



Silica/aluminum oxide hybrid as a filler for photocurable composites



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ABSTRACT

In this study silica/alumina hybrid (COK 84) was tested as filler for photocurable composites dedicated for protective coatings and was compared to fumed nanosilica (Aerosil 200). The model monomer was polyethylene glycol diacrylate. The effect of the filler type and content on the photopolymerization kinetics was followed; the kinetic studies were accompanied by measurements of thermal and mechanical characteristics of the composites produced. Polymerization rates and polymerization rate coefficients (propagation k_p and termination k_t^b) were determined as functions of double bond conversion. At low filler contents the acceleration of the polymerization was observed; higher loadings had detrimental effect both on the polymerization rate as well as on final conversion, the latter effect was stronger in the case of COK 84. The influence of the filler on the curing kinetics was discussed in terms of the behavior of the polymerization rate coefficients which is associated with filler/polymer interactions in the interphase. Tensile testing showed that COK 84 better improves mechanical characteristics of the poly-PEGDA matrix as compared to Aerosil 200, but only in a limited range of content.

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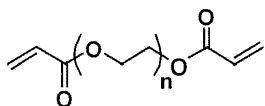
1. Introduction

Ultraviolet (UV) curable materials have aroused substantial interest in the past decade because of their merits in environmental protection, high processing speed, excellent film properties, low temperature cure and energy efficiency [1]. These unique solvent-free compositions cure (harden) in a fraction of a second upon exposure to a UV source, which makes them commonly used as coatings, inks, adhesives and other applications. Most commercially UV curable coatings are based on acrylate chemistry that cures via free radical polymerization. These liquid formulations often contain additives which improve thermal stability and mechanical properties of the arising protective layers. In recent years many attention has been devoted to modification of coatings by nanofillers. Among the diverse inorganic particles, silica has been widely used as functional filler [2–7]. Although the potential of nanosilicas as reinforcements for polymers composites with poly(meth)acrylate matrices was investigated intensively [8–11], the reports concerning alumina as the potential filler are much more limited even though alumina-based materials are significantly harder than those containing silica [12].

In our continuing investigations on preparation and properties of photocurable composites [13–15] we undertook research concerning a special hybrid filler—Aerosil®COK 84 (COK 84) being a mixture of fumed silica Aerosil®200 (A 200) and highly dispersed aluminum oxide (AEROXIDE®Alu C) in the 5:1 ratio. The primary particles consist of either SiO₂ or pure Al₂O₃ [16]. COK 84 is synthesized by high-temperature hydrolysis of the corresponding gaseous metal chlorides (SiCl₄, AlCl₃) in an oxyhydrogen flame [17]. Due to the pyrogenic synthesis method, all fumed oxides possess unique properties: high-chemical purity, nanoscale spherical primary particles and large specific surface area [18]. COK 84 provides strong thickening effects in aqueous media and is used in coatings pastes, water-based coatings and aqueous coatings. On the other hand, introduction of aluminum oxide and silica into the composite significantly helps to increase polymer hardness and wear resistance [19]. Therefore, it is of interest to test COK 84 as filler for UV-curable polyacrylate-based composites addressed for protective coatings.

While many studies have investigated formation of silica-containing nanocomposites in a UV-induced process, there are no detailed reports on the photocuring behavior of systems containing mixture of nanosilica and alumina. Our paper is intended to complement this gap and is devoted to photopolymerization kinetics and properties of compositions (and derived composites) based on a model acrylate monomer (polyethylene glycol diacrylate, PEGDA) filled with various amounts of COK 84. Curing kinetics of COK 84 dispersions in PEGDA were compared to curing kinetics of A 200

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Scheme 1. PEGDA.

dispersions; the deeper analysis included determination of polymerization rate coefficients: (propagation k_p and termination k_t^b) as a function of double bond conversion. Kinetic studies were accompanied by measurements of thermal properties of the composites formed as well as their selected physical and mechanical properties. Such investigations enable comparison of the photocuring and physical behavior of A 200-filled systems with and without aluminum oxide, and can help to design formulations and conditions for industrial applications.

2. Materials and methods

2.1. Materials

The monomer, polyethylene glycol diacrylate with MW = 575 (PEGDA, Scheme 1) was purchased from Aldrich and was purified by column chromatography before use. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651) was a gift from Ciba. COK 84 (82–86% silica A 200, 14–18% Al_2O_3) has specific surface area of 155–215 m^2/g [20] and average particle diameter 2–200 nm [16]. The specific area of A 200 is 175–225 m^2/g and average primary particle size is 12 nm [17]. The both fillers were kindly donated by Evonik. The fillers were dried at 110 °C for 2 h before use. The monomer/filler mixtures containing 2–15 wt.% of A 200 or 2–10 wt.% of COK 84 and 0.2 wt.% of the photoinitiator were homogenized by ultrasonication through 2–20 h.

2.2. Viscosity

Viscosities of photocurable systems were measured with DV-II+ PRO Brookfield Digital Viscometer (40 °C, 0–160 rpm, cone-and-plate geometry).

2.3. Photopolymerization kinetics

Reaction rate profiles (enabling determination of the reaction rates R_p and conversion degrees p) were measured by DSC under isothermal conditions at 40 ± 0.01 °C in a high-purity argon atmosphere ($<0.0005\%$ of O_2) using the Pyris 6 instrument (Perkin-Elmer) equipped with a lid specially designed for photochemical measurements. The 2-mg samples were polymerized in open aluminum pans with the diameter of 6.6 mm. The polymerizations were initiated by the light from a LED Hamamatsu LC-L1 lamp ($\lambda = 365$ nm, light intensity at the sample pan position 2.75 $mW\ cm^{-2}$). All photopolymerization experiments were conducted at least in triplicate. The reproducibility of the kinetic results was about $\pm 3\%$. For computations, the heat of polymerization of the acrylate group 86 kJ/mol per one double bond was taken [21].

Polymerization rate coefficients: propagation (k_p) and bimolecular termination (k_t^b) rate coefficients were calculated from experimental data obtained from postpolymerization processes, which were registered after stopping the irradiation at various degrees of double bond conversion. The calculations were performed over the first 10 s of the dark reaction. The coefficients were calculated according to the bimolecular termination model [22] from the following equations:

$$\frac{[M]_t}{(R_p)_t} = \frac{2 \cdot k_t^b}{k_p} \cdot t + \frac{[M]_0}{(R_p)_0} \quad (1)$$

$$(R_p)_0 = \frac{k_p}{(k_t^b)^{0.5}} \cdot [M]_0 \cdot (\phi \cdot I_a)^{0.5} \quad (2)$$

where $(R_p)_t$ and $[M]_t$ are the polymerization rate and double bond concentration at time t of the dark reaction, respectively, and $(R_p)_0$ and $[M]_0$ are the parameters at the moment of breaking the irradiation, ϕ denotes quantum yield of initiation and I_a is intensity of the light absorbed.

The rate coefficients were calculated in the form of $k_p \cdot F$ and $k_t^b \cdot F$, where $F = (\phi \cdot I_a)^{0.5}$; F was assumed to be constant in the range of conversions studied.

2.4. Thermal properties

Glass transition temperature T_g was measured with DSC instrument (DSC1 Mettler Toledo) under nitrogen atmosphere at the heating rate of 10 °C/min. T_g was evaluated from the second run of two separate DSC measurements at two temperature ranges: (a) from –80 °C to 40 °C (the sample was kept 3 min at 40 °C) and (b) from –80 °C to 110 °C (the sample was kept 5 min at 110 °C).

The thermal resistance was investigated with TG 209 F3 Tarsus thermogravimetric analyzer (NETZSCH-Geratebau GmbH, Germany). 10 mg samples were heated in Al_2O_3 crucibles from 40 to 800 °C at a scan rate of 10 °C/min under nitrogen atmosphere (purge of 10 ml/min of N_2 protection gas and 20 ml/min of N_2 sample gas).

2.5. Mechanical properties

The samples for mechanical tests were cured in a two-part stainless steel mold. The samples in the mold were covered with poly(ethylene terephthalate) foil. The PEGDA/filler compositions were irradiated with the whole spectrum of the Dymax UV 5000 Flood lamp for 300 s. The mechanical properties were investigated at 25 °C. The tensile properties were measured according to PN-EN ISO 527-1:1998 (crosshead speed of 5 mm/min) with Zwick/Roell universal testing machine model Z020 (Zwick GmbH & Co. KG, Germany). The Shore D hardness was measured according to DIN 53 505.

2.6. Water sorption

Samples of composites for water sorption characterization were prepared under the same conditions as for mechanical measurements. Water sorption studies were performed in accordance with PN-EN ISO 62:2008. Dried samples (12 h, 50 °C) were submerged in distilled water at room temperatures. The samples were taken out periodically and weighed immediately, after wiping out the water on the surface of the sample, using a precise four-digit balance to find out the content of water absorbed. The measurements were conducted over an equal time period, until a stable sample mass value was obtained.

The percentage of water sorption at any time (t) X , was calculated by the equation:

$$X = \frac{m_2 - m_1}{m_1} \cdot 100\% \quad (3)$$

where m_2 is the weight of the sample at time t and m_1 is the weight of the dried sample.

3. Results and discussion

3.1. Appearance

All the dispersions showed good monomer/filler compatibility which is promoted by intermolecular interactions between ether and carbonyl groups of the monomer and hydroxyl groups on

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