Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 1, 125–132

TG AND DSC STUDIES OF FILLED POROUS COPOLYMERS

Y. N. Bolbukh[1], *V. A. Tertykh*[1*] *and B. Gawdzik*[2]

[1]Institute of Surface Chemistry of National Academy of Sciences of Ukraine, Gen. Naumov Str. 17, 03164 Kyiv, Ukraine
[2]Faculty of Chemistry, Maria Curie-Skłodowska University, M. Curie-Skłodowska Sq. 3, 20031 Lublin, Poland

A complex approach including thermogravimetry, differential thermal analysis and differential scanning calorimetry was applied to study characteristics of non-filled and filled porous copolymers of divinylbenzene with styrene or some acrylic monomers: di(methacryloyloxymethyl)naphthalene, methacrylic ester of *p*,*p*'-dihydroxydiphenylpropane diglycidyl ether, and dimethacrylglycolethylene. High disperse silicas with the grafted methyl and silicon hydride groups in the surface layer were used as fillers. The kinetic parameters of thermal degradation for composites obtained were determined by different methods.

Keywords: *chemically modified silicas, degradation kinetics, DSC, fillers, methacrylic monomers, porous copolymers, TG*

Introduction

Polymeric microspheres and microcapsules are widely used materials for a wide range of applications including stationary phases for chromatographic separation, biomedical devices, and controlled release systems. Improving the mechanical and thermal properties of these materials can be achieved by introduction of fillers, in particular high disperse silica. It is well known [1] that the chemical modification of silica surface allows one to improve the compatibility of the system's components, and to obtain more uniform filler distribution and, in favourable cases, to provide chemical cross-linking of the filled composite. In recent years we have shown that grafted surface silicon hydride groups can have an influence on the cross-linking of the filled polymers and on the polymerization of unsaturated monomers, owing to the formation of covalent bonds between the filler surface groups and the functional groups of the polymer [2]. Additionally, the presence of methyl groups on the modified silica surface enables the distribution of the filler to be more homogeneous [3].

Thermal degradation of non-filled and modified silica-filled porous copolymers of divinylbenzene with styrene and some acrylic monomers was studied by DTA and DSC in this research. The kinetic parameters of thermal degradation of composites have been determined.

Experimental

The non-filled polymers were obtained by combined suspension–emulsion polymerization [4]. Two types silica fillers were used for preparation of the filled polymers: high disperse fumed silica (specific surface area 300 $m^2 g^{-1}$) with the methylsilyl groups in the surface layer (contents of grafted $-CH_3$ groups 0.21 mmol g^{-1}) and the methyl hydride-containing silica prepared by treatment of the previously synthesized methyl-containing silica with triethoxysilane (concentration of bound $\equiv$SiH groups 0.25 mmol g^{-1}). The silica with surface methylsilyl groups was obtained by reaction with hexamethyldisilazane vapour. Fumed silica (10 g) and $(H_3C)_3SiNHSi(CH_3)_3$ (0.475 cm^3, 0.25 mmol) were placed in a leak-proof reactor with stirring at 20°C for 24 h. After modification the methyl-containing silica was heated at 150°C for 30 min. Silica with grafted methylsilyl and silicon hydride groups (methyl,hydride-containing silica) was prepared by interaction of the methyl-containing silica (10 g) with triethoxysilane (0.9 mL, 5.0 mmol) in ethanol (70 cm^3) at room temperature with stirring for 24 h.

For copolymerization with divinylbenzene (DVB, Fluka) the following monomers were used: styrene (St, Fluka), di(methacryloyloxymethyl)naphthalene (DMN, Cosden Chemical Co.), methacrylic ester of *p*,*p*'-dihydroxydiphenylpropane diglicydylether (MEDDE), and dimethacrylglycolethylene (DMGE, Fluka). All porous copolymers were obtained by suspension-emulsion polymerization as described in paper [5]. In particular, for synthesis of copolymer DVB–St a mixture containing DVB (1.20 cm^3) and St (3.94 cm^3) (molar ratio 0.2:0.8) and α,α'-azobisisobutyronitrile (0.047 g) as an initiator was dissolved in a pore-forming diluent containing 20% toluene (1.53 cm^3) and 80% *n*-decyl alcohol (6.12 cm^3). The homogeneous mixture was immediately poured into the aqueous solution of polyvinyl alcohol (1 g in 50 cm^3 H_2O). The poly-

---

* Author for correspondence: tertykh@public.ua.net

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

merization was carried out at 80°C in a round-bottomed three-neck glass reactor equipped with a mechanical stirrer and condenser. For synthesis of copolymer with the monomers in molar ratio 0.5:0.5 the amount of DVB and St was 2.8 and 2.3 cm^3, respectively. For synthesis of nanocomposites the fillers were introduced into the copolymer mixture with diluents and then the initiator was added. For all compositions the total mass of monomers was 4.686 g. The filler contents was 15 mass% (0.7 g). After polymerisation, the products were washed with hot water and extracted in a Soxhlet apparatus for 15 h using acetone. Then, the samples were dried at 150°C.

The synthesized composites were studied by derivative thermogravimetry using a MOM device (Paulik and Erdey, Hungary) in the temperature range 20–1000°C and by differential scanning calorimetry (Netzsch Thermal Analysis, Selb, Germany) in the temperature range 20–500°C at a heating rate 10°C min^{-1}. The initial decomposition temperature was determined from the TG curve.

Calculation of the kinetic parameters

The thermal degradation of polymers is a complex process. The mechanism of polymer decomposition is still unclear. It is very difficult to obtain the exact kinetic parameters of each reaction involved in the decomposition process. In the filled systems there is a superposition of thermooxidative destruction of the polymer and of the surface layer of inorganic particles [6]. In addition, the presence of functional groups on the silica surface can change a course of the thermooxidative process and destruction of polymeric chains.

Thermogravimetric analysis (TG) is widely applied for determination of the kinetic parameters of composite degradation. Complexities in identification of the temperature intervals of the individual reactions are due to superposition of different stages of reaction and the shift in temperatures of thermal effects on DTA curve, caused by difficulties of gaseous products removal [7]. More exact information can be obtained by combined application of the TG and DSC methods.

Methods for determination of the kinetic parameters of the decomposition reactions use the general equation [8, 9]:

$$-\frac{\mathrm{d}w}{\mathrm{d}t}=A\exp\left(-\frac{E}{RT}\right)w^{\mathrm{n}} \tag{1}$$

where w is the fractional residual sample mass, t is time, T is the absolute temperature, R is the universal gas constant, A is the pre-exponential factor, E is the activation energy, and n is the order of reaction.

Although a common approach to calculation of kinetic parameters of decomposition processes is used, essential differences occur in the kinetic results for identical systems [6]. Therefore in this work the calculation of kinetic parameters was performed by several approaches with the application of the Freeman–Carrol [10], Friedman [10, 11] and Coats–Redfern [12] methods.

The equation for the Freeman–Carrol method is as follows:

$$\frac{\Delta\ln\mathrm{d}\alpha/\mathrm{d}t}{\Delta\ln(1-\alpha)}=n-\left(\frac{E}{R}\right)\frac{\Delta(1/T)}{\Delta\ln(1-\alpha)} \tag{2}$$

where α is the fraction of unreacted polymer. Values of $\Delta\ln(\mathrm{d}\alpha/\mathrm{d}t)$ and $\Delta\ln(1-\alpha)$ are taken at the regular $1/T$ interval (in this work the interval was 0.0002 K^{-1}).

The equation for the Friedman method has the following form:

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\ln A+n\ln(1-\alpha)-\left(\frac{E}{RT}\right) \tag{3}$$

Additionally, the E values were determined by the Coats–Redfern equation:

$$\ln\left[\frac{g(\alpha)}{T^2}\right]=\ln\left(\frac{AR}{\beta E}\right)-\frac{E}{RT} \tag{4}$$

where α is the fractional loss of mass at temperature T; $g(\alpha)$ is a function related to the order of the reaction; β is the heating rate.

Results and discussion

For all compositions studied, thermal degradation in air occurs through a fast stage (at about 280–400°C) and is followed by a slower stage (above 400°C) (Figs 1–6, a). Thermal degradation of the copolymers in a nitrogen atmosphere (DSC curves) proceeds in one stage at the range 340–475°C (Figs 1–6, b and c).

For the DVB–St copolymer the first degradation stage consists of two steps with maximum mass loss rate at 320 and 360°C (DTG curves in Fig. 1a). In accordance with literature data [13] in the DVB–St copolymer mass loss observed at 280–320°C may be attributed to decomposition of the side groups of polymer chains. Also mass losses in this interval are caused by removal of weakly bound groups to the chain. Such bonds are easily broken at relatively low temperatures and can initiate further thermal degradation of copolymer. Such bonds are formed between styrene blocks and divinylbenzene blocks [11].

Copolymer thermooxidative degradation mainly takes place in the range 300–400°C with the maximum mass loss rate at 360°C. Changes in the TG curve at this temperature can be used to characterize the polymer–filler interaction [14].

A large mass loss at the second stage of degradation (above 400°C) can be related to the decomposition of products of the copolymer thermooxidative degradation. The absence of thermal effects on all DSC curves above 450°C at the first heating and any effects at the second heating (the curve of second heating is not illustrated here) supports this interpretation.

In the non-filled DVB–St copolymers a decrease of the material cross-linking degree (the decrease of the divinylbenzene contents) has resulted in a shift (10°C) of the endothermic effect at 427°C (DSC curve) to a lower temperature (Fig. 1b). Also, for the less cross-linked copolymer (molar ratio DVB–St is 0.2:0.8) the prevalence of exothermic effects on the DTA curve and absence of a decomposition rate peak splitting on the DTG curve were detected. It testifies a difference in proceeding of the copolymers decomposition. Similar changes on DTA curves were observed after an introduction of the modified silica with methyl and silicon hydride groups into the DVB–St (0.5:0.5) copolymer (Fig. 2c). But the splitting of the peak on the DTG curve is not detected also (Fig. 2a). It provides evidence to a decrease in the side chains unbound to the polymer network. In this case the endothermic effect on the DSC curve is displaced to a higher temperature range and the rate of the material degradation is decreased (Fig. 2b). Such a shift may be related to the copolymer cross-linking arising from the interaction of monomers with active groups of the filler surface during polymerization.

Studies of the effect of various functional groups of the filler on the thermooxidation of the DVB–St (0.2:0.8) copolymer (Fig. 3) established that the presence both modified fillers (methyl- or methyl,hydride-containing silica) reduces the initial rate of the composite degradation in comparison with non-filled copolymer. Besides, the maximum on the DSC curve is shifted to a higher temperature by 10°C for the filled copolymers.

Decrease in area of the endothermic peak on the DSC curves (Figs 3b and c) was noted for the filled copolymer. At a first sight, this may appear to correspond to a decrease in the thermal stability of the material. However, if the endothermic peak area is calculated on the mass of pure copolymer (without the filler mass (15 mass%)), the endothermic peak area is changed insignificantly. It may testify that filling affects weakly on the copolymer thermal degradation. At the same time the filling with the methyl- or methyl,hydride-containing silicas leads to strongly marked exothermal or endothermal effects (DTA curves, Fig. 3c), respectively. According to TG data the main effect of the grafted functional groups appears above 450°C, at the stage of the copolymer thermooxidation products degradation.

Comparison of TG and DSC results reveals that temperature of endo-effects maximum on the DSC

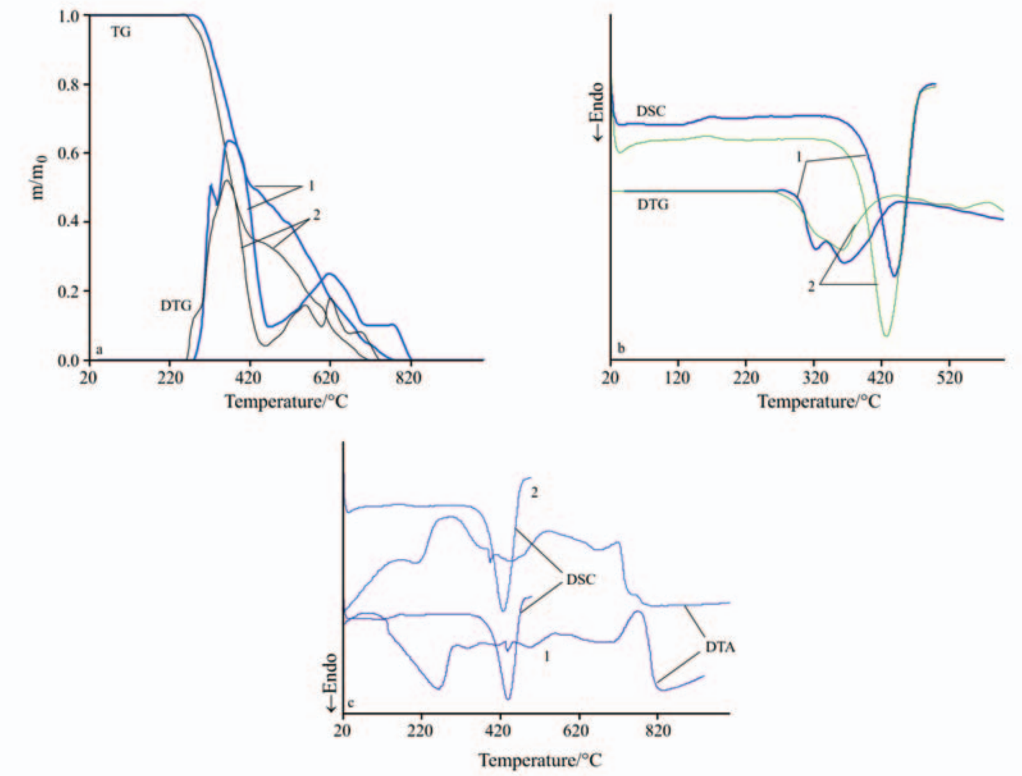

Fig. 1 a – TG/DTG, b – DSC/DTG and c – DSC/DTA curves for thermal degradation of non-filled DVB–St copolymer with molar ratio 1 – 0.5:0.5 and 2 – 0.2:0.8

Table 1 Kinetic parameters of thermooxidative degradation process for DVB–St copolymers

Composite	Temperature range/°C	Freeman–Carrol		Friedman method	
		E/kJ mol^{-1}	n	E/kJ mol^{-1}	n
DVB–St with molar ratio 0.5:0.5	300–320 320–360	84.9 39.9	1.2 0.9	287.1 109.9	0.8 0.6
DVB–St with molar ratio 0.2:0.8	280–380	33.8	0.9	46.5	0.5
DVB–St (0.2:0.8) filled with methyl-containing silica	280–380	58.3	1.1	61.9	0.6
DVB–St (0.2:0.8) filled with methyl,hydride-containing silica	280–360	53.2	1.3	51.0	0.8

curve (420–430°C) coincides with the minimal thermooxidation rate on the DTG curve. This observation was used for analysis of the DTG curves to more strictly define the intervals of various destruction stages for calculation of the kinetic parameters. It is known, that breakage of the bonds in the benzene ring occurs at 400–450°C [15]. Taking into account the decrease of mass loss within the temperature range 400–440°C, this part of the TG curve may be attributed to polymer transformations related to rearrangements and formation of the new bonds.

It is necessary to note a significant difference between activation energy values (E) calculated for the same temperature intervals by Freeman–Carrol and Friedman methods (Table 1). However, both methods demonstrate the identical trend of the E values change after copolymers filling.

Correlation coefficients (R^2) of the linearized TG curves derived using Eqs (2) and (3) were 0.89 and 0.95, respectively. Obtained results are in agreement with the literature data [6, 11, 16], where the activation energy of the DVB–St copolymer thermooxidative degradation was 85–289 kJ mol^{-1}. The filling leads to increase in E values and to a decrease in the composites decomposition rate at the initial stage. It indicates a decrease in the pendant chains (unbound in polymeric network) content. The increase of E value was less at filling with the methyl,hydride-containing silica than at filling with the methyl-containing silica. Probably, the ≡SiH groups promote immobilization of the copolymer chain with formation of the rigid strained bonds in the filler surface layer [9]. Furthermore, carbonaceous residue for copolymer filled with methyl-containing silica was larger in

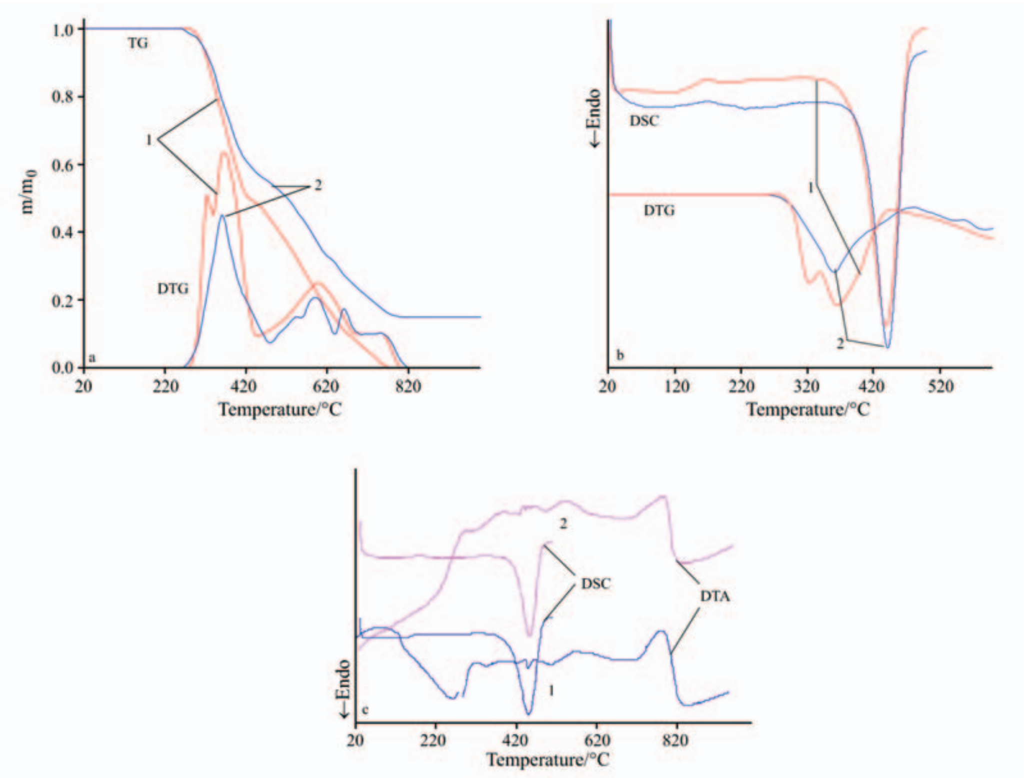

Fig. 2 a – TG/DTG, b – DTG/DSC and c – DSC/DTA curves for decomposition of non-filled DVB–St copolymer with 1 – molar ratio 0.5:0.5 and 2 – composite with methyl,hydride-containing silica

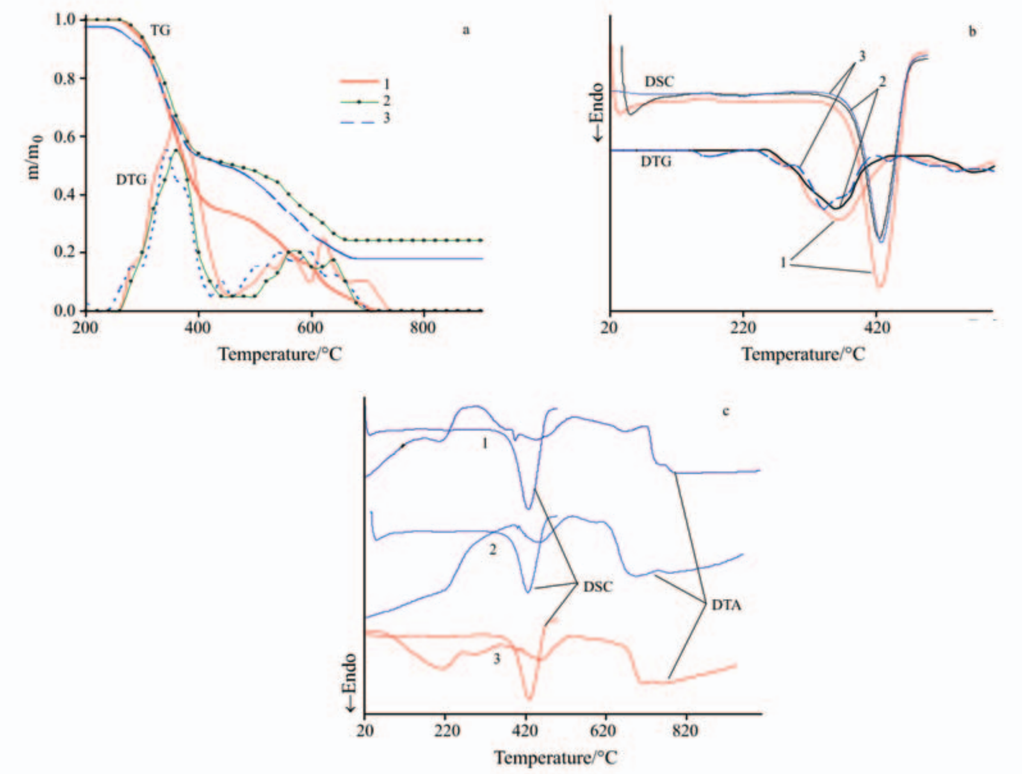

Fig. 3 a – TG/DTG, b – DSC/DTG and c – DSC/DTA curves for decomposition of non-filled DVB–St copolymer with 1 – molar ratio 0.2:0.8 and after filling with 2 – methyl- or 3 – methyl,hydride-containing silicas

comparison with the copolymer filled with methyl,hydride-containing silica.

According to the DSC analysis results, the greatest increase in cross-linking degree was registered for filled DVB–St copolymers with molar ratio of monomers 0.5:0.5 (Figs 2 and 3). Based on these data the mentioned ratio of monomers was chosen for further study of copolymers of divinylbenzene with methacrylates.

For the DMGE–DVB copolymer (Figs 4a and b) on the first stage (TG curve, 300–440°C) two maximum decomposition rates at 360 and 400°C (DTG curve) were observed. At the same time two endo-effects at 400 and 450°C were registered on the DSC curve (Fig. 4c). The decomposition rate peak at 300–360°C is representative for organic materials and was interpreted as destruction of the copolymer network [17]. A minimum at 400–450°C may be attributed to decomposition of both the filler-polymer blocks and linear fragments of the polymer chain [18]. Since the value of the endothermic peak in the range of 420–450°C (DSC curves) for the filled DMGE–DVB copolymer changes insignificantly, the peak near 450°C may be attributed to the benzene rings degradation. Hence, maxima at 360 and 400°C on the DTG curve may be assigned to the decomposition of the *poly*-DMGE and the DMGE–DVB blocks. The temperature intervals for kinetic parameter calculation were determined by a curve-fitting procedure of the right half of both peaks on the DTG curve taking into account the minima of the endothermic peaks on the DSC curve (Fig. 4b) [16].

In accordance with obtained results a reduction of the endothermic peak area at 400°C (DSC curve), which occurs at the filling with methyl-containing silica, indicates a decrease in the copolymer thermal stability (Fig. 4c). However, conformation transformations of the copolymer chains (significant decrease of the mass loss rate at 400–480°C) take place under the smaller degree of polymer thermooxidation and the maximum decomposition degree occurs at the lower temperatures (Fig. 4a).

Intensive exothermic peaks observed on the DTA curve indicate an intensification of thermooxidative processes at the filling with methyl-containing silica. Introduction of the silica filler with grafted ≡SiH groups provides a formation of more cross-linked polymer. It is confirmed by an increase of endothermic peak area on DSC curve, temperature of the maximum decomposition rate, and activation energy in the interval of chains polymer thermooxidation. It is necessary to note also that a decrease of the activation energy at 360–400°C (Table 2) and the increase of copolymer thermooxidation products decomposition rate occur at filling with the methyl,hydride-containing silica. It may testify that surface silicon hydride groups assist to the benzene rings decomposition.

Another character of fillers' influence on the thermodegradation process was noted for the

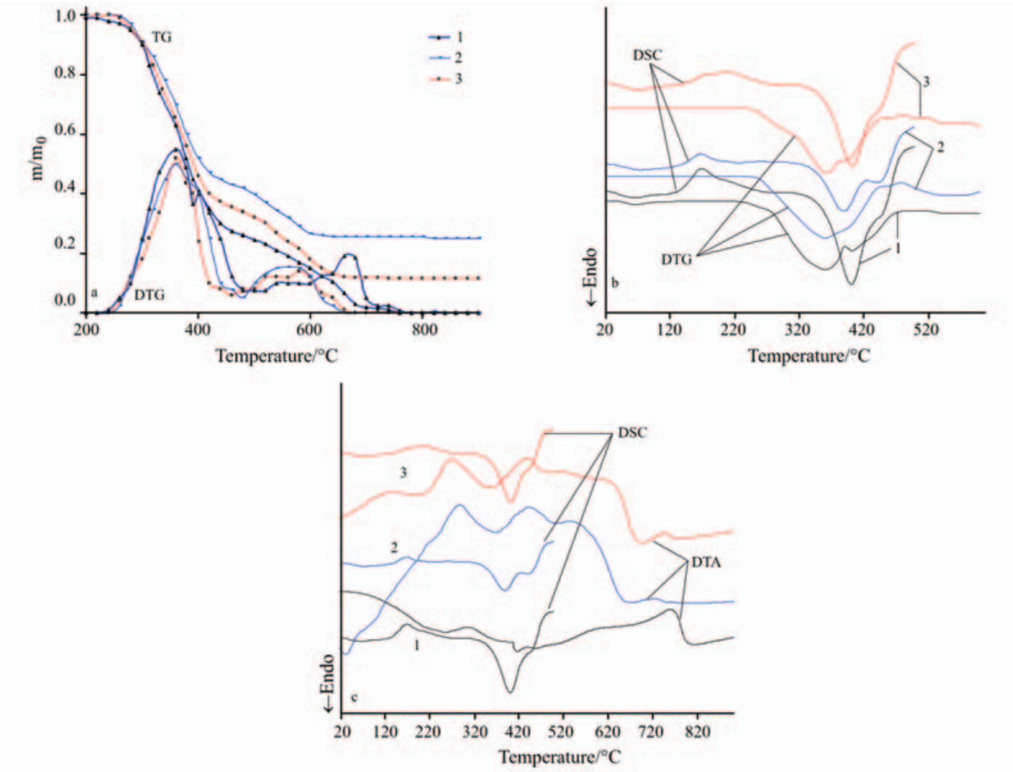

Fig. 4 a – TG/DTG, b – DSC/DTG and c – DSC/DTA curves for decomposition of non-filled DMGE–DVB copolymer with 1 – molar ratio 0.5:0.5 and filled with 2 – methyl- or 3 – methyl,hydride-containing silica

DVB–MEDDE copolymer (Fig. 5). Namely, introduction of the methyl-containing silica results in substantial increase of the activation energy in the temperature interval of polymer chain degradation (300–360°C) (Table 2).

The activation energy at filling with methyl,hydride-containing silica was lower, however the maximum destruction rate was detected at the higher temperature (Fig. 5a). The splitting of the decomposition rate peak on the DTG curve at 300–450°C was not observed in the fillers' presence. It testifies to decrease in the thermodegradation temperature of benzene rings. As well as for the filled DVB–St copolymers, for filled DVB–MEDDE copolymer the maximum destruction degree was registered at the lower temperature (in comparison with non-filled copolymer). However in this case the appreciable change of the thermooxidation

Table 2 Activation energy of copolymers thermooxidative decomposition calculated by the Friedman method

Composite	Temperature range/°C	E/kJ mol^{-1}	Temperature range/°C	E/kJ mol^{-1}
DVB–DMGE (0.5:0.5)	320–360	58.8	360–400	67.7
DVB–DMGE filled with methyl-containing silica	320–360	38.5	360–400	75.7
DVB–DMGE filled with methyl, hydride-containing silica	320–360	64.6	360–400	38.3
DVB–MEDDE (0.5:0.5)	300–360	23.7	360–440	30.63
DVB–MEDDE filled with methyl-containing silica	300–360	96.94	360–440	56.49
DVB–MEDDE filled with methyl,hydride-containing silca	300–360	85.7	360–440	56.8
DVB–DMN (0.5:0.5)	300–340	160.2 (136.7*)	320–360	142.3 (136.0*)
DVB–DMN filled with methyl-containing silica	300–360	121.1 (141.1*)	340–380	88.7 (101.5*)
DVB–DMN filled with methyl,hydride-containing silica	280–320	101.4 (107.3*)	300–360	71.2 (85.5*)

*E values were calculated by the Coats–Redfern equation at first order

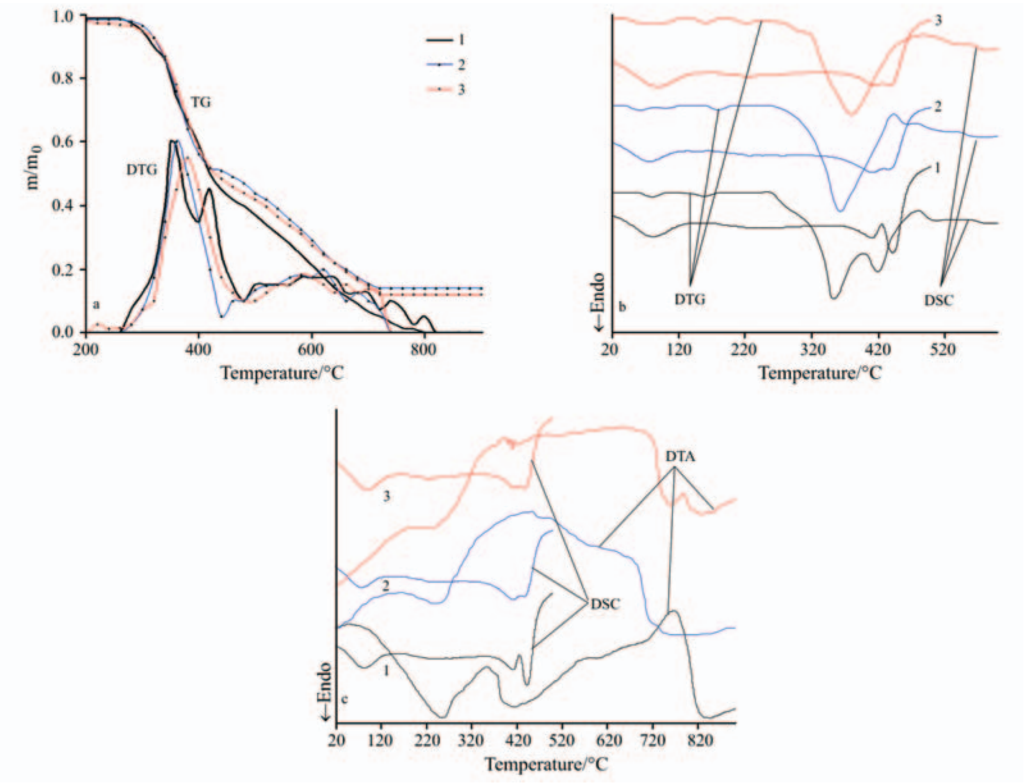

Fig. 5 a – TG/DTG, b – DSC/DTG and c – DSC/DTA curves for decomposition of non-filled MEDDE–DVB copolymer with 1 – molar ratio 0.5:0.5 and filled with 2 – methyl- or 3 – methyl,hydride-containing silica

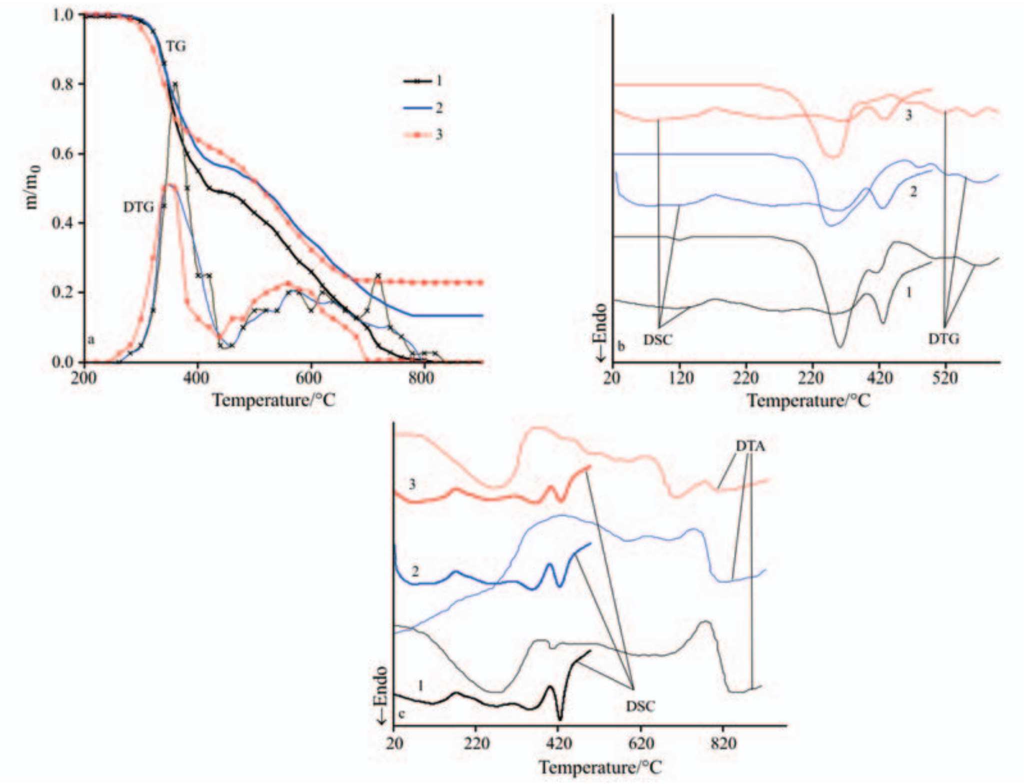

Fig. 6 a – TG/DTG, b – DSC/DTG and c – DSC/DTA curves for decomposition of non-filled DMN–DVB copolymer with 1 – molar ratio 0.5:0.5 and filled with 2 – methyl- or 3 – methyl,hydride-containing silica

products destruction rate (over 450°C) and formation of the carbonaceous residue were not marked.

Filling of the DVB–DMN copolymer with the modified silica leads to a significant decrease of the thermooxidative degradation rate in the range 300–360°C and to an increase of the maximum destruction rate temperature (Fig. 6a).

Apparently from the DSC curves the increase of the endothermic peak area corresponding to the polymer chains thermal degradation (on the DSC curve) was more significant at filling with the methyl-containing silica (Figs 6b and c). However, the activation energy of the filled DVB–DMN copolymers thermooxidation was reduced (Table 2). At filling with the methyl,hydride-containing silica the decrease of the degradation rate in the range 320–380°C (Fig. 6a) and a peak compression effect on the DTG curve were noted. At the same time a formation of the carbonaceous residue was observed only for the DVB–DMN copolymers filled with the methyl,hydride-containing silica. It can testify the presence of thermally stable filler-polymer bonds in the surface layer. Thus, the samples of the filled DVB–DMN copolymer possess the lower thermal stability, the high char-formation ability and more stable surface bonds.

According to the results obtained, the studied fillers have the more significant influence on the thermooxidation process in comparison with thermal degradation of the copolymers in a nitrogen atmosphere. Since the copolymer thermooxidative degradation consists of the reaction sequence, in which the following reaction is initiated by product of the previous process [17], it is possible to assume that for the investigated composites a decrease of the effective decomposition rate has been caused by delay just in the proceeding of the secondary processes.

The filling with the modified silica, on the one hand, results in a decrease of the pendant chains content due to a cross-linking of the copolymer, and on the other hand, it leads to a formation of the zones with different polymer links density and more rigid bonds in the surface layer. A comparison of the obtained results with literature data [16–18] provide evidence that a trend in the filler influence is caused by an affinity of the silica modifying layer to the copolymer and macromolecules rigidity. In a case of chemical grafting of the polymer molecules to the filler surface the increase in the activation energy of the decomposition process was realized for the copolymers with less rigidity of the macromolecular chains.

Conclusions

The filling of the copolymers with the modified silica was shown to promote the copolymer cross-linking and has more significant influence on the thermooxidation process in comparison with the thermal degradation in a nitrogen atmosphere. The presence of filler leads to a decrease of decomposition rate on the initial stage and it can indicate a decrease of the pendant chains content.

A decrease in the activation energy of the decomposition process of the filled composites is probably connected with the formation of rigid strained bonds in the silica surface layer. Character of the filler influence depends on an affinity of the silica modifying layer to the copolymer and a rigidity of the polymeric macromolecules.

References

1 G. Schmidt and M. M. Malwitz, Curr. Opin. Colloid Interface Sci., 8 (2003) 103.
2 Y. Bolbukh, Y. Mamunya and V. Tertykh, J. Therm. Anal. Cal., 81 (2005) 15.
3 Y. N. Bolbukh, V. A. Tertykh and B. Gawdzik, Abstracts of III Polish-Ukrainian Conference on Polymers of Special Applications, Radom, June 15–18, 2004, p. 22.
4 B. Gawdzik and T. Matynia, Reactive Polymers, 5 (1987) 197.
5 B. Gawdzik and J. Osypiuk, J. Chromatogr. A, 898 (2000) 13.
6 R. Aguado, M. Olazar, B. Gaisan, R. Prieto and J. Bilbao, Chem. Eng. J., 92 (2003) 91.
7 B. V. L'vov, J. Therm. Anal. Cal., 79 (2005) 151.
8 S. S. Pavlova, I. V. Zhuravleva and Yu. I. Tolchinskii, Thermal Analysis of Organic and Macromolecular Compounds, Moscow, Khimiya 1983, p. 15.
9 A. Hazra, D. Dollimore and R. Alexander, Thermochim. Acta, 392–393 (2002) 221.
10 M. V. Kök and C. Keskin, Thermochim. Acta, 369 (2001) 143.
11 X.-G. Li, React. Funct. Polym., 42 (1999) 53.
12 S. N. Swain, K. K. Rao and P. L. Nayak, J. Therm. Anal. Cal., 79 (2005) 33.
13 F. Sediri, F. Touati, N. Etteyeb and N. Gharbi, J. Sol-Gel Sci. Technol., 26 (2003) 425.
14 L. Sierra, B. L. Lopez and J. L. Guth, Mater. Res. Innovations, 5 (2002) 268.
15 A. V. Pastukhov, V. A. Davankov, L. D. Belyakova, N. N. Alekseenko, M. P. Tsurupa and A. M. Voloshchuk, Struct. Dynamics Mol. Systems, X (2003) 29.
16 J. Yang, R. Miranda and C. Roy, Polym. Degrad. Stab., 73 (2001) 455.
17 A. Gultec, T. Seckin, Y. Onal and M. G. Icuygy, Turk. J. Chem., 26 (2002) 925.
18 S. Madorskii, Thermal Destruction of Organic Polymers, Moscow, Mir 1967.

DOI: 10.1007/s10973-006-7587-1