

DSC study of polyhydroxyethylmethacrylate filled with modified silicas

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Abstract Effects of the nature of functional groups (namely, hydroxyl, methyl, silicon hydride, amino, and vinyl) on the surface of pristine and modified silicas on polymerization of 2-hydroxyethylmethacrylate (HEMA) and on structural characteristics of the filled composites have been studied. DSC, FTIR spectroscopy and equilibrium water sorption (ESI) techniques were applied for the composites characterization. Results obtained testify that the chemical nature of the grafted groups has a strong influence on the monomer orientation in the surface layer of the filler. More uniform and cross-linked structures were detected in the composites with particularly methylated silica. Filler with chemically active silicon hydride groups promotes formation of ordered structure with rigid macromolecules. The presence of amino and vinyl groups on the silica surface results in formation of flexible polymer chains with a low cross-linking density or with a low polymerization degree, even at 2 wt% filling degree. Water uptake for composites with vinyl- and amine-containing silicas was low, indicating the close-packing of polymeric molecules in the filled polyHEMA.

Keywords 2-Hydroxyethylmethacrylate (HEMA) · Silica fillers · Surface groups · DSC · Composite structure

Introduction

Polymers based on 2-hydroxyethylmethacrylate (HEMA) are widely used for preparation of permanent hydrogels, drug delivery systems, cell carriers and other biomedical applications. The great interest in HEMA is determined by easiness of polymerization, as with a majority of methacrylic derivatives, and the presence of primary alcohol in the structure, that allows one to execute the substitution reactions with the monomer or appropriate polymer (polyHEMA) [1–3]. In addition, polyHEMA displays significant physical properties, such as permeability of its membranes to oxygen, mechanical and viscoelastic behavior, thermal and dielectric properties [4]. Some restrictions are caused by stiff and brittle nature of the polymer in the dry state and its poor mechanical strength [5]. In order to improve the polymer characteristics and physical properties of HEMA-based materials the copolymerization of HEMA with other types of monomers is often applied [6, 7]. Improving the mechanical and thermal properties of polymeric materials can be achieved by introduction of fillers, in particular highly dispersed silicas [8, 9]. It is well known that chemical modification of the silica surface allows one to improve the compatibility of the system components, to obtain more uniform filler distribution and in favorable cases to provide chemical cross-linking of the filled composite [10–12]. Polymer structure controlling can be achieved by polymerization in the presence of silica fillers.

This study was directed toward the investigation of the effects of the nature of functional groups (namely, hydroxyl, methyl, silicon hydride, amino and vinyl) on the surface of pristine and modified silicas on polymerization of HEMA and on structural characteristics of the filled composites.

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Experimental

Fumed silica with a specific surface area of 300 m²/g (Kalush, Ukraine) was used as initial hydrophilic filler. Hydrophobization of silica surface was performed via gas-phase silylation using trimethylchlorosilane (Kremnepolimer, Ukraine) as was previously described [13]. Modification of silica surface with triethoxysilane, 3-aminopropyltriethoxysilane, and vinyltriethoxysilane was performed by liquid-phase process (solution of appropriate alkoxy silane in toluene or ethanol) as was described in [14]. The degree of substitution of isolated silanols on the silica surface with functional groups was controlled by IR spectroscopy.

2-Hydroxyethylmethacrylate polymerization was carried out in an open reactor at 90 °C in the presence of azobisisobutyronitrile (0.01 wt%). Next to pristine fumed silica (A300), five more types of silica fillers, obtained on the basis of fumed silica, were employed for preparation of the filled composites: silicas with grafted methylsilyl groups (samples ACH₃20 and ACH₃100, degree of surface silanol groups displacement of 20 and 100 %, respectively), silicas with bound amino groups (ANH₂20 and ANH₂100, degree of SiOH groups displacement of 20 and 100%, respectively), silicas with anchored silicon hydride and vinyl groups (ASiH30 and ACH=CH₂30, degree of SiOH groups displacement of 30 % for both samples). The filling degree was in all cases 2 wt%.

Differential scanning calorimetry (DSC) was performed under nitrogen atmosphere in the temperature range from 0 up to 150 °C using a TA Q200 series DSC instrument. Samples of ~8 mg in mass, cut from the produced plate, were closed in standard Tzero aluminum pans. Cooling and heating rates were 10 °C/min. During the 1st and 2nd heating scan the samples stayed at 120 °C for 3 min (isothermally) in order to stabilize the materials.

Fourier-transform infrared (FTIR) spectroscopy (Termo Nicolet Nexus FTIR) has been used to characterize modified silica, unfilled polymer and silica-filled composites. The dry powdered samples were mixed with KBr (1:10). The FTIR spectra were obtained by recording 50 scans between 4,000 and 400 cm⁻¹ with a resolution of 8 cm⁻¹.

Isothermal water sorption curves were recorded at room temperature by exposing the samples to water vapor atmospheres in sealed jars. Various water activities were achieved with the appropriate saturated salt solutions in distilled water. The samples were exposed for 7 days to atmosphere with water activities of 0.02 (phosphorus

pentoxide), 0.40 (local ambience), 0.85 and 0.98. Attainment of equilibrium was determined via recording of the sample weight. A Metler Toledo balance with 10⁻⁵ g sensitivity was employed for these measurements. The weights after equilibrating over P₂O₅ were considered as dry weights ($m_{\text{dry sample}}$). Once the equilibrium was attained, the hydration (h) was calculated on the wet basis through the expression:

$$h = \frac{m_{\text{water}}}{m_{\text{hydr. sample}}} = \frac{m_{\text{hydr. sample}} - m_{\text{dry sample}}}{m_{\text{hydr. sample}}}$$

Results and discussion

Silica fillers

The filler surface chemistry (Scheme 1) is responsible for the structure of the resulting composite material. Interaction of the monomer with the surface sites of silica particles determines the mechanism of macromolecules attachment, namely, physical adsorption, chemical adsorption, “grafting to” or “grafting from” surface-initiated polymerization, as well as the degree of monomer conversion, especially in the surface layer, and macromolecules orientation relative to each other and to the filler particles. Fig. 1 shows the infrared spectra of silica with relatively chemically inert groups (*a*) and fillers with chemically active groups in the surface layer (*b*, *c*). Pristine (unmodified) silica (A300) contains on surface isolated hydroxyl groups (3,745 cm⁻¹), the OH-groups perturbed with hydrogen bonds (3,660 cm⁻¹), as well as physically adsorbed and coordinatively bound water with a broad band with maximum of absorption at 3,450 cm⁻¹ (Fig. 1a). Interaction of the monomer HEMA with hydrated surface can be realized mainly through the hydrophilic groups of adsorbed molecules. In this case, hydrophobic methacrylate groups directed from surface are available to participate in the radical polymerization process. When analyzing the role of the filler in such system, the influence of the surface hydrate covering on HEMA polymerization process should be also taken into account [15].

For the filler with 20% substitution of surface silanols with trimethylsilyl groups (ACH₃20), hydroxyl (3,745 cm⁻¹) and methyl groups (2,966 and 2,906 cm⁻¹) are present (Fig. 1a), with the result that both hydrophilic and hydrophobic interactions with monomer can be realized. Full surface hydrophobization with trimethylsilyl groups (ACH₃100) reduces

Scheme 1 Structure of fillers surface layer

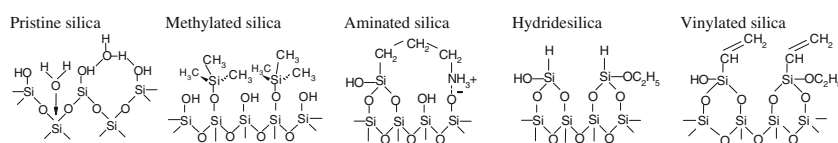
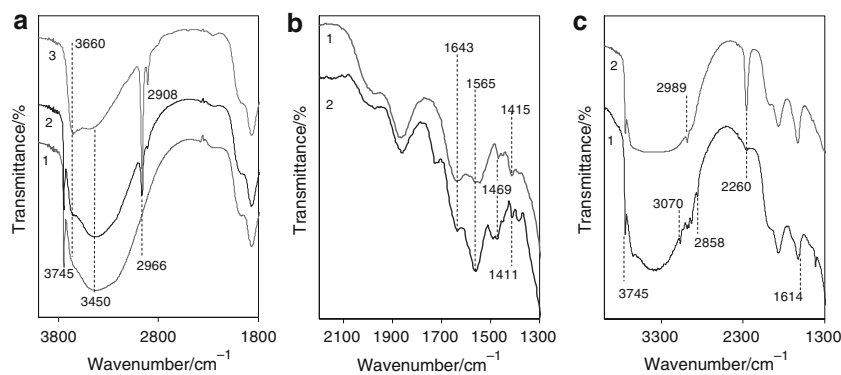


Fig. 1 FTIR spectra of fillers: A300 (a, 1), ACH₃20 (a, 2) ACH₃100 (a, 3), ANH₂20 (b, 1) and ANH₂100 (b, 2), ASiH30 (c, 1) and ACH=CH₂30 (c, 2)



the degree of silica particles aggregation, which results in better dispersability of this filler in the monomer medium. However, at executing of hydrophobic interactions of the monomer with methylated surface the hydrophilic groups of HEMA are directed into the volume that can hinder the participation of the methacrylate groups of the adsorbed molecules in the polymerization process.

Using silicas with chemically active groups promotes polymer structurization not only due to orientation effects but also through covalent attachment of macromolecules to the filler surface. In this case, the reactivity and accessibility of the grafted surface groups is of great importance. As known, grafted aminopropyl radicals can form bridge-like structures via interaction of amino groups with protons of surface hydroxyl groups or adsorbed water molecules. Because of this the surface layer of aminosilica (ANH₂20) contains NH₂-groups with different protonation degree (1,643 and 1,565 cm⁻¹). The degree of protonation is determined by NH₂-groups basicity. As the degree of silica modification increases (ANH₂100), the ratio of strongly and weakly basic amino groups is changed, and the band at 1,565 cm⁻¹ dominates in the spectrum (Fig. 1b). At filling with aminosilica, interaction of surface amino groups with functional groups of the monomer (polymer) can be realized.

In the presence of silicon hydride (2,260 cm⁻¹) or vinyl groups (3,070, 1,614 cm⁻¹) on the silica surface (Fig. 1c) grafting of macromolecules occur through the formation of hydrolytically stable Si–C bonds via the hydrosilylation reaction or radical polymerization, respectively. In both cases, however, the surface groups can both promote and interrupt the growth of the polymeric chain.

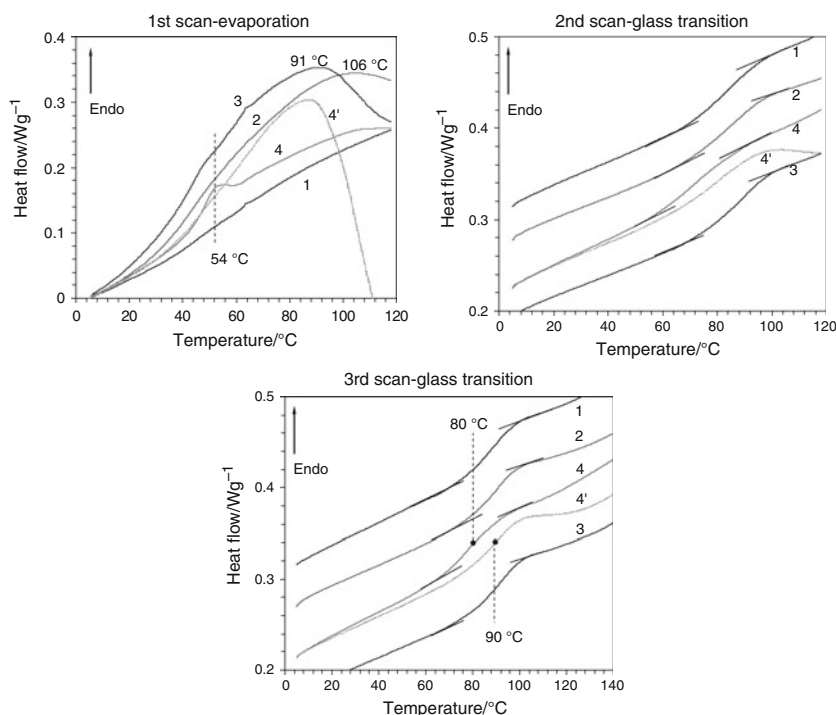
Composites with chemically inert fillers

The DSC curve for unfilled polyHEMA (Fig. 2, 1st scan, curve 1) shows smooth heat consumption during the volatile matter (unreacted monomer) and moisture eliminating with an extremum near 150 °C (according to Gaussian fitting). The filling with pristine silica leads to an increase

in intensity of the endothermic peak with a shift to 106 °C (Fig. 2, 1st scan, curve 2). This is caused by a decrease in the mobility of the evaporating molecules as a consequence of low conformational mobility of the polymer molecules. The composite structure formed exhibits less enthalpy changes in comparison with unfilled polyHEMA. The above mentioned change tendency in the DSC curve profile with a decrease in the mobility of macromolecules is retained for the composite filled with partially methylated silica ACH₃20 (Fig. 2, 1st scan, curve 3). For the composites filled with ACH₃100, the presence of areas with varying cross-linking degree was detected (Fig. 2, 1st scan, 4 and 4'). For loosened structure of the material a broad endotherm of volatile matter evaporation with maximum at about 110 °C and β -relaxation stage in the range of 40–60 °C (curve 4) were obtained. This conformation transition (β -relaxation) is the local rotational motion of the segments of the flexible macromolecules in the interlayer between lamellar phases. At the greater macromolecules bending convolution this transition is more significant and appears at a lower temperature. In the absence of local tension (Fig. 2, 1st scan, curve 4'), this transition was not observed, the endotherm being narrower with an extremum at 88 °C. A possible explanation is that the less homogeneous structure of the sample was caused by different rates of polymerization of the monomer near the particle surface and in the bulk, resulting in a “cell effect” [16]. This leads to discreteness of the thermodynamic and thermokinetic parameters of structure. However, at the 3rd scan the changes in heat capacity after α -relaxation (glass transition) in both cases were similar (Table 1). Activation energy (E_a) [17] of the volatile matter removal (Table 1) was higher for the composites than for the unfilled polymer. This could have been caused by a change in the macromolecules packing density, in particular for the composites with methylated silicas.

The glass transition temperatures of composites with the relatively chemically inert fillers (Fig. 2, second and third scans) are increased independently of the liophilicity of the silica surface (Table 1). Along with this, the change in heat

Fig. 2 DSC scans of heat flow versus temperature for polyHEMA (1) and composites filled with various silicas: untreated (2), methylated with 20% (3) and 100% (4) degrees of substitution of surface hydroxyl groups. Interrupted line refers to the repeated measurement



capacity (ΔC_p) at the glass transition is decreased compared with unfilled HEMA. Among the composites with chemically inert fillers, the lowest ΔC_p was obtained for the material with hydrophilic silica (A300). ΔC_p can be interpreted in terms of the fraction of polymer participating to the glass transition (α -relaxation). This result suggests then that the hydrophilic filler has a stronger ability to cause immobilization of the polymer chains. However, the cohesion energy [18] for the polyHEMA-A300 composite at the third scan (Table 1) was similar to that for the polyHEMA-ACH₃20 composite. This provides an indication of similarities in the mutual arrangement of the macromolecules after the structure relaxation.

Analysis of IR spectra [14–22] in the range of CH₂ and CH₃-groups vibrations confirms the changes in macrostructure and macromolecules conformation for the composites with inert fillers (Table 2). The presence in the spectra of composites filled with ACH₃20 or ACH₃100 bands at 2,996 cm⁻¹ and in the range 3,023–3,008 cm⁻¹ attributed to stretching vibrations of CH bonds in the methacrylate groups [23] indicates an incomplete conversion of the monomer. It should be noted that these peaks were more intense in spectrum of composite with ACH₃100 that indicates the lower monomer conversion degree. According to the infrared spectra the filling with hydrated silica A300 leads to formation of a more uniform structure with close packing of macromolecules. The presence of 10% trimethylsilyl groups on the silica surface provides an increase of the distance between the macromolecules, while maintaining uniformity of the material,

whereas the fully methylated surface leads to composite structure loosening.

The water sorption capacity of composites in air of 98% relative humidity decreases in the following sequence: A300 > ACH₃20 > ACH₃100 (Table 3). The resulting dependences of the water sorption are characteristic of materials with low energy interaction of adsorbent–adsorbate. Since the absorption in this system occurs mainly through penetration of water molecules between the macromolecules of disordered regions [24], it can be assumed that the content of disordered regions increases with increasing hydrophobicity of the filler. The gel formed in these areas suppresses the diffusion of water molecules inside the material.

Composites with chemically active fillers

The endotherm of the composite filled with ANH₂20 at the first scan (Fig. 3, curve 1) is wider and more intense in comparison with unfilled polymer. This result indicates a decrease in the molecules mobility of the volatile products in bulk of the polymer formed [25]. It explains also the increase (in comparison with the unfilled polymer and polyHEMA-A300) in the activation energies of the volatile matter elimination below 50 °C. Attention is drawn to the presence of an endothermic process in the range of 95–110 °C with activation energy that is comparable with activation energy of covalent bonds destruction. The composite with ACH₃100 and the material with ANH₂20 have discrete structural properties (Fig. 3, curves 1 and 1').

Table 1 DSC data (T_g , ΔC_p), cohesion energy (E_c) and effective activation energy (E_a) of main stage of evaporation for polymeric composites based on polyHEMA and silicas

No	Sample	Scan	$T_{on}/^{\circ}C$	$T_{end}/^{\circ}C$	$T_g/^{\circ}C$	$\Delta C_p/J\ g^{-1}\ C^{-1}$	$E_c/kJ\ mol^{-1}$	$E_a/kJ\ mol^{-1}$		
								<50 °C	50–80 °C	>80 °C
1	polyHEMA	i	–	–	–	–		11	10	12
		ii	72	95	83	0.41	92			
		iii	78	97	88	0.37	114			
<i>Composites with chemically inert fillers</i>										
2	polyHEMA-A300	i	–	–	–	–		19	14	–
		ii	76	96	86	0.34	107			
		iii	82	97	90	0.30	146			
3	polyHEMA-ACH ₃ 20	i	–	–	–	–		22	42	–
		ii	79	98	89	0.35	115			
		iii	82	100	91	0.35	146			
4	polyHEMA-ACH ₃ 100	i	–	–	–	–		51	19	–
		ii	64	85	74	0.33	95			
		iii	71	89	80	0.34	115			
4'		i	–	–	–	–		25	39	101
		ii	73	93	83	0.32	105			
		iii	80	99	90	0.33	115			
<i>Composites with chemically active fillers</i>										
1	polyHEMA-ANH ₂ 20		–	–	–	–	–	22	25	74
			60	70	65	0.15	190			
			63	77	70	0.19	140			
1'		i	–	–	–	–	–	7	25	61
		ii	39	56	48	0.23	101			
		iii	40	61	51	0.29	83			
2	polyHEMA-ANH ₂ 100	i	–	–	–	–	–	23	26	–
		ii	–	–	–	–	–			
		iii	–	–	–	–	–			
2'		i	–	–	–	–	–	45	47	18
		ii	46	61	54	0.22	119			(80–90 °C), 33
		iii	50	75	63	0.32	75			(95–105 °C)
3	polyHEMA-ASiH ₃ 30	i	–	–	46	–	–	37	38	67
		ii	74	95	85	0.35	101			
		iii	78	97	88	0.35	114			
4	polyHEMA-ACH=CH ₂ 30	i	–	–	–	–	–	14	36	–
		ii	58	94	76	0.43	56			
		iii	62	93	77	0.41	66			
4'		i	–	–	–	–	–	18	34	67
		ii	61	82	72	0.32	94			
		iii	65	89	77	0.37	85			

$E_a/kJ\ mol^{-1}$ is the effective activation energy of process pass during first scan determined using Friedman model [17], the coefficient of determination (R^2) for all samples was in the range 0.9700–0.9990

In these composites structural heterogeneity may be due to reactions in the filler surface layer below the temperature of initiation of radical polymerization. In this case, sequence of filler-monomer and monomer-monomer interaction depends on the sample heating depth and uneven heat

penetration leads to a difference in the structure of the sample near and far from the plane of the heat. It is also possible that alcohols formed during acetylation of amino groups react with the methacrylate groups forming C–O–C bonds, the destruction of which causes the increase in

Table 2 Characteristic bands in FTIR spectra of polymeric composites based on polyHEMA and silicas

polyHEMA	polyHEMA-A300	polyHEMA-ACH ₃ 20	polyHEMA-ACH ₃ 100	Assignment
–	–	2,996	3,023–3,008	$\nu(\text{CH})$ in =CH ₂
2,985	2,989	2,981	2,989	$\nu_{\text{as}}(\text{CH})$ in –CH ₃
	2,962	2,958	2,954	$\nu_{\text{as}}(\text{CH})$ in –CH ₃
2,950	2,950	–	2,950	$\nu_{\text{as}}(\text{CH})$ in –CH ₂ –
	2,915	–		$\nu_{\text{as}}(\text{CH})$ in –CH ₂ – (close packing)
		2,923		$\nu_{\text{as}}(\text{CH})$ in –CH ₂ – (loose packing)
		2,904	2,904	$\nu_{\text{s}}(\text{CH})$ in terminal –CH ₃
	2,896			$\nu_{\text{s}}(\text{CH})$ in –CH ₃
2,888	2,885	2,885	2,888	$\nu_{\text{s}}(\text{CH})$ in –CH ₃
			2,880	$\nu_{\text{s}}(\text{CH})$ in –CH ₃
2,840				$\nu_{\text{s}}(\text{CH})$ in –CH ₂ –
	2,846	2,852	2,846	$\nu_{\text{s}}(\text{CH})$ in –CH ₂ – (close packing)
		2,834		$\nu_{\text{s}}(\text{CH})$ in O–CH ₂ –
polyHEMA	polyHEMA-ANH ₂ 20	polyHEMA-ASiH30	polyHEMA-ACH=CH ₂ 30	Assignment
1,724	1,724	1,743	1,731	$\nu(\text{C}=\text{O})$ in O–C=O–
–	1,650	–	–	Amide I
1,640	1,635 _w	1,635 _{st}	–	$\nu(\text{C}=\text{C})$ in –C(CH ₃)=CH ₂
–	1,540	–	–	Amide II
1,484	1,484	–	1,488	$\delta(\text{CH})$ in –CH ₂ –C (scissoring)
1,477	–	–	–	$\delta(\text{CH})$ in –CH ₂ –CH ₂ – (scissoring)
1,454	1,454	1,457	1,454	$\delta(\text{CH})$ in –CH ₂ – (bending)
1,392	–	1,392	1,390	$\delta(\text{CH})$ in –CH ₃ (trans-conformation)
1,373	–	–	1,365	$\delta(\text{CH})$ in –CH ₃ (gosh-conformation)
	1,360	–		$\nu_{\text{s}}(\text{CN})$ in –CH ₂ –NH–CH ₂ –
	1,340	–		$\delta(\text{CH})$ in C–CH(C)–C (trans)
1,322	–	–	1,322	$\delta(\text{CH})$ in =CH ₂
1,276	1,272	1,288	1,280	$\delta(\text{CO})$ in O=C(O)–
	1,249	–	1,257	$\nu(\text{CO})$ in primary alcohol
	1,187	1,203	1,183	$\delta(\text{COC})$ in O=C(O)–
1,176	1,180	–	1,168	$\nu_{\text{as}}(\text{COC})$ in O=C(O)–
1,079	–	1,095	1,060	$\delta(\text{CO})$ in –O–CH ₂ –(gosh)
1,022	–	1,040	1,022	$\delta(\text{OH})$
–	1,014	–	–	$\delta(\text{CO})$ in C–O–C (gosh-conformation)

Table 3 Samples hydration ($h \times 10^{-3}$, wt) at equilibrium water sorption (ESI) $\Delta h = 0.5\%$

Samples	Initial dry mass/g	Relative humidity			
		0.02 (P ₂ O ₅)	0.40 (ambience)	0.85 (KCl)	0.98 (K ₂ SO ₄)
polyHEMA unfilled	0.3825	0	38	116	187
polyHEMA-A300	0.3051	0	36	115	184
polyHEMA-ACH ₃ 20	0.3575	0	43	115	180
polyHEMA-ACH ₃ 100	0.3429	0	43	114	182
polyHEMA-ANH ₂ 20	0.7484	0	33	103	165
polyHEMA-ANH ₂ 20	0.6754	0	35	97	163
polyHEMA-ASiH30	0.7393	0	21	88	165
polyHEMA-ACH=CH ₂ 30	0.5097	0	34	114	180

activation energy of the endothermic process above 95 °C (Table 1). At such conditions, some methacrylate groups are not involved into the process of radical polymerization. On DSC curve the α -relaxation transition is expressed slightly and detected at a temperature that is considerably below the glass transition temperature of the unfilled polymer (Table 1).

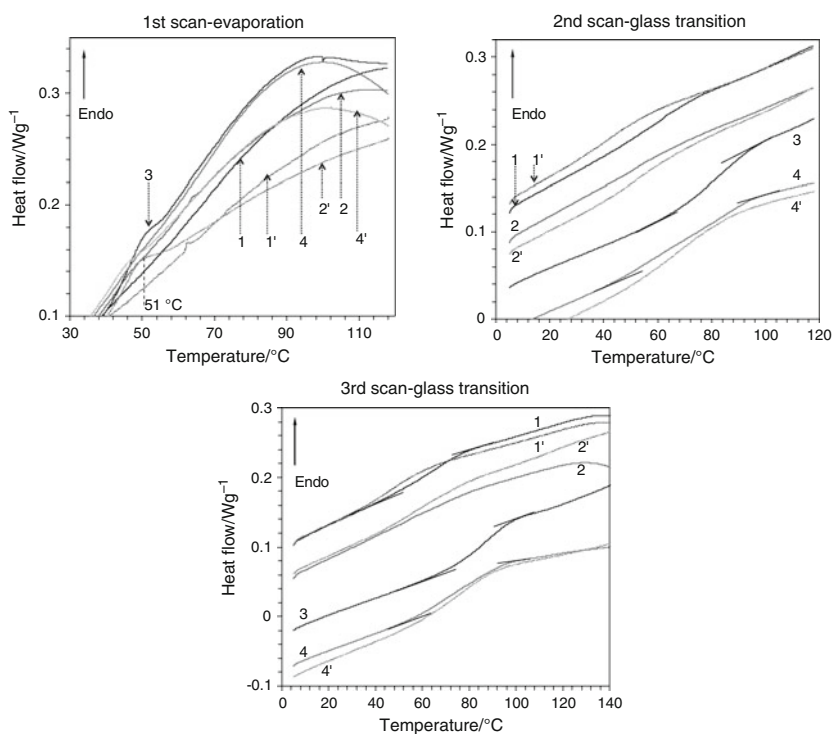
With a rise of surface amino groups concentration heterogeneity of the composite is increased, but the tendency to form the structure with flexible mobile macromolecules is still retained. On the DSC curve there is a step of β -relaxation near 50 °C (Fig. 3, 1st scan, curve 2'), which indicates the presence of torsion stresses in the macromolecules. In addition to this, the high value of cohesion energy indicates a strong intermolecular interaction, realized due to the low molecular weight products formed in the process of amino group and HEMA interaction. After their removal (3rd scan), the cohesion energy is reduced (Table 1).

In comparison with polyHEMA, in the spectra of composites with aminated silicas the intensity profiles of the characteristic vibrations of ester groups (1,100–1,300 cm^{-1}) and deformation vibrations of (CH) bonds (1,300–1,500 cm^{-1}) have changed significantly. The absorption band at 1,079 cm^{-1} ($\delta(\text{CO})$ in $-\text{O}-\text{CH}_2-(\text{gosh})$) and 1,022 cm^{-1} ($\delta(\text{OH})$) was not observed, but amide groups vibrations at 1,650 and 1,540 cm^{-1} and the absorption peak of $-\text{CH}(\text{C})-$ groups (1,340 cm^{-1}), as well as new band of ether-groups vibration (1,014 cm^{-1}), were detected in the spectra (Table 2). This indicates the passage of the acetylation reaction and interaction of alcohols

eliminated with methacrylate groups. An interaction of the alcohol with methacrylate groups (or radicals) can result in the polymer chain breakage. The presence in the spectrum of the band at 1,360 cm^{-1} (Table 1) points the amino groups alkylation during polymer formation that can improve filler-matrix interaction. The water adsorption for the composites with aminated silicas at relative humidity of 40% was the same as for the unfilled polymer (Table 3), but with increasing vapor pressure the magnitude of adsorption was reduced, probably due to the peculiarities of packaging of flexible macromolecules.

The presence of silicon hydride groups on the filler surface was found to promote cross-linking of the composite structure. The DSC curve for polyHEMA-ASiH30 (Fig. 3, 1st scan, curve 3) shows the β -relaxation step at about 46 °C, as well as for the composite HEMA-ACH₃100, but for this composite the glass transition temperature was lower (Table 1). The values of effective activation energy of elimination of volatile products indicate a high density of macromolecules packing. However, the cohesion energy, in comparison with other composites with chemically active fillers, is not high. Small change in E_c magnitude after heating-cooling cycle indicates the presence of stable network of the polymer macromolecules with low water adsorption capacity (Table 3). The material contains unreacted methacrylate groups (1,635 and 1,395 cm^{-1}), but the intensity profile of bands in the region of deformation vibrations of CH_2 -groups indicates the conformational homogeneity of the macromolecules (Table 2).

Fig. 3 DSC scans of heat flow versus temperature for polyHEMA-ANH₂20 (1, 1') polyHEMA-ANH₂100 (2, 2'), polyHEMA-ASi-H30 (3) and polyHEMA-ACH=CH₂30 (4, 4') composites. Interrupted lines (1', 2', 4') refer to the repeated measurements



The high homogeneity of the structure was also detected for the composite with vinylated silica (polyHEMA-ACH=CH₂30). But unlike the previous composite, during polymerization flexible macromolecules are formed. Among the samples under study, the change in heat capacity at α -relaxation was the greatest for this material, along with the lowest value of cohesion energy (Table 1). Besides, the effective activation energy is reduced that gives an indication of the considerable distance between the macromolecules, which is unusual for materials with flexible polymer chains. In IR spectrum of the composite (Table 2) the band at 1,639 cm⁻¹ was not observed, which indicates a high degree of monomer conversion. Some shift of bands attributed to the characteristic vibrations of the ester and hydroxyl groups in molecules HEMA was detected, which testifies to some change in the macromolecules environment. Along with the polymer filled with aminated silicas, this composite is also characterized by flexible polymer chains and the adsorption capacity of this material is higher (Table 3). Higher glass transition temperature indicates the presence of rigid network of flexible macromolecules.

Conclusions

Low degrees of cross-linking were observed for all composites based on polyHEMA and silicas. The glass transition temperatures of polymers filled with methylated silica or silica with grafted silicon hydride groups increase slightly as compared to the unfilled polymer. Filling with amino- or vinyl-containing silicas leads to significant drop in glass transition temperature of composites, especially in the case of aminated silica. This indicates the formation of flexible polymer chains with low cross-linkage or with low polymerization degree. Consequently, even at filling degree of 2 wt% amino and vinyl groups of silica surface can be involved into reactions of polymer formation. Surface silicon hydride groups can provide filler-polymer chemical interaction. In addition, such composite has the lowest capacity for water sorption. Water adsorption for composites with vinyl- and amine-containing silicas was also low, which indicates the close-packing of polymeric molecules in the filled polyHEMA.

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