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Effect of Surface Hydride, Vinyl, and Methyl Groups on Thermal Stability of Modified Silica-Divinylbenzene-Di(Methacryloyloxymethyl)Naphthalene Composites

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Divinylbenzene (DVB)-di(methacryloyloxymethyl)naphthalene (DMN)/modified silica composites were studied by means of IR spectroscopy, thermogravimetric analysis, and differential scanning calorimetry. The results show that filling with modified fumed silica decreases the initial temperature of DVB-DMN copolymer thermal-oxidative degradation; however, the activation energy of this process generally increases. The partial modification of silica surface turned out to be more efficient than the total functionalization and silicas containing surface methyl in combination with hydride groups were found to be the best fillers for DVB-DMN copolymer among all those investigated.

Keywords: composites, DMN, DSC, DVB, modified silica, surface groups, TGA

INTRODUCTION

Embedding of inorganic nanoparticles in polymeric systems affords materials with advanced characteristics. The most commonly used filler for such systems is highly-dispersed silica [1]. However, large

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amount of surface silanol groups leads to particles agglomeration. Due to high inter-aggregate interaction silica has the ability to form a percolation network immobilizing a large volume of liquid [2]. At the same time hydrophilic silica particles are difficult to disperse in the organic monomer and polymer media without surfactant [3]. A possible way to improve the compatibility of inorganic particles with polymer matrix could be the total or partial organophilization of their surface. The authors have found that acceptable penetration of filler particles into the organic monomer medium during the suspension-emulsion polymerization is obtained at filling with partially methylated silica [4]. It was also found that in the presence of surface silicon-hydride groups a crosslinked structure is achieved due to formation of hydrolytically stable polymer-silica bonds during hydrosilylation of unsaturated monomer groups [5]. Because polymers crosslinked with modified silica can demonstrate an enhancement in internal structure [6] and thermal stability [7–10], the presence of methyl and hydride groups on silica surface presumably will allow obtaining high filler dispersion and chemical structurization of a composite.

The effect of surface hydrophobization with the possibility of polymer-filler chemical interaction is also achieved via vinyl groups grafting onto silica surface [11]. However, during chemical interaction in the surface layer, overstrained bonds are formed resulting in material weakening [12]. The intensity of interfacial bonds network may be varied by the quantity of functional groups at the filler surface. The present work is devoted to studies of the effect of the amount of hydride, vinyl, and methyl groups grafted to fumed silica surface on the thermal stability of porous spheres based on copolymer of divinylbenzene with di(methacryloyloxymethyl)naphthalene. Such spheres are used in gas chromatography and their thermal stability and strong solvents resistance are important for this application. Presumably filling with crosslinking organophilic silica aside from keeping high thermal stability will stabilize their swelling parameters in aggressive media.

EXPERIMENTAL

Materials

Divinylbenzene (DVB), di(methacryloyloxymethyl)naphthalene (DMN), α,α' -azoisobutyronitrile (Fluka) were used without further purification. Poly(vinyl alcohol), *n*-decanol, ethanol, acetone and toluene (Merck), fumed silica with a specific surface area of 200 m²/g (Kalush, Ukraine), trimethylchlorosilane, vinyltrichlorosilane, vinyltriethoxysilane, and triethoxysilane (Kremnepolimer) were applied.

Synthesis and Characterization

The filler samples with varied concentration of surface vinyl, methyl or hydride, as well as methyl in combination with hydride groups were obtained via gas-phase and/or liquid-phase chemical modification of fumed silica surface by vinyltrichloro- or vinyltriethoxy-, trimethylchloro- and/or triethoxysilane, respectively (Figure 1).

Gas-phase modification was performed in a reactor with stirring at 200–230°C. In brief, the silica powder was placed into the reactor and mixed with appropriate quantity of modifying agent (trimethylchlorosilane or vinyltrichlorosilane). After that, the samples were heated at 200°C for 1 h to remove from the surface the reagents and/or the by-products.

Liquid-phase modification was carried out in ethanol medium. Hydridesilylated silica was obtained by a reaction of triethoxysilane with unmodified or methylated fumed silica at room temperature under stirring for 24 h. Vinyl-containing silica was synthesized via interaction of fumed silica with vinyltriethoxysilane under similar conditions. Then modified silica samples were dried at 100°C.

Divinylbenzene-modified silica was obtained by a reaction of surface silicon-hydride groups with divinylbenzene via solid-phase hydrosilylation under stirring at 80°C with Speier catalyst (Figure 2).

The degree of surface modification was varied by the quantity of add-on modifying agent. All types of grafted groups were found in IR spectra of modified silica. The quantity of vinyl and silicon-hydride groups was determined by titrimetric analysis, and trimethylsilyl groups—by means of IR spectroscopy.

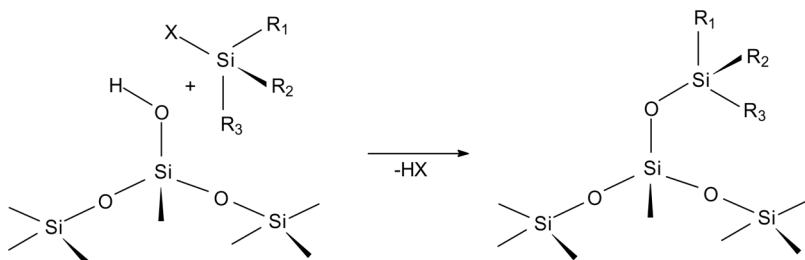


FIGURE 1 The scheme of silica surface silylation via electrophilic substitution of proton in terminal silanol group [13]. Trimethylsilylation: X = Cl, R₁ = R₂ = R₃ = CH₃; vinylsilylation: R₁ = CH=CH₂, X = R₂ = R₃ = Cl (gas-phase modification) or OC₂H₅ (liquid-phase modification); hydridesilylation: R₁ = H, X = R₂ = R₃ = OC₂H₅.

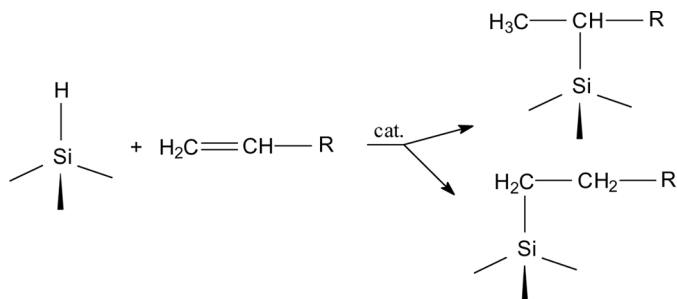


FIGURE 2 Nucleophilic addition of the silicon-hydride group hydrogen to the divinylbenzene vinyl group [14], $\text{R} = \text{C}_6\text{H}_4\text{CH}=\text{CH}_2$.

Porous spheres were obtained via suspension-emulsion polymerization [15] (DVB and DMN molar ratio 0.5:0.5) at filler presence (13 wt% with respect to composite mass) or absence. Synthesized composites were studied by means of IR spectroscopy (Perkin-Elmer 1700 FTIR spectrometer), differential scanning calorimetry (DSC) (NETZSCH Thermal Analysis, Bavaria) in an interval 20–500°C and differential thermogravimetric analysis (MOM, Paulik and Erdey, Budapest) in an interval of temperatures 20–1000°C both at heating rate 10°C/min. Second heating at DSC analysis was also performed but because no effects were observed, second DSC curves are not presented.

The degradation temperature (T_d) was determined by extrapolation of the initial degradation portion of the thermogravimetric (TG) curve; the temperature at the maximum weight-loss rate (T_{dm}) was determined by derivative thermogravimetry (DTG) curve; the activation energy of thermo-oxidative degradation (E_a) was calculated according the Friedman's equation [16]:

$$\ln \frac{d\alpha}{dt} = \ln A + n \ln(1 - \alpha) - \left(\frac{E_a}{RT} \right),$$

where α is the fractional loss of weight at absolute temperature T , R is the universal gas constant, A is the pre-exponential factor, and n is the order of reaction.

RESULTS AND DISCUSSION

Presumable schemes of the copolymer grafting onto modified silica surface during copolymerization are given in Figure 3. It should be noted that surface silicon-hydride and vinyl groups as well as attached DVB molecules can react both with DMN and DVB.

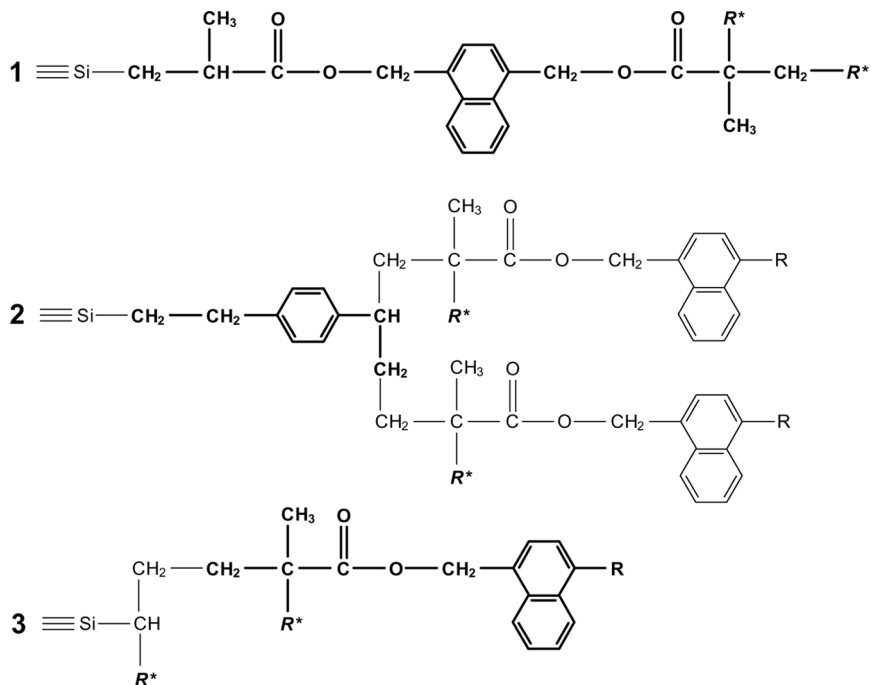


FIGURE 3 The schemes of modified silica—DVB-DMN copolymer interface structure: **1**—DMN is grafted to a surface via its hydrosilylation reaction by filler silicon-hydride group, **2**—DMN is attached to DVB grafted onto the filler surface, **3**—DMN (and DVB) attached to a filler surface via pre-grafted vinyl group. $\text{R} = \text{CH}_2\text{OC}(\text{O})\text{C}(\text{CH}_3) = \text{CH}_2$, $\text{R}^* = \text{DVB}$ or DMN .

Table 1 summarizes the results of thermogravimetric analysis (TGA) data on thermo-oxidative degradation of DVB-DMN composites in air. According to the TGA results of filler particles studies it is evident that at the filling degree used, filler weight loss contribution to total weight loss of the composites was not more than 1%. Therefore, the higher the value of composite char residue, the higher is the influence of filler surface on copolymerization process and composite structure. As seen from Table 1, in some cases the value of char residue is less than 12% (the lowest expected value at a condition of total filler inertness). It is related to some filler loss during the composites preparation.

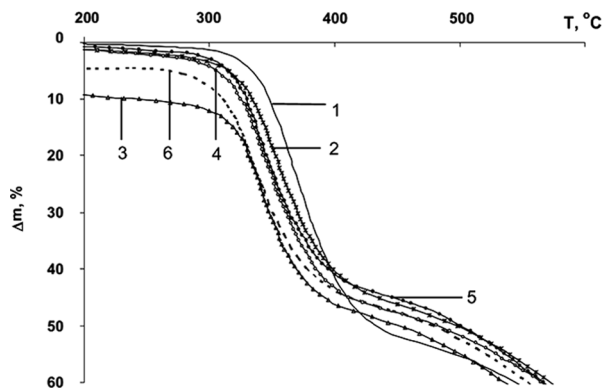
DVB-DMN/Trimethylsilylated Silica Composites

Modification with alkyl groups is known to improve the inorganic filler dispersion in the organic monomer medium, but the influence of the

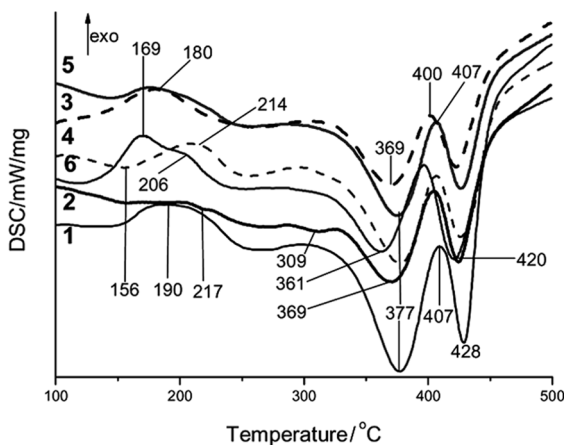
TABLE 1 Thermal Degradation Characteristics of DMN-DVB/Modified Silica Composites

N	Relative amount of grafted groups at filler surface, %	$T_d/T_{dm1}/T_{dm2}/T_{dm3}$ °C		Total weight loss, %	$T, ^\circ\text{C} / E_a, \text{kJ/mol}/n$
		T_d	T_{dm1}		
1	Unfilled copolymer	330/370/610		100	300–400/98/0.9
2	10% of $\equiv\text{Si}(\text{CH}_3)_3$ groups	320/360/580		91	300–380/103/1.2
3	20% of $\equiv\text{Si}(\text{CH}_3)_3$ groups	300/360/580		83	300–380/116/2.4
4	30% of $\equiv\text{Si}(\text{CH}_3)_3$ groups	320/360/560		92	300–380/97/1.2
5	80% of $\equiv\text{Si}(\text{CH}_3)_3$ groups	320/360/580		88	300–360/146/1.1
6	100% of $\equiv\text{Si}(\text{CH}_3)_3$ groups	300/360/580		84	300–360/96/1.4
7	20% of $\equiv\text{Si}(\text{CH}_3)_3$ and 10% of $\equiv\text{SiH}$ groups	320/360/570		73	300–380/126/2.4
8	20% of $\equiv\text{Si}(\text{CH}_3)_3$ and 30% of $\equiv\text{SiH}$ groups	300/350/580		80	300–400/61/0.9
9	20% of $\equiv\text{Si}(\text{CH}_3)_3$ and 80% of $\equiv\text{SiH}$ groups	330/370/600		88	300–380/129/2.1
10	30% of $\equiv\text{Si}(\text{CH}_3)_3$ and 10% of $\equiv\text{SiH}$ groups	320/360/600		88	300–380/94/0.9
11	30% of $\equiv\text{Si}(\text{CH}_3)_3$ and 30% of $\equiv\text{SiH}$ groups	310/360/570		83	300–380/95/0.7
12	30% of $\equiv\text{Si}(\text{CH}_3)_3$ and 70% of $\equiv\text{SiH}$ groups	320/360/580		92	300–360/118/1.2
13	30% of DVB	310/380/600		92	300–400/114/1.5
14	100% of DVB	150/200/380/600		90	120–200/53/1.2 320–380/159/8
15	30% of vinylsilyl groups (gas-phase modification)	320/360/590		88	300–380/119/1.4
16	30% of vinylsilyl groups (liquid-phase modification)	320/360/580		87	320–380/108/1.2
17	100% of vinylsilyl groups (liquid-phase modification)	320/350/600		84	300–380/85/0.7

degree of silica surface hydrophobization on homogeneity of polymeric composites structure is not well understood. From the literature (in particular [17–20]), it is clear that there is a direct relation between thermal stability and homogeneity of polymeric composite filled with highly-dispersed silica. The TGA results obtained (Figure 4a) demonstrate a decrease of the initial degradation temperature (T_d) of DVB-DMN/methylated silica composite relative to the unfilled copolymer. This decrease has an extreme dependence on the degree of filler surface modification with T_d minima (and thermal oxidation reaction order (n) maxima) at filling with 20 and 100% trimethylsilylated silica (Table 1). For the forementioned samples the authors also noted the weight loss within 100–200°C that may be attributed to solvent removal from the pores that has remained after preliminary washing



(a)



(b)

FIGURE 4 TG curves for thermal-oxidative degradation (a) and DSC curves for thermal decomposition (b) of copolymer DVB-DMN: unfilled (1) and containing fumed silica with a degree of surface trimethylsilylation 10 (2), 20 (3), 30 (4), 80 (5), and 100% (6).

and drying of synthesized composites. All this indicates that filling changes the material macrostructure.

The loss in thermal stability as a result of DVB-DMN filling with silica of varied degrees of surface trimethylsilylation may be related to material structure disordering in the presence of filler with chemically inactive functional groups. On the other hand, the degradation activation energy (E_a) of composites filled with trimethylsilylated

silica within 300–380°C generally increases. It is in accordance with the theory of formation of harder polymer layer at filler surface, which has higher thermal stability in comparison with bulk polymer [8,21]. Thus, the expected increase of the degree of structure homogeneity and therefore thermal stability of DVB-DMN/methylated silica composite with an increase of the degree of filler inorganic particles hydrophobization is not observed.

It is known that inorganic disperse filler decreases heat evolution at organic polymer curing as well as it can inhibit the polymerization process. The presence of methyl groups on silica surface in spite of the absence of chemical binding with polymeric matrix leads to an increase of polymerization exo-effect providing full polymer curing at the interface [21]. For DVB-DMN/methylated silica composites under study (samples 2–6) this assertion is only partly valid. The analysis of DSC curves shows that for unfilled copolymer (Figure 4b, curve 1) the broad peak of exo-effect with maximum at 190°C is typical consisting of at least two processes and is due to material post-curing involving unsaturated terminal groups of DMN and/or DVB links. Two endo-effects at 377 and 428°C corresponding to decomposition of methacrylate and divinylbenzene units, respectively [15] were also observed. Such effects are typical for all the composites under study with some shift of temperature maxima. Ten-percent trimethylsilylation of filler surface increases the degree of monomers transformation during the copolymerization process since the exo-effect at 190°C does not appear on DSC curve 2 (Figure 4b). However, here the structure decomposition begins at lower temperature and it is accompanied by weakly expressed endo-effect at 309°C, which may be related to overstrained bonds breaking.

With further increase of the degree of filler surface modification the intense exo-effect peak within 150–250°C is observed again (Figure 4b, DSC curves 3-6). In particular, at 20% trimethylsilylation of filler surface (sample 3) the low-temperature post-curing process prevails (peak maximum at 180°C), 30% (sample 4)—high-temperature process (peak maximum at 214°C), 80% (sample 5)—the contribution of both processes equalizes with a subsequent increase of low-temperature process contribution in the case of 100% trimethylsilylation (sample 6). Therefore, a prevalence of low-temperature post-curing process related to DVB-DVB interaction leads to a decrease of thermal stability of DVB-DMN copolymer in case of its filling with methylated silica.

DVB-DMN/Trimethylsilyl,hydridesilylated Silica Composites

The structure of near-surface layer plays a primary role in material reinforcement [8]. This structure is defined by polymer-filler

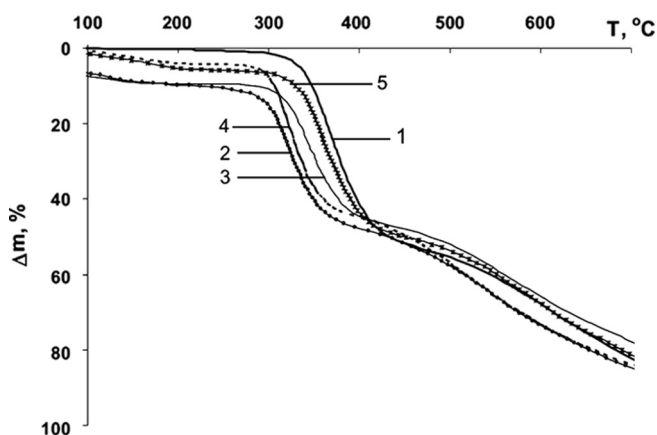
interaction, which could be separated into two components: weak (orienting, dispersion) and strong (crosslinking, chemical). The presence of hydride groups on silica surface in combination with methyl groups gives both components. Their contribution to the total value of polymer-filler interaction may be adjusted by varying the concentration of these groups: methyl groups will relax stresses at filler surface, and silicon-hydride groups will participate in macromolecules grafting.

DVB-DMN/Trimethylsilyl(20%),hydridesilylated Silica Composites

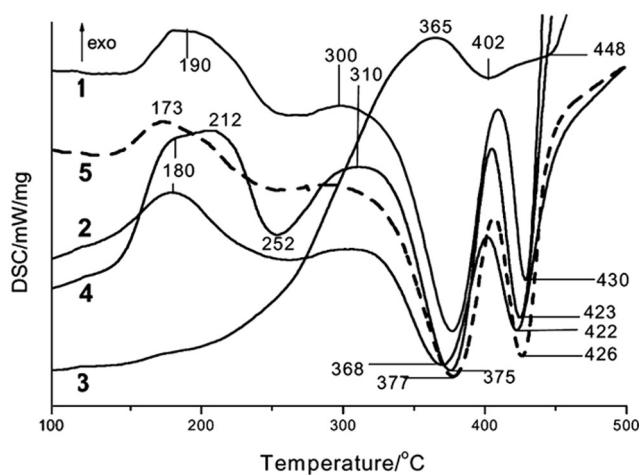
According to TGA data (Figure 5a) embedding of nanoparticles with 20% of surface trimethylsilyl groups and different amount of silicon-hydride groups into DVB-DMN copolymer (samples 7–9) slightly decreases the initial degradation temperature of material, as it was in the case of filling with methylated silica (samples 2–6). Sample 9 with silica containing maximum hydride groups is the only exception (Table 1)—its thermal stability is not worse than that for unfilled copolymer. The minimum T_d (as well as the maximum E_a and n) is observed at 30% hydridesilylation of filler surface (sample 8) and is close to T_d of composite 3 whose filler does not contain $\equiv\text{SiH}$ groups. At the same time 10% and total hydridesilylation leads to an increase of thermal characteristics of DVB-DMN copolymer. It should be noted that within 100–200°C there is a weight loss on TG curves of samples 7–9.

The DSC curves analysis (Figure 5b) shows that, in comparison with unfilled copolymer, for the composite 8 the broadening of post-curing exo-effect peak is observed with the prevalence of a high-temperature component. It indicates to a decrease in the degree of monomers transformation during the copolymerization process. The expressed exo-effect peak with maximum at 310°C is also noted and attributed to post-curing reactions involving the groups of filler surface. At maximal $\equiv\text{SiH}$ groups content, the DSC curve of the composite is identical to that for sample 3 but the temperatures of copolymer units decomposition are higher and close to those for unfilled material.

The most interesting case is the composite 7 containing filler with 20% of trimethylsilyl and 10% of silicon-hydride groups on the surface. Despite the fact that according to TGA results its thermal stability is lower than that of unfilled copolymer (Table 1) aberrant behavior of DSC curve 2 in Figure 5b indicates to the essential filler effect on thermal decomposition processes under inert atmosphere. It allows assuming that in this case the most homogeneous structure among all the composites under study is achieved. Exo-effect is not observed on the DSC curve within 150–250°C yet the authors noted



(a)



(b)

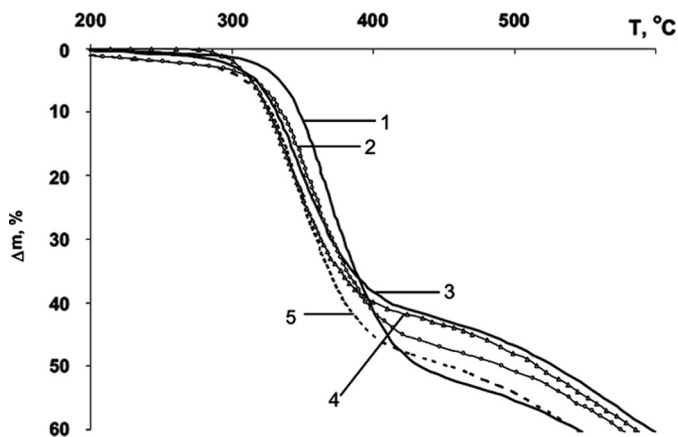
FIGURE 5 TG curves for thermal-oxidative degradation (a) and DSC curves for thermal decomposition (b) of copolymer DVB-DMN: unfilled (1) and containing trimethylsilylated (by 20%) fumed silica with a degree of surface hydridesilylation 0 (2), 10 (3), 30 (4), and 80% (5).

the evident exo-effect peak at 365°C. On the one hand it may be related to high degree of monomers transformation resulting in copolymer macromolecules reconstruction occurring at higher temperatures

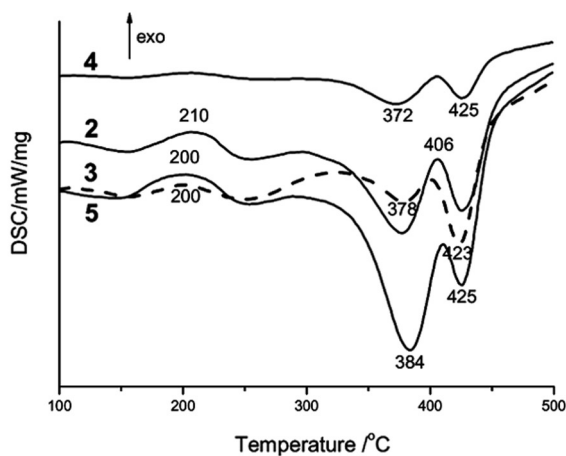
and accompanied by the breakage of weak bonds and the formation of more thermally stable ones. On the other hand, exo-effect of copolymer post-curing involving unsaturated bonds may shift into the region of higher temperatures owing to considerable effect of filler surface. Probably at this concentration of surface methyl and hydride groups the highest degree of filler dispersancy was obtained already at the polymerization stage and the maximal contact area as well as the optimal quantity of monomer (polymer)-filler chemical bonds were achieved. It promoted the formation of structural network, which has sites of filler particles with high crosslink density of polymer at the surface. In this case, the surface has a considerable immobilizing effect on the macromolecules participating in sites junction and/or having unsaturated groups; as a result of this the activation energy and correspondingly the temperature of post-curing process are increased. An intense exo-effect at 365°C has an influence on peaks resolution on DSC curve attributed to decomposition of copolymer units. As a consequence the observed endo-effects maxima are shifted into high-temperature region (402 and 448°C, respectively). Estimating generally the effect of the amount of silicon-hydride groups of 20% trimethylsilylated filler it should be noted that minimum of thermal stability observed for sample 8 is probably related to the ability of $\equiv\text{SiH}$ groups to both initiate and break off the polymer chain growth [22]. Here the degree of polymerization is relatively low and intense exo-effect of post-curing within 150–250°C may be an additional evidence in this favor. In the case of total hydridesilylation of partially methylated silica surface a more crosslinked structure is formed and the thermal stability of the material increases.

DVB-DMN/Trimethylsilyl(30%),hydridesilylated Silica Composites

TGA analysis (Figure 6a) shows that, as in previous cases, filling leads to a decrease of copolymer T_d , the minimum T_d and n is again at 30% hydridesilylation of silica surface (sample 11). Maximal and 10% grafting of silicon-hydride groups onto filler surface practically do not change the T_d of a composite (samples 12 and 10, respectively) as compared with sample 4 whose filler does not contain $\equiv\text{SiH}$ groups. It also should be noted that in comparison with sample 4, for the composites 10 and 12 a decrease of thermal oxidation reaction order is observed down to the value close to that for unfilled copolymer without essential change of E_a . At the same time, in the case of totally hydridesilylated filler the activation energy increases and the value of reaction order is close to n for 30% trimethylsilylated silica (Table 1). The



(a)



(b)

FIGURE 6 TG curves for thermal-oxidative degradation (a) and DSC curves for thermal decomposition (b) of copolymer DVB-DMN: unfilled (1) and containing trimethylsilylated (by 30%) fumed silica with a degree of surface hydridesilylation 0 (2), 10 (3), 30 (4), and 70% (5).

weight loss within 100–200°C was not observed on TG curves of the samples under consideration.

On the DSC curve of the composite 10 (Figure 6b, curve 3) the authors noted the appearance of low-intensity exo-effect peak at

200°C and the evident maximum at 325°C that testifies to the passage of several reactions: post-curing between polymer units in bulk and at the filler surface. It is interesting to note the change in ratio of peaks intensities attributed to endo-effects of polymer methacrylate and divinylbenzene units decomposition (378 and 423°C) that was not so evident for the composites filled with 20% trimethylsilylated hydride-silica. For the composite 10 on the DSC curve the peak prevails related to endo-effect of divinylbenzene units decomposition. As the $\equiv\text{SiH}$ groups content increases, the ratio of first and second peaks intensity changes (Figure 6b, curves 3–5), that is, in the case of sample 11 (30% hydridesilylation of filler surface) the intensities equalizing occurred and for sample 12 (maximum hydridesilylation of filler surface) the peak attributed to methacrylate units decomposition (384°C) prevails. A minimum of exo-effect peak intensity at 200°C is noted on the DSC curve of the sample 11. The composite structural change observed may be related to change of specificity and increase of selectivity of monomers adsorption on the filler surface. Presumably, at low (10%) surface $\equiv\text{SiH}$ groups content, the adsorption of DVB molecules is preferable. Because chemically active silicon-hydride groups initiate the copolymerization process from the surface it, resulted in compaction of near-surface layers and prevention of radical migration into the bulk, that is, the cell effect occurred [23,24] and therefore the polymerization of DVB molecules prevails. Not crosslinked DMN is washed out at samples posttreatment. Similar mechanism is presumed for the structure formation of the DVB-DMN composite 12 but in this case the immobilization of DMN molecules at filler surface prevails.

The influence of filler surface on the structure of the composites obtained is also confirmed by IR spectroscopy data. In the spectra of filled composites (Figure 7, sp. 2–4) the absorption band at 466 cm^{-1} appears, indicating a spiral macromolecules conformation [25]. The composite filled with totally hydridesilylated pre-methylated silica is the only exception in whose spectrum, as in the case of unfilled copolymer, the band at 466 cm^{-1} is absent. Probably here a secondary modifying layer is formed on the filler surface in which the macromolecules are oriented not from the surface with spiral conformation but along the surface. At that the fraction of unreacted double bonds increases, which is confirmed by a relative increase of band intensity at 1624 cm^{-1} corresponding to $=\text{CH}-$ bond vibrations.

DVB-DMN/DVB-Modified Silica Composites

Because the presence of silicon-hydride groups has an ambiguous influence on the completeness of hydrosilylation and copolymerization

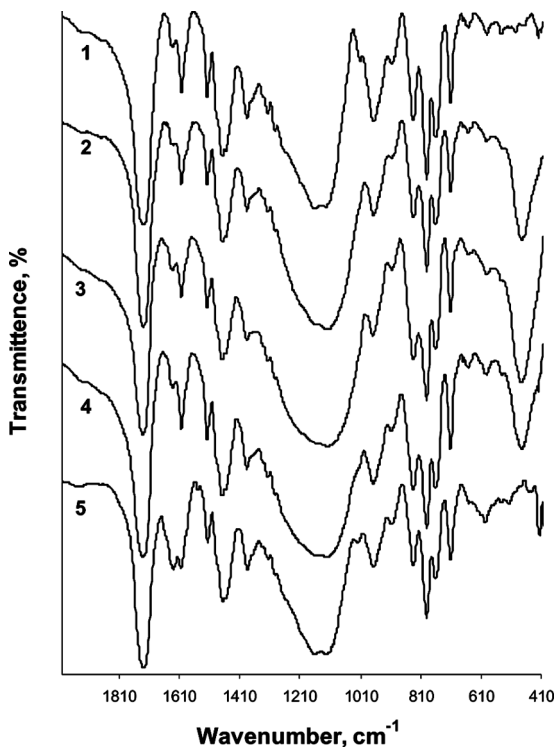
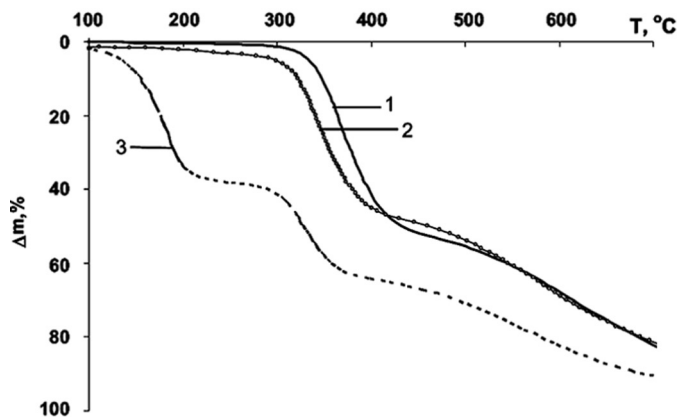


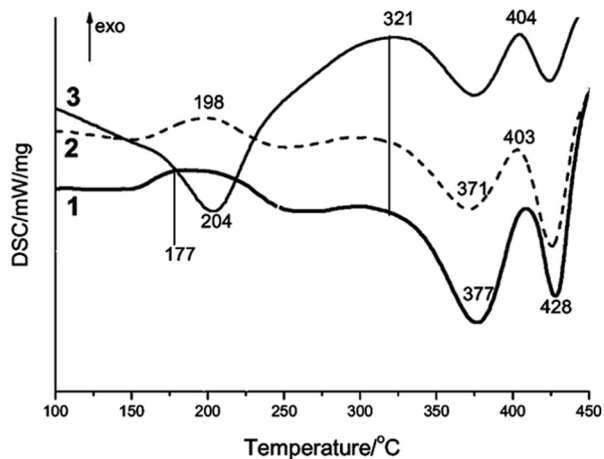
FIGURE 7 IR-spectra of copolymer DVB-DMN: unfilled (1) and containing trimethylsilylated (by 30%) fumed silica with a degree of surface hydridesilylation 0 (2), 10 (3), 30 (4), and 70% (5).

processes, and therefore on structure and characteristics of the composites obtained, the authors decided to carry out the hydrosilylation stage separately, as well. Before the synthesis of copolymer composite the DVB molecules were grafted onto the hydridesilica surface. Such modification should have ensured compatibility and homogeneity of polymer-silica chemical binding.

From the results of TGA analysis (Figure 8a) it is seen that in this case as well, filling leads to a decrease of T_d value. However, comparing the composites with the same modification degree of filler surface (Table 1, samples 4, 7, and 13) one may conclude that at 30% substitution of surface hydroxyls the nature of grafted groups has the main influence on the parameters of composites thermal degradation, the presence of chemically active groups leads to an increase of the activation energy and thermal degradation reaction order. The composite



(a)



(b)

FIGURE 8 TG curves for thermal-oxidative degradation (a) and DSC curves for thermal decomposition (b) of copolymer DVB-DMN: unfilled (1) and containing DVB-modified fumed silica with a degree of surface modification 30 (2) and 100% (3).

13 has shown unexpectedly low T_d in sequence under comparison. Therefore, a rigid modifying organic layer, although distant from the filler surface, is less efficient than that formed as a result of partial functionalization with trimethylsilyl and silicon-hydride groups. This is confirmed by a considerable worsening of thermal

stability of the composite 14. On TG curve 3 within 100–400°C two parts are noted corresponding to the removal of uncrosslinked monomer (oligomer) and degradation of thermally mobile (most likely adsorbed) surface layer. Apparently, it is related to the presence of large amount of grafted DVB groups, which leads to their chemical interaction with each other that decreases considerably the degree of filler surface participation in the process of composite structure formation. This assumption is in accordance with the data of DSC analysis and IR spectroscopy. An intense endo-effect peak on DSC curve 3 (Figure 8b) at 204°C indicates the presence of low-molecular polymer fractions weakly crosslinked into the polymer network. At maximal concentration of DVB molecules grafted onto the filler surface in IR spectrum of the composite 14 (Figure 9, sp. 3) the conformationally sensitive bands at 668, 646, and 420 cm^{-1} characterizing the structure order were not observed. At the same time on DSC

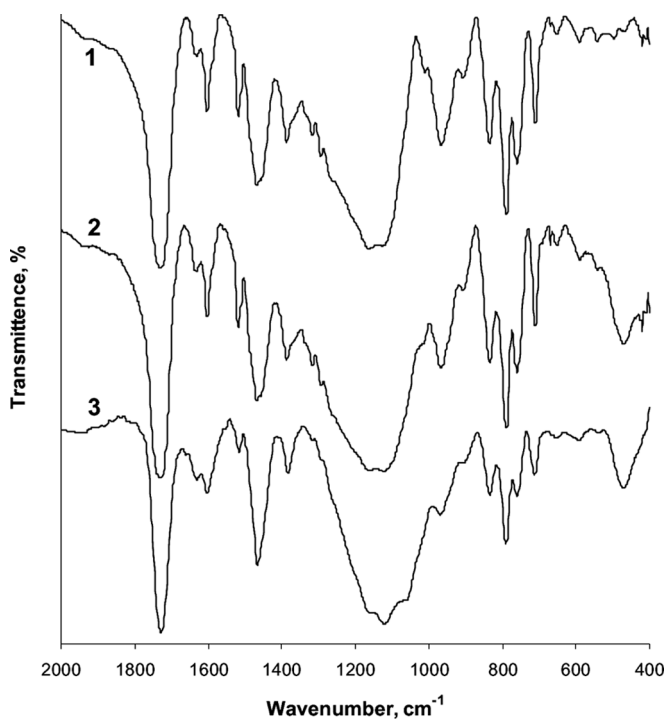


FIGURE 9 IR spectra of copolymer DVB-DMN: unfilled (1) and containing DVB-modified fumed silica with a degree of surface modification 30 (2) and 100% (3).

curve 3 in Figure 8b the exo-effect peak at 321°C is noted indicating the participation of filler surface in the process of material post-curing. It is evident that the efficiency of polymer-filler binding is restrained by steric factors occurring when large amount of DVB groups are grafted onto the filler surface. As seen from curve 2 (Figure 8b), steric factor is not evident in the case of 30% DVB groups content on the filler surface (sample 13). However, in this case a drastic change in peaks intensity at 377 and 428°C, attributed to the decomposition of methacrylate and divinylbenzene units respectively, is noted. A similar effect, as mentioned earlier, is also observed for the composite 10 that confirms the assumption that predominantly DVB molecules are present at the surface and participate in material structurization process. However, at the sample 13 formation the polymerization apparently progresses from the surface and DVB units are mainly generated. In the IR spectrum of the composite obtained (Figure 9, sp. 2) the presence of bands at 1548 and 1650 cm^{-1} is noted, indicating that there are terminal aromatic groups with unreacted double bonds in the material.

DVB-DMN/Vinylsilylated Silica Composites

The results of these investigations have shown the low efficiency of fillers with grafted DVB during the formation of DVB-DMN composite structure, in particular due to steric factor. To decrease it while keeping the filler functionality, vinylsilyl groups were grafted onto silica surface. In IR spectra of vinylsilica-filled DVB-DMN (Figure 10) a decrease of band intensity at 1620 cm^{-1} corresponding to the =CH-stretching vibrations is observed with an increase of grafted functional groups concentration. It confirms the assumption on a larger influence of vinylsilylated filler on the degree of monomers transformation in comparison with DVB-modified one. The IR spectroscopy data is the evidence that the method of filler surface modification has also an influence on the structure of the copolymer obtained. At filling in spectrum of the composite 15, the bands at 670 and 648 cm^{-1} appear that are typical for the unfilled material but they are absent in the spectra of composites 16 and 17. Therefore, gas-phase modified silica surface has less effect on macromolecules conformation. This is possibly related to a smaller influence of this modification method on the fractal structure of filler aggregates.

According to the TGA results (Figure 11a) for vinylsilicas neither method nor the degree of surface modification has an influence on the initial degradation temperature of the composites. At the same time, as the degree of filler surface modification increases, the

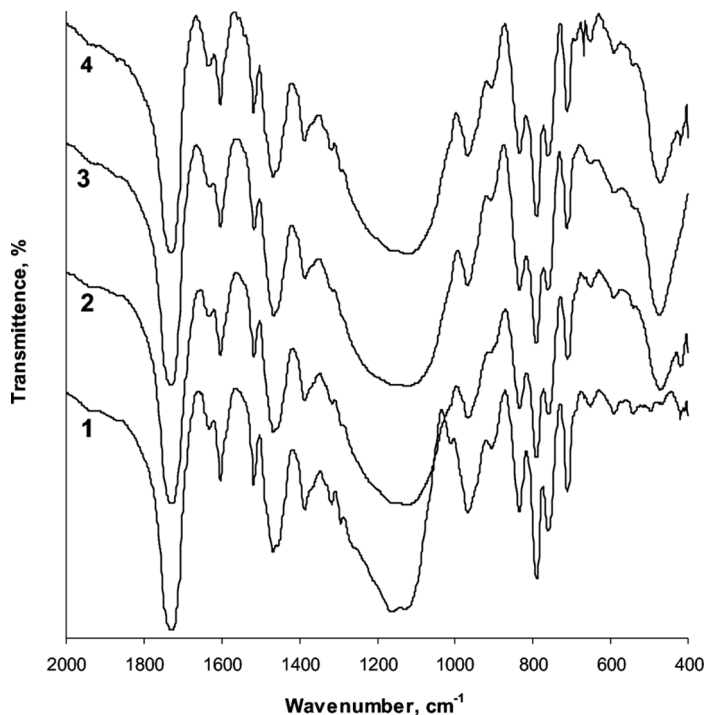


FIGURE 10 IR spectra of copolymer DVB-DMN: unfilled (1) and containing fumed silica with a degree of surface vinylsilylation 30 (2), 100% (3) (liquid-phase modification) and 30% (4) (gas-phase modification).

activation energy and reaction order decrease, becoming even less than those for unfilled copolymer (Table 1). It is, again, evidence in favor of better efficiency of partial in comparison with total modification of filler surface.

On the DSC curve of composite 17 (Figure 11b, curve 4) an intense exo-effect peak at 168°C is noted. This peak is probably related to the regrouping reactions involving thermally labile terminal groups of macromolecules, crosslinks between them as well as the surface structures. Such a process is possible only with active participation of the surface both in reaction of chain transfer and in activation of radical interaction between macromolecules fragments. As in the case of maximum degree of surface modification with DVB molecules, total surface coverage with vinyl groups leads to the formation of compounds with strained bonds in a composite and their decomposition starts already at 227°C. Here, the observed broad endo-effect peak

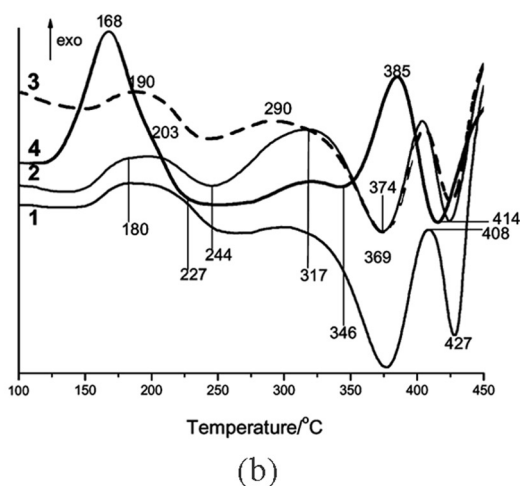
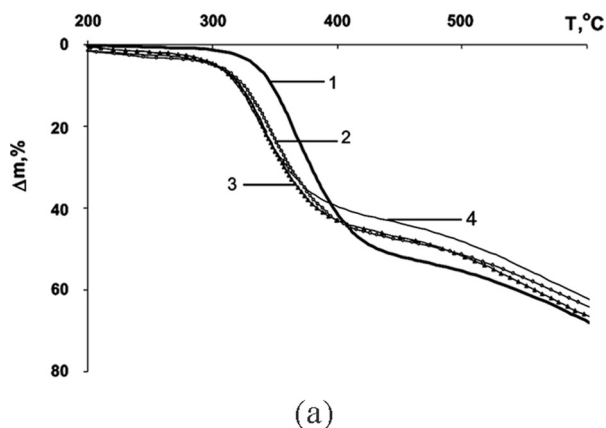


FIGURE 11 TG curves for thermal-oxidative degradation (a) and DSC curves for thermal decomposition (b) of copolymer DVB-DMN: unfilled (1) and containing fumed silica with a degree of surface vinylsilylation 30% (2) (gas-phase modification), 30 (3), and 100% (4) (liquid-phase modification).

indicates to a broad distribution of binding energies in structures that were formed under the influence of the surface and are subject to decomposition. Shifting and decrease in intensity of endo-effect peak attributed to methacrylate units decomposition allows one to assume that they are involved in surface reactions. Therefore, on the surface of totally modified vinylsilica the sorption of DMN molecules occurs,

preventing their binding to the network. Here, the temperature of endo-effect of divinylbenzene units decomposition decreases, providing the evidence for the formation of rigidly crosslinked compounds.

CONCLUSIONS

1. Filling with modified silica generally decreases the initial temperature of DVB-DMN copolymer degradation but increases the activation energy of its thermal oxidation. A decrease of the initial degradation temperature of the composites has an extreme dependence on the concentration of chemically inactive trimethylsilyl groups grafted onto the filler surface, and at their constant concentration—upon the amount of chemically active silicon-hydride groups.
2. Total functionalization of silica surface leads to worsening of its efficiency as filler for DVB-DMN copolymer. The composites filled with silica having less size of surface groups chemically active in copolymerization process demonstrate better thermal stability. At the same amount of grafted active groups the composites filled with silica having lower degree of surface hydroxyls substitution show better thermal characteristics. At the same degree of silica surface coverage with modifying layer, the primary parameter of its efficiency is the nature of the grafted chemically active groups. Mixed modification with trimethylsilyl and silicon-hydride groups was found to be the most efficient.
3. Modification of methylated silica with silicon-hydride groups improves the thermal stability of filled DVB-DMN composites. Thus, in the case of 20 or 100% trimethylsilylation of silica surface, the minima of the initial temperature of the material degradation are observed whereas the surface layer of totally modified filler with 20% of trimethylsilyl and 80% of silicon-hydride groups promotes its increase up to the value closed to T_d of unfilled DVB-DMN copolymer.
4. Variation of the degree of silica surface modification and the nature of grafted functional groups has a direct effect on the DVB with DMN copolymerization process. The highest influence of filler surface on the copolymerization process and thermal characteristics of DVB-DMN copolymer is observed at filling with methylated silica having 10% of surface hydride groups: for 30% hydrophobization the ratio of methacrylate and divinylbenzene units in the cross-linked copolymer is drastically changed and in the case of 20% trimethylsilylation the most homogeneous distribution of filler in copolymer is presumably achieved.

5. The concentration of vinyl groups on filler surface affects weakly the thermal stability of DVB-DMN composites in contrast to the modification method: gas-phase vinylsilylated silica is more efficient filler than that obtained via liquid phase modification.

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