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THERMOMECHANICAL PROPERTIES OF POLYMERIC COMPOSITES BASED ON 2-HYDROXYETHYLMETHACRYLATE AND FUMED SILICAS

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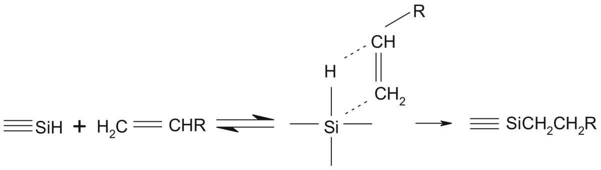
Thermomechanical properties have been investigated for the composites synthesised by the thermal polymerization of 2-hydroxyethylmethacrylate or its polymerization initiated with acrylamide complex of cobalt nitrate in the presence of the fumed silica or silicon hydride-containing silicas. The effect of the filler surface nature on temperature dependencies of deformability of the polymeric composites has been studied.

Keywords: *fumed silica, 2-hydroxyethylmethacrylate, silicon hydride-containing silica, thermal and initiated polymerization, thermomechanical properties*

Introduction

Chemically modified silicas with grafted silicon hydride groups are of special interest for the olefin-containing systems since they open up new opportunities in formation of the surface compounds with hydrolytically stable Si–C bonds by using the hydrosilylation reaction in the presence of the Speier catalyst or by heating [1, 2]:



Earlier we investigated the reaction of catalytic solid-phase hydrosilylation of 2-hydroxyethylmethacrylate (HEMA) [3] and the particular behaviour of modified silicas with the surface ≡SiH groups as fillers in the processes of HEMA polymerization [4]. The results obtained show that the introduction of the hydride-containing silicas at the thermal or initiated with acrylamid complex of cobalt nitrate HEMA polymerization increases the rate and the degree of polymerization with increasing surface ≡SiH group concentration. This clearly demonstrates chemical interaction of ≡SiH groups of the filler surface with C=C groups of the monomer resulting in additional cross-linking of the composite network. In such a case it was reasonable to expect changes in the physicomechanical properties of the filled systems. This work is intended to study thermomechanical properties of composites obtained by thermal and initiated radical polymerization of HEMA in the presence of silica fillers.

Experimental

Hydride-containing silica was obtained by reaction between triethoxysilane (1 mL) (Kremnepolymer, Zaporizhya) and fumed silica (10 g) with a specific surface area of 300 $m^2 g^{-1}$ (Oriana, Kalush,) at room temperature in the medium of ethyl alcohol (70 mL) under stirring for 24 h. After solvent evaporation in a water bath the modified silica was dried at 100°C. The ≡SiH groups concentration was determined by the bromide-bromate and iodometric methods [5] based on reaction of silicon hydride groups with water solution of halogens and following titration with sodium thiosulfate. 2-Hydroxyethylmethacrylate (Fluka) was used without additional purification. Acrylamide (AAm) complex of cobalt nitrate with the composition $4AAm{\cdot}Co(NO_3)_2{\cdot}2H_2O$ was synthesized according to the recommendations of the paper [6].

Thermal polymerization of HEMA was carried out in an open reactor at 106°C. Polymerization of the

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monomer was performed both in the presence of starting fumed silica and hydride-containing silicas with ≡SiH group concentrations of 0.25 and 0.64 mmol g^{-1}. Filler content was 16 mass%. Radical HEMA polymerization initiated with acrylamide complex of cobalt nitrate was performed at 106°C. The initiator:monomer ratio was 1:10 (2.4 g of HEMA and 0.24 g of the initiator). Before polymerization the initiator and filler were carefully mixed and then added to the monomer. The initiated polymerization in filled systems was conducted with a silica content of 16 mass%.

Thermomechanical analysis was carried out using the home-made penetration device with an accuracy of 0.001 mm on samples of 3–4-mm thickness and 1 cm diameter; the rate of heating was 1.0–1.5°C min^{-1} in air under constant applied load σ_0 (kgf cm^{-2}). In accordance with the accepted ICTA terminology [7], measurements of deformation ε as a function of temperature change under conditions of constant applied loading may be referred to as thermomechanical analysis and appropriate thermomechanical curves of the polymeric compositions synthesised. The flat-ended indenter with edge diameter 0.30 cm was used. Investigations by an indenter penetration method were carried out at 20–200°C, with an applied load of 15 kgf cm^{-2}. The specimen thickness was measured by a micrometer. The density of the composites ρ (g cm^{-3}) was determined by picnometry.

Specimen deformation ε (%) was calculated according to the formula

$$\varepsilon = \left(\frac{\Delta L}{L_0}\right)100$$

where ΔL (cm) represents the probe displacement when the temperature is changed, L_0 is the initial specimen thickness (cm). The determination of the thermal expansion coefficient was performed at 20–120°C in the dead-load mode 0.1 kgf cm^{-2}. The thermal expansion coefficient α (K^{-1}) below the glass-transition temperature was calculated by the equation

$$\alpha = \frac{\Delta L}{L_0 \Delta T}$$

where $\Delta T = T_g - T_0$; T_g is the glass-transition temperature and T_0 is the initial temperature [7]. The glass-transition temperature was determined from a knee point appeared in the experimental curve $\varepsilon = f(T)$ (σ_0=0.1 kgf cm^{-2}) at the transition from expansion to compression of samples [8]. When studying the characteristics by an indenter penetration method (σ_0=15 kgf cm^{-2}), the glass-transition temperature is determined as a point on the curve corresponding to transition from the resilient to highly elastic strain [7] (Fig. 1).

Calculation of the Young's modulus E_{eq} (Pa) in the region of the high elastic deformation was performed by a conventional method [9] adapted for penetration:

$$E_{eq} = \frac{\sigma_0 L_0 (1 + \alpha \Delta T)}{L_0 (1 + \alpha \Delta T) - (L_0 - \Delta L_d)}$$

where ΔL_d is the depth of indenter penetration at the temperature of the specimen thermal destruction (T_d) (Fig. 1).

The equation for calculation of the compression degree λ (%) [7] was transformed into λ=100–ε. The molecular mass of a polymer chain segment between a site of polymer network M_s g mol^{-1}) and number of segments n (mol cm^{-3}) was calculated by the following Eqs [8, 9]:

$$M_s = \frac{3RT_d\rho}{E_{eq}}, \qquad n = \frac{\rho}{M_s}$$

where R is the universal gas constant (J mol^{-1} K).

Results and discussion

Figure 1 illustrates the deformation change during heating in a mode of penetration (thermomechanical curves) for the composites obtained by the thermal polymerization of pure HEMA and in the presence of starting fumed silica and modified silicas with different concentrations of surface ≡SiH groups. Judging from the curve (Fig. 1, curve 1) the product of pure HEMA polymerization is a high-molecular polymer, which follows from the presence of a horizontal portion in the region of the high elastic deformation.

The character of the deformation change in the regions of glass-transition temperature and high elastic deformation is defined by cross-linking density of polymer chains [10–12]. In the composites prepared by the polymerization of the monomer in the presence of fumed silica the total deformation increases. But in this case the filled system has a lower glass-transition temperature and the horizontal portion in the region of the high elastic flow is less pronounced (Fig. 1, curve 2). Often transition area is less marked at thermomechanical analysis of the filled polymers [8–10, 13]. In this case the formed network can be mechanically unstable and destructive processes are possible. As a result instead of a well-defined horizontal platform, a rise of the branch of highly elastic strain on the thermomechanical curve can be observed. From these data, the composite obtained is a material with the low-molecular flexible polymeric chains [8]. By analogy with reported results [13], it may be attributed to a considerable polymer-filler adsorption

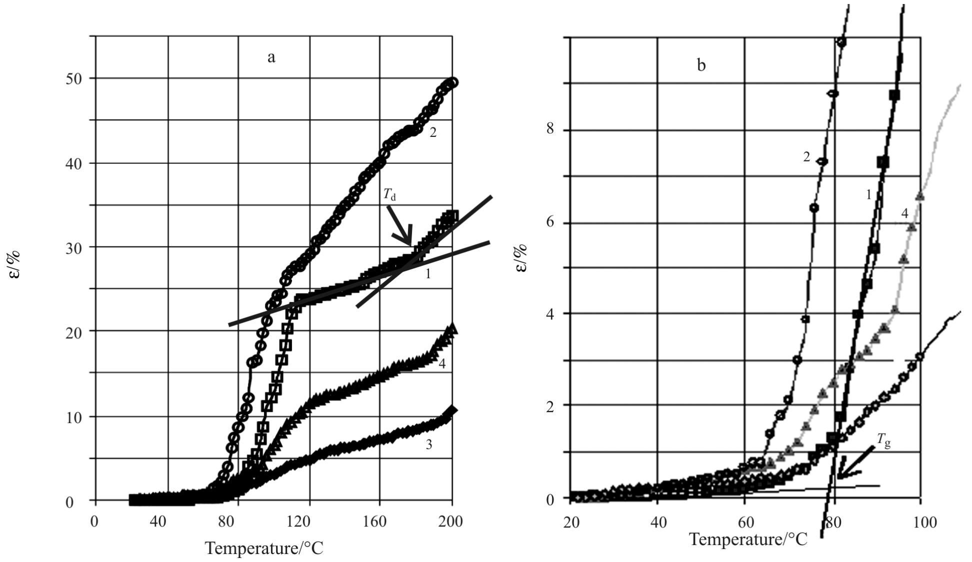

Fig. 1 a – Thermomechanical curves (σ_0=15 kgf cm^{-2}) of polymer obtained by thermal polymerization of pure HEMA (1), composite of HEMA with fumed silica (2), composites of HEMA with modified silicas containing 0.25 (3) and 0.64 mmol g^{-1} of grafted silicon hydride groups (4); b – enlarged section of the initial parts of thermomechaical curves

interactions, which inhibit the formation of the cross-linked structure. However, a decrease of the thermal expansion coefficient (Table 1) was detected.

The thermomechanical curve of the polymer filled with the silicon- hydride- containing silica (Fig. 1, curve 3) and data of Table 1 show that the composite obtained has rigid polymeric chains and a higher cross-linking density compared with the composite fumed silica–HEMA.

In this case the ordered (non-defected) network with the strong bonds is formed. Although an increase in the number of the cross-linking bonds sometimes results in loosening of the packing of macromolecules [14], composites with the high density structure are formed in the polymer filled by silica with grafted ≡SiH groups. It is conceivable that the surface ≡SiH groups interacting with vinyl groups of HEMA render an orienting effect on polymer macromolecules and their packing in the composite. However, when determining of the thermal expansion coefficient at the load 0.1 kgf cm^{-2} in the temperature range 70–104°C, a substantial expansion of the sample (even after the treatment at 200°C) was detected. This result is assigned to the fact that there is considerable inner stress in the composite obtained.

With increasing concentration of surface silicon hydride groups from 0.25 to 0.64 mmol g^{-1} the polymer chains become more flexible (Fig. 1, curve 4). But in this case a loosening of the macromolecule packing and a decrease of the material density were also detected (Table 1). However, according to [9], the two knees (at 69 and 94°C) on the curve in the vicinity of the glass-transition temperature related to an additional cross-linking. The decrease observed in the glass-transition temperature at the additional cross-linking may point to formation of a composite with non-uniform structure involving the loosened domains and regions with a high density of cross-links. The thermal coefficient of expansion (Table 1) was not changed. One can assume that the additional cross-linking takes place in the microregions formed by the macromolecule aggregates bound with the filler surface. In this case the polymer chain flexibility increase levels down the filler surface effect and prevents the occurrence of inner stresses.

Based on the obtained experimental data the interaction between surface ≡SiH and C=C groups of monomer (hydrosilylation reaction) may lead to some immobilization of macromolecules and to a decrease in a degree of the chains termination and thus to an increase of cross-links density.

As can be seen from the published data [6], the presence of acrylamide complex in the composite is often favourable for the formation of the branched structures.

The results of our investigation give evidence to the fact that the availability of the acrylamide complex during the HEMA polymerization leads to formation of composites with the rigid framework and high density of cross-links but with the loosened macromolecule packing (Fig. 2, curve 1; see also Table 2). Introduction of fumed silica into monomer causes the cross-linking as shown by an increase of the glass-transition temperature [13] (Fig. 2, curve 2) and a decrease in M_s. This may be assigned to a lowering of the silica–HEMA adsorption interactions due to the competing adsorption with the initiator molecules. As a result, composites with the high density of

Table 1 Thermomechanical characteristics of composites obtained by thermal HEMA polymerization

No.*	Composition	ρ/g cm^{-3}	σ_0=0.1 kgf cm^{-2}		σ_0=15 kgf cm^{-2}				
			T_g/°C	$\alpha \cdot 10^4$/K^{-1}	T_g/°C	$E_{eq} \cdot 10^{-4}$/Pa	M_s/g mol^{-1}	$n \cdot 10^3$/mol cm^{-3}	λ/%
1	Pure HEMA	1.19	50	0.75	78	527.1	2565	0.47	77
2	HEMA + fumed silica	1.09	48	0.66	63	345.8	3569	0.31	63
3	HEMA+ modified silica with C_{SiH}=0.25 mmol g^{-1}	1.26	50	0.40	72	1618.4	904	1.39	96
4	HEMA+ modified silica with C_{SiH}=0.64 mmol g^{-1}	0.81	50	0.35	81	873.3	1057	0.76	88

*numbers of composites in Fig. 1

cross-links and loosened packing of polymer macromolecules are formed.

Incorporation of hydride-containing silica (C_{SiH}=0.25 mmol g^{-1}) in the case of the radical HEMA polymerization initiated with acrylamide complex of cobalt nitrate results in formation of a composite which is characterised by different strengths of the formed bonds (Fig. 2, curve 3). Taking into account a decrease in the glass-transition temperature at 15 kgf cm^{-2} and increase in density of macromolecule packing (Table 2), one would expect a manifestation of the surface orienting effect on the HEMA molecules, which leads to appearance of the dense macromolecule packing [14]. Because the additional cross-linking in the surface layer (two knees at a resilient strain of 0.1 kgf cm^{-2}) and dense packing are balanced by a formation of structure network with the flexible macromolecules, the composite overstrains are not observed. It is not improbable that the unbound polymer chains can exert a plasticizing effect [15].

As expected, an increase in the surface ≡SiH groups concentration (Fig. 2, curve 4) leads to a growth of the cross-linking density (Table 2). At the same time, the obtained composite has the loosened packing of macromolecules. This is supported by the fact that the material density is lowered and the thermal expansion coefficient is increased.

Thus, at further enhancement of polymer–filler interaction a rigidity of polymeric chains grows and loosening of the structure occurs. It leads to counterbalanc-

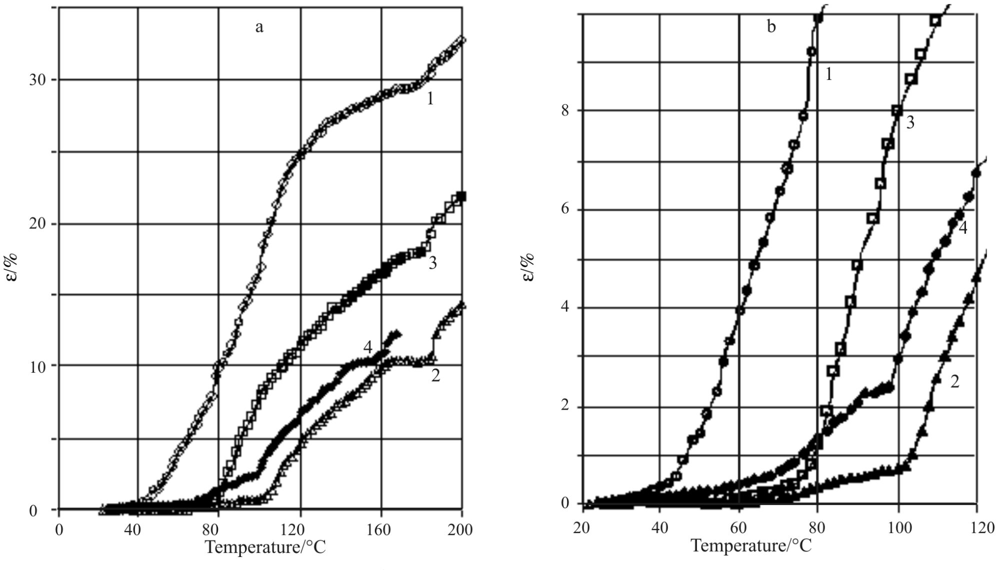

Fig. 2 a – Thermomechanical curves (σ_0=15 kgf cm^{-2}) of the polymer obtained by the HEMA polymerization initiated with acrylamide complex of cobalt nitrate (1), composite of HEMA with fumed silica (2), composites of HEMA with modified silicas containing 0.25 (3) and 0.64 mmol g^{-1} (4) of grafted silicon hydride groups; b– enlarged initial portions of the thermomechanical curves

Table 2 Thermomechanical characteristics of composites obtained by the HEMA polymerization initiated with acrylamide complex of cobalt nitrate

No.*	Composition	ρ/g cm^{-3}	σ_0=0.1 kgf cm^{-2}		σ_0=15 kgf cm^{-2}				
			T_g/°C	$\alpha\cdot10^4$/K^{-1}	T_g/°C	$E_{eq}\cdot10^{-4}$/Pa	M_s/g mol^{-1}	$n\cdot10^3$/mol cm^{-3}	λ/%
1	HEMA +initiator	0.98	48	1.11	48	529.0	2094	0.47	76
2	HEMA +initiator +fumed silica	0.77	36 52	1.62 0.64	96	1334.5	661	1.16	96
3	HEMA +initiator +modified silica with C_{SiH}=0.25 mmol g^{-1}	1.35	50 80	0.78 0.78	75	857.8	1777	0.76	87
4	HEMA +initiator +modified silica with C_{SiH}=0.64 mmol g^{-1}	0.85	46	1.34	84	1310.4	703	1.22	92

*numbers of composites in Fig. 2

ing of inner strains. The loosened structures with rigid macromolecules and high cross-link concentration are formed, which is typical for effect of acrylamide complexes of metals on material structure.

In parallel with additional cross-linking, such an interaction with functional groups of the modified filler, especially under the conditions of the thermal polymerization of the system monomer–hydride-containing silica, can lead to breaking of formed polymeric chains. In the presence of acrylamide complex of cobalt nitrate the vinyl group concentration in the surface layer increases substantially and there are more favourable possibilities for formation of the network with rigid polymeric chains and high cross-linking density.

Conclusions

The results achieved provide evidence for the fact that an introduction of hydride-containing silica during the thermal or initiated polymerization of HEMA can provide cross-linking of composite system due to interaction between C=C groups of the monomer and ≡SiH groups attached to the filler surface. The enhancing effect of the above-mentioned modified fillers of polymer composites has a complex character that depends on interface adsorption of system components and concentration of silicon-hydride groups.

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