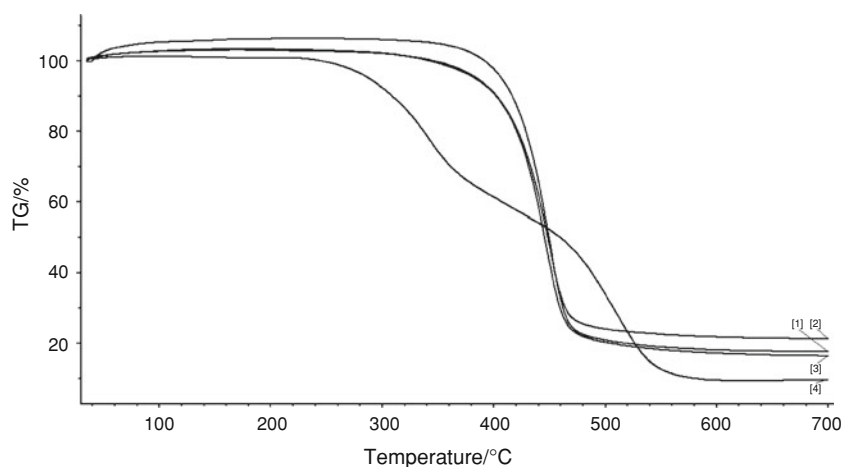

Fig. 7 TG curves of VP–DVB (*1*); VP–DVB/C (*2*); VP–DVB/Si (*3*); VP–DVB/MCM (*4*) determined in air

complete [24]. In order to find the conversion degree, the infrared spectroscopy was applied. Intensities of peaks responsible for stretching vibrations of the C=C (1,637 cm^{-1}) group before and after polymerization were compared. As an internal standard, the peak responsible for the stretching vibration of the aromatic ring (1,610 cm^{-1}) was used (Fig. 4). The degree of conversion (DC) was calculated by the following equation:

$$DC = 100\,\% - \left(\frac{\left(\frac{I_{C=C}}{I_{C=C_{Ph}}} \right)_{polymer}}{\left(\frac{I_{C=C}}{I_{C=C_{Ph}}} \right)_{monomer}} \times 100\,\% \right)$$

The obtained values of double bond conversion are summarized in Table 4. Thus, one can assume that presence of the fillers significantly diminishes the conversion of the double bond. It is especially visible in the case of carbon black. The conversion of the double bond in the material obtained with the presence of this filler is almost 20 % lower than in the pure VP–DVB copolymer. The presence of the unreacted double bond was also confirmed during DSC measurements in helium. On the DSC curves of the filled copolymers, an exothermic reaction at 220°

can be observed (Fig. 5). It can be attributed to thermal polymerization of double bonds. The enthalpies of the reactions are equal to −159 J g^{-1} for the VP–DVB/C material, −93.48 J g^{-1} for VP–DVB/Si and −34.88 J g^{-1} for VP–DVB/MCM. In the case of pure VP–DVB copolymer, no exothermic peaks are observed on the DSC curve. The differences in thermal properties of pure and filled copolymers also appeared during TG analysis. Table 3 presents the initial decomposition temperature (IDT), $T_{50\,\%}$ of mass loss, final decomposition temperature (FDT) and the temperature of the maximum of mass loss (T_{max}) in helium. From this data, one can see that addition of inorganic fillers lowers the initial decomposition temperature of the copolymers. This effect is especially visible in the case of the VP–DVB/MCM material. Its initial temperature is more than 100 °C lower than in the case of pure VP–DVB copolymer. This fact is caused not only by the lower degree of conversion but also by the different chemical composition. In the VP–DVB/MCM material, the amount of VP incorporated into the polymer network is the highest amongst all the materials under study. In the case of VP–DVB/Si and VP–DVB/

Fig. 8 The DSC curves of VP–DVB (*1*); VP–DVB/C (*2*); VP–DVB/Si (*3*); VP–DVB/ MCM (*4*) determined in air
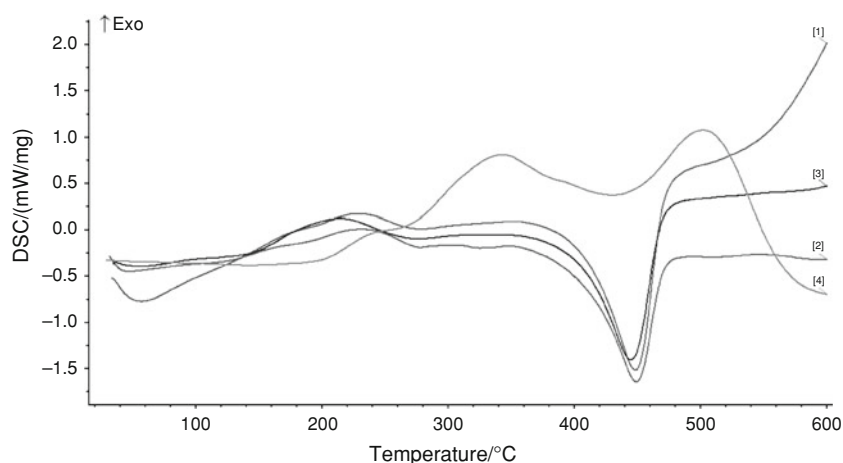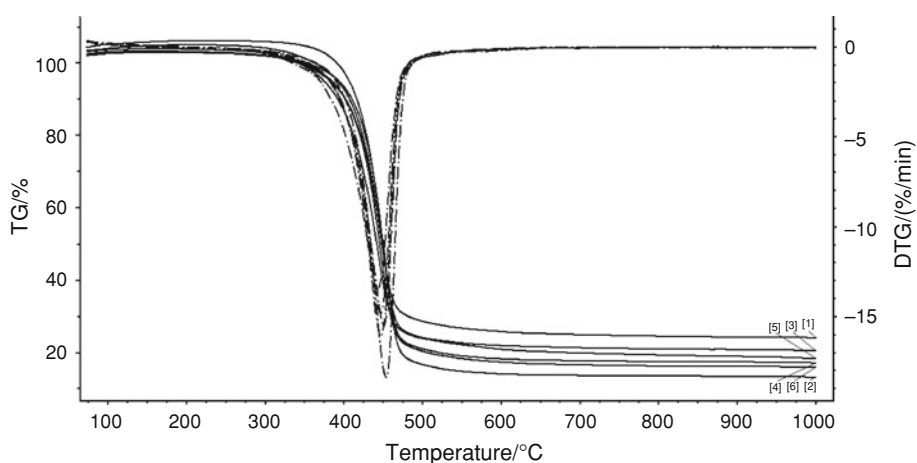

Fig. 9 TG and DTG curves of VP–DVB/C copolymers synthesized with 1 % (*1*); 2.5 % (*2*); 4 % (*3*); 5.5 % (*4*); 7 % (*5*); and 8.5 % (*6*) of carbon black filler


C materials, their IDTs are also lower than pure VP–DVB, but the differences are about 20 °C. The temperature of the maximum of mass loss of pure VP–DVB copolymer is 452 °C. The addition of fumed silica and carbon black to the copolymers has not changed significantly the position of the decomposition temperature. The situation was different when MCM-41 was used as a filler. In this case, thermal degradation of the material proceeds through two stages. The first step at 417 °C is followed by the second stage above 633 °C. It is suggested that the copolymer can contain blocks of polyvinylpyrrolidone. Graphical representation of the thermal behaviour of the discussed material in helium atmosphere is presented in Fig. 6.

Figure 7 presents the thermal degradation of the copolymers under study in air. What is interesting is that the initial decomposition temperature for all investigated materials is higher than in helium (Table 4). For VP–DVB, VP–DVB/Si and VP–DVB/C, this difference is equal to about 30 °C; in the case of VP–DVB/MCM, about 17 °C. The temperature of 50 % mass loss and the temperature of the maximum of mass loss are almost the same in air and in helium for VP–DVB, VP–DVB/Si and VP–DVB/C

materials. Thermal degradation of VP–DVB/MCM proceeds otherwise. Similarly, as in helium atmosphere, there are two steps of the degradation process: The first one has the maximum at 417 °C, the second at 633 °C. The differences between the influence of MCM and the two other fillers were also clearly visible during the DSC measurements conducted in air. DSC curves of the composites and pure copolymer are presented in Fig. 8. The addition of carbon black filler as well as fumed silica to the copolymer has not change significantly the position of the decomposition peaks (450 °C). The only change is that the enthalpy of decomposition (ΔH_d) has a lower value due to the presence of fillers. The situation is completely different in the case of VP–DVB/MCM. On the DSC curve determined for this material, one can observe two exothermic peaks. Their values correspond with T_{max1} and T_{max2} determined during the thermogravimetric analysis. On this basis, it can be assumed that thermal degradation of the VP–DVB/ MCM composite occurs through the process of oxidation. In order to evaluate the influence of filler concentration on the thermal properties, a series of block copolymers with carbon black as the filler was prepared. The concentration
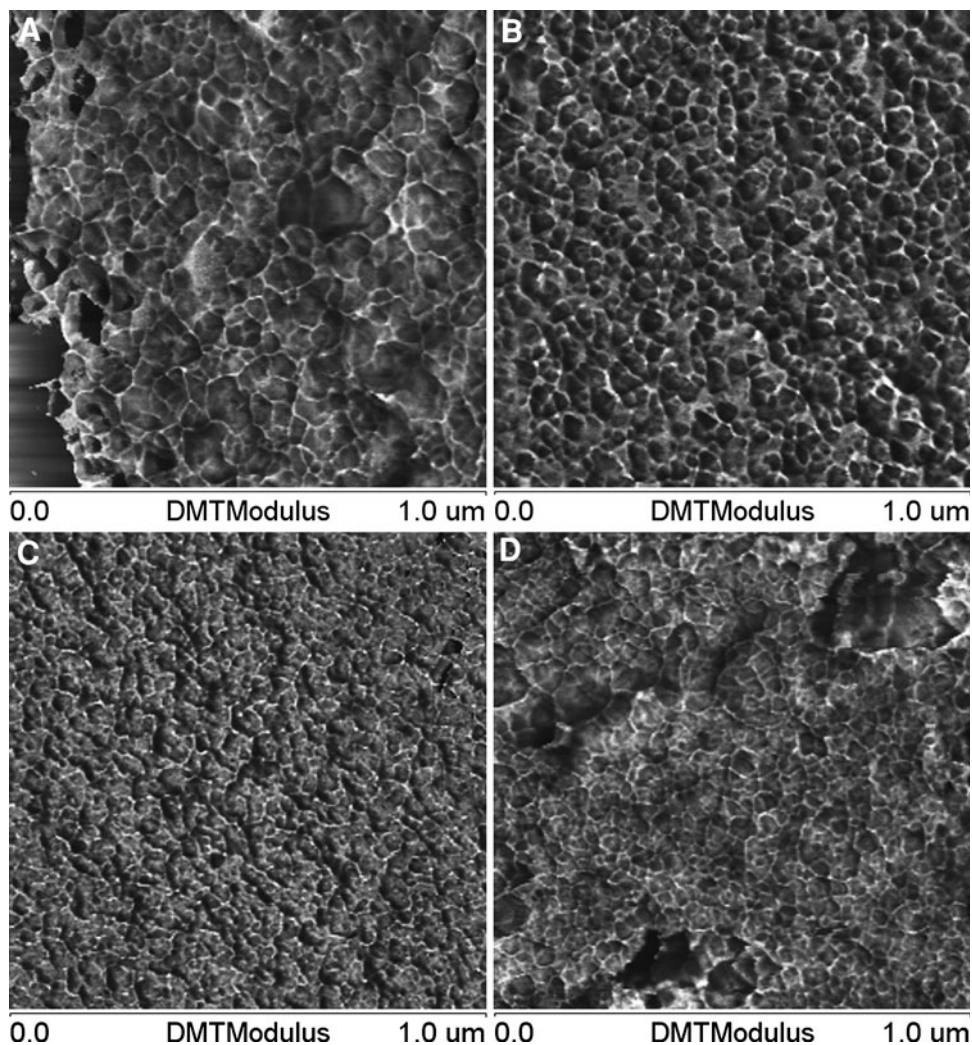
of carbon black was changed from 1 to 8.5 % of the total mass of the monomers. Figure 9 presents the TG and DTG curves of the obtained materials. As can be seen in this figure, increasing the concentration of carbon black filler has not changed the position of the decomposition peaks.

Differences in the degree of conversion and the chemical composition of the obtained materials are also reflected in the mechanical properties. Young's modulus is one of the important parameters of mechanical properties of materials. In our work, atomic force microscopy (AFM)-based mechanical mapping techniques were applied to determine the Young modulus. The Derjaguin–Müller–Toporow (DMT) theory was used for the calculation. The morphologies of the samples under study are visualized in Fig. 10. Unfortunately, the addition of fillers, resulting in dismissing the double bond conversion, also decreases the Young modulus. Its average value for the pure copolymers is equal to 3.1 GPa, 2.8 GPa for VP–DVB/MCM material, 1.7 GPa for VP–DVB/Si and 1.4 GPa for VP–DVB/C.

Conclusions

In the presented work, we synthesized pure and filled with inorganic fillers porous copolymers of 1-vinyl-2-pyrrolidone–divinylbenzene. We intend to lower the cost of the synthesis and improve thermal and mechanical properties of the obtained materials. It turned out that during the synthesis, in the presence of inorganic filler, the phase separation occurs earlier in the system and consequently the value of the porous surface area and the degree of double bond conversion are much lower than in the case of pure copolymers. The difference reflects in the deterioration of the thermal and mechanical properties of the materials. Especially, significant differences were visible in the case of the MCM-41-filler. What is valuable is that it promotes the incorporation of VP into the polymer network. As a consequence, the textural and thermal properties are quite different compared with the pure copolymer as well as materials obtained in the presence of high dispersed fumed silica with the methylsilyl groups in the surface layer and carbon black.

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