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Effect of Unmodified and Surface Treated Fumed Silica on the Polymerization of HEMA

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Summary: Thermal polymerization of 2-hydroxyethylmethacrylate (HEMA) and radical polymerization initiated by an acrylamid complex of cobalt nitrate in the presence of unmodified and surface treated silicas have been investigated. It has been found that the introduction of fillers, especially silicas with grafted silicon hydride groups, makes an essential effect on the rate and degree of the HEMA polymerization.

Keywords: cross-linking; fillers; hydride-containing silicas; 2-hydroxyethylmethacrylate (HEMA); radical polymerization

Introduction

In many cases essential strengthening of a filled polymeric system can be achieved when active sites of modified surface of a silica filler are able to interact chemically with functional groups of polymer macromolecules, which results in chemical cross-linking. Such a chemical cross-linking was realized for plastic binders and filled polymeric systems with the help of finishing agents with active functional groups for surface modification of glass fibers and disperse silicas.[1, 2] Among modifying reagents, organosilanes with amino-, methacryl-, epoxy- or vinyl groups have much use, and their filler/polymeric matrix interface structures have been widely studied. Studies of behavior of silicon hydride-containing silicas as active fillers of polymeric systems are practically absent. Recently, systematic study of the hydrosilylation reaction of functional olefins by silicon hydride groups attached to silica surface under the action of catalysts and heat treatment were carried out.[3-5] The proceeding of surface chemical reaction involving the grafted surface $\equiv$SiH groups and olefin molecules is effected according to the following general scheme:

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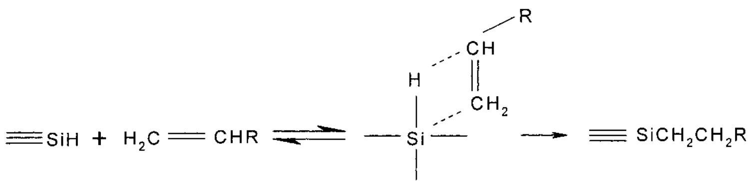

where *R* is a suitable organic radical. In line with these data, silicas with the grafted silicon hydride groups on the surface layer are of particular importance as chemically active fillers of the olefin-containing polymers.

Investigation of the interaction of silicon hydride-containing silicas with derivatives of methacrylic acid is of special interest. The aim of this work is to study the role of hydrosilylation reaction on the thermally induced self-polymerization and initiated polymerization of HEMA to obtain data concerning the effect of surface groups on the polymerization.

Experimental

Hydride-containing silicas were prepared by the reaction of triethoxysilane (Kremnepolymer, Zaporizhya) with fumed silica (Oriana, Kalush, 300 m^2/g) at room temperature in ethyl alcohol under stirring for 24 h. Then the modified silicas were dried at 100 °C.

2-Hydroxyethylmetacrylate (Fluka) was used without any additional purification.

Acrylamide (AAm) complex of cobalt nitrate of composition $4AAm \cdot Co(NO_3)_2 \cdot 2H_2O$ was synthesized in accordance with the recommendations of Savost'yanov et al.[6]

Thermal HEMA polymerization was conducted in an open reactor at 106 °C. The polymerization was carried out in the presence of unmodified fumed silica or hydride-containing silicas with concentration of bound ≡SiH groups of 0.25 and 0.64 mmol/g. Filler content was equal to 16 wt.% of composite.

Radical HEMA polymerization initiated by acrylamide complex of cobalt nitrate was performed at contents of the initiator of 2, 5, 10, 20 wt.% at 96 °C and at the initiator–monomer mass ratio of 1:10 at 96, 106, 116 °C. The polymerization of filled systems was carried out for 10 wt.% of the initiator and content of the silica filler of 16 wt.%. Prior to the polymerization the initiator and filler were carefully mixed and then added to the monomer.

The concentration of C=C groups in the composite system was determined by a titrimetric (bromide-bromate) method by analyzing water extracts of the appropriate samples after separation of the polymer.

Results and Discussion

Thermal HEMA polymerization

When studying kinetics of the thermal HEMA polymerization at 106 °C (Fig. 1, *a*) we observed a considerable scatter between individual determinations of C=C group concentrations (*C*, mol/L). As in the case of other vinyl monomers[7], it may be related to formation of the low-molecular adducts which affect the polymerization rate. Kinetic curves have a plateau-like section corresponding to an induction period with a subsequent acceleration of the polymerization process. The monomer contains hydroquinone monomethyl ether as a stabilizer, which may at least influence the start of the reaction and it is possibly the reason for the induction period.

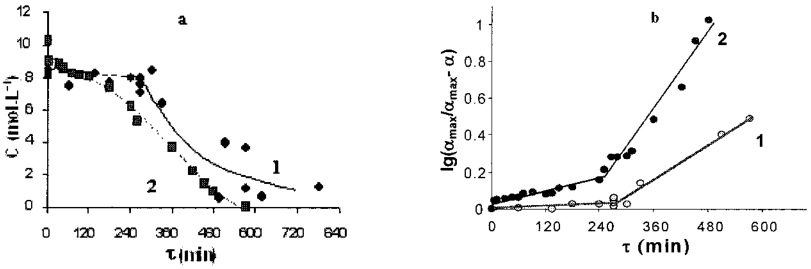

Figure 1. Kinetics of HEMA polymerization at 106 °C (*a*) and anamorphosis of the kinetic curves (*b*) in the absence (*1*) and in the presence (*2*) of acrylamide complex of cobalt nitrate.

The polymerization rate constant calculated[8,9] from the equation:

$$k = \frac{2.303}{\tau} \cdot \lg \frac{C_o}{C}$$

where C_o is the initial concentration of vinyl groups in the monomer and C is the concentration of C=C groups at time τ, was found to be equal to $5.55 \cdot 10^{-5}$ sec^{-1}. The construction of the logarithmic anamorphosis of kinetics curves[10] $\log \alpha_{max}/(\alpha_{max} - \alpha) = f(\tau)$, where $\alpha = (C_o - C)/C_o$ is the degree of polymerization at time τ and α_{max} is the maximum degree of the monomer transformation, allowed us to discriminate more distinctly both sections of the kinetic curves (Fig. 1, *b*). As it is seen, the introduction of the initiator leads to stabilization of the polymerization process.

Effect of fillers on thermal HEMA polymerization

The study of thermal polymerization of a system on the basis of the monomer and fumed silica (Fig. 2, curve *1*) showed that introduction of the filler resulted in an increase in the polymerization degree. At the same time, it made only a slight effect on the polymerization rate in comparison with pure monomer and led to formation of impure structures. This can be explained by the strong monomer adsorption on the filler surface since the adsorption inhibits formation of the cross-linked structures.[11]

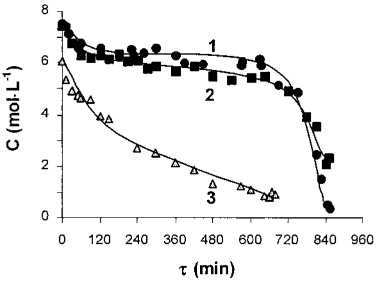

Figure 2. Kinetics of the thermal HEMA polymerization in the presence of as-received fumed silica (*1*) and modified silicas at ≡SiH group concentrations of 0.25 (*2*) and 0.64 mmol/g (*3*) at 106 °C.

Table 1. Time of polymerization and degree of conversion of C=C groups in products of the thermal and initiated HEMA polymerization in the presence of silica fillers at 106 °C.

Composition*	*a*	*b*	*c*	*d*	*e*
Time, h	14	11	6.5	5.5	4.5
$100\cdot(C_o-C)/C_o$, %	69	85	71	74	86

**a*, *b*: HEMA + modified silica with C_{SiH}=0.25 and 0.64 mmol/g respectively;
c: HEMA + acrylamide complex of cobalt nitrate+silica;
d, *e*: HEMA + acrylamide complex of cobalt nitrate+modified silica with C_{SiH}=0.25 and 0.64 mmol/g respectively.

Introduction of hydride-containing silica into the monomer leads to an increase in the polymerization degree. Thus, the concentrations of C=C groups in the resulting composites filled with modified silicas at ≡SiH group concentrations of 0.25 and 0.64 mmol/g were equal to 2.31 and 0.91 mol/L respectively. As the concentration of ≡SiH groups increases, the time of the polymerization decreases from 14 down to 11 h (Table 1).

Accordingly, under the reaction conditions the hydride groups attached to silica surface interact with vinyl groups of the monomer and promote the HEMA polymerization. On the basis of the experimentally observed dependencies it is possible to assume that hydrosilylation of monomer molecules by surface silicon hydride groups results in immobilization of macromolecules, which leads to an increase in the rate and degree of polymerization (Figure 2, curve *3*).

Initiated HEMA polymerization

According to the results achieved, with increasing temperature the polymerization rate decreases, which may be attributed to an influence of the medium viscosity.

Figure 1 shows the effect of acrylamide complex of cobalt nitrate on kinetics of the initiated HEMA polymerization in the comparison with the thermal polymerization in the absence of the initiator at the same temperature. In the presence of the initiator the curve section corresponding to the induction period of the process is diminished and an increase in the polymerization rate is observed.

Because the acrylamide complex of cobalt nitrate is rarely applied as an initiator of the olefin polymerization, the order of the initiation reaction was determined experimentally. The initiation order was equal to 0.53 ± 0.07, which is in agreement with literature data for such widely used radical polymerization initiators as benzoyl peroxide or azobisisobutyronitrile.[12] The inference about the HEMA polymerization by the radical mechanism in the presence of acrylamide complex of cobalt nitrate is corroborated by the linear dependence of the polymerization time on the square root of the initiator concentration.

Initiated polymerization in a filled system

The literature data about an effect of filler surface on initiated polymerization processes are contradictory. In accordance with the work of Tsubokawa et al.[13] the introduction of fumed silica into methylmethacrylate does not influence the degree of polymerization initiated by benzoyl peroxide. However, according to the data of Almazova et al.[14] the fumed silica is an active filler accelerating the formation of the cross-linked structure. Our experimental data give evidence to the fact that the introduction of fumed silica leads to a decrease in the polymerization time from 9.0 down to 6.5 h as compared to the corresponding system without any filler.

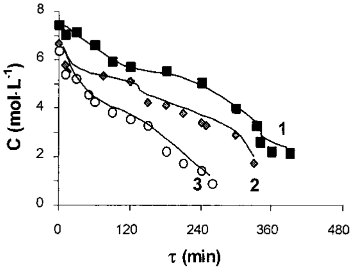

Figure 3. Kinetics of the initiated HEMA polymerization in the presence of the as-received fumed silica (*1*) and modified silicas at ≡SiH group concentrations of 0.25 (*2*) and 0.64 mmol/g (*3*) at 106 °C.

Introduction of silicon hydride-containing silicas promotes an increase in rate and degree of the HEMA polymerization, which may assigned to the presence of additional active surface sites reacting with polymer macromolecules (Figure 3). As an example, the introduction of the hydride-containing silica at a concentration of the grafted ≡SiH groups of 0.25 mmol/g decreases the polymerization time to 5.5 h at the residual C=C groups content of about 1.71 mol/L. If the concentration of ≡SiH groups in the modified filler is 0.64 mmol/g, the polymerization time and the C=C groups content are 4.5 h and 0.89 mol/L, respectively. The presence of silicon hydride groups on the filler surface practically eliminates an induction period of the polymerization reaction.

Conclusions

The results achieved give evidence for the fact that the introduction of the hydride-containing silicas in the case of the thermally induced self-polymerization or initiated polymerization of HEMA provides cross-linking of composite systems due to the reaction between C=C groups of the monomer and ≡SiH groups attached to the filler surface. During the polymerization initiated by the cobalt complex the process of grafting of HEMA molecules onto the filler surface may be affected by grafting acrylamide complexes of cobalt nitrate or by adding of HEMA molecules. The presence of acrylamide ligands contributes to immobilization of HEMA macromolecules and to formation of cross-linked structures. As the ≡SiH group concentration on the silica surface increases, the rate and degree of polymerization become higher.

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