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SYNTHESIS AND APPLICATION OF MACROPHOTOINITIATORS OBTAINED VIA BENZOIN TETHERING WITH COPOLYMERS OF MALEIC ANHYDRIDE

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Abstract. A new approach to the synthesis of macrophotoinitiators (MPI) on the basis of benzoin was developed; it was grounded on the tethering of benzoin to copolymers of methyl methacrylate and maleic anhydride. This process occurred as a polymer-modification reaction due to interaction of the anhydride groups in polymer structure with hydroxyl functionality of benzoin and resulted in formation of benzoin monomaleate units. Chemical structure of MPI and content of benzoin moieties tethered were determined using IR- and UV-spectroscopies. It was found that the MPI synthesized had a high affinity towards surfaces of the dispersed mineral fillers, namely TiO_2 and nano $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; that allowed to immobilize MPI at these filler surfaces. It is important that photoinitiation activity increased in the range: benzoin < MPI < MPI immobilized at TiO_2 < MPI immobilized at nano $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. The MPI immobilized at the filler surface could be considered as promising initiator for diverse photopolymer composites.

Keywords: macrophotoinitiator, benzoin, photoinitiation, photocuring, Titanium dioxide, nano hydroxyapatite, poly(methyl methacrylate-co-maleic anhydride).

1. Introduction

Polyfunctional peroxide macroinitiators were found to be very effective modifiers of the diverse by chemical nature surfaces and for creation of various polymer composite materials [1, 2]. Their essential drawback is the necessity to apply high temperatures, although nowadays there is a strong demand in composite materials which could quickly harden at room temperature and at same time they should have quite long shelf life at ambient conditions. Such materials can find many applications,

especially in medicine (e.g. as filling materials), in diverse lithographic processes, electronics production, and so on.

This task can be solved via creation of polymer materials whose formulation includes a photoinitiator that brings about their hardening under UV-irradiation [3, 4]. Macrophotoinitiators have a number of advantages comparing with their low-molecular analogs; besides initiating of polymerization process they behave as surface modifiers due to their high adsorbability and polymerophilicity. Another benefit appeared owing to their polymeric nature is that photoinitiation activity can be improved as the result of energy absorption and transferring along the polymer chain, as well as due to intramolecular reactions responsible for the formation of more reactive species. On the other hand the macromolecular chain can protect the active species similarly to a cage effect [3-7].

Macrophotoinitiators are defined as polymer systems containing pendant or in-chain chromophores, which through the light absorption process can generate active species capable of initiating the polymerization and crosslinking of mono- and multi-functional monomers and oligomers [3, 7-11]. All of the free-radical photoinitiators can be divided into two main types: i) those capable of photofragmentation (Norrish type I), and ii) those capable of generating free radicals through hydrogen-abstraction mechanism (Norrish type II). Examples of the Norrish type I photoinitiators are polymers bearing side-chain benzoin methyl ether moieties [8], polymeric trichloro- and α -amino-acetophenones [9]. In the last years, new polymeric systems with tethered thioxanthone, anthraquinone, camphorquinone or benzyl moieties are intensively developed [7]. Most popular polymeric photoinitiators of the Norrish type II are based on benzophenone, first of all because of its relatively low cost [10, 11].

A principal possibility of introduction of the benzoin fragments into the structure of copolymer namely poly(methyl methacrylate-co-maleic anhydride) (MMA-MA) using polymer-modification reaction grounded on acylation mechanism of alcohol by anhydride have been demonstrated in our previous works [12]. This paper is focused on the notable properties of this novel macrophotoinitiator, namely its surface-activity, adsorbability, and initiation of radical polymerization.

2. Experimental

2.1. Reagents

Maleic anhydride (MA), methyl methacrylate (MMA), benzoin (Bz), and 4-dodecylbenzenesulfonic acid (DBSA) were supplied by Sigma-Aldrich Co. Ethyl acetate, hexane, *o*-xylene as well as other organic solvents from diverse origins were purified before their use as reported by Weissberger *et al.* [13].

As inorganic fillers rutile Titanium dioxide (TiO₂) of pigment grade R-706 (Sherwin Williams Co.) with specific surface area of 5.4 m²/g and nanoparticles of hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) (HA) with specific surface area of 100 m²/g self-synthesized in accordance with [14] were applied.

Components of photopolymer compositions involved unsaturated polyester resin PE-246, triethylene glycol diacrylate TGM-3, paraffin, aerosil A-200 (Degussa GmbH); and as photoinitiator either benzoin, either MPI either MPI immobilized at the TiO₂ surface, or MPI immobilized at the HA surface was used.

2.2. MPI Synthesis

2.2.1. Synthesis of poly(methyl methacrylate-co-maleic anhydride)

The MMA-MA copolymer was obtained *via* free-radical copolymerization of methyl methacrylate with maleic anhydride at their mole ratio as 1:1 in ethyl acetate in the presence of 2 % lauryl peroxide as an initiator and 10 % dodecyl mercaptan as a chain transfer agent at 333 K. The process was carried out in three-neck flask fitted with reflux condenser, mechanical stirrer, and inert-gas inlet. Copolymerization time was of 8 h; and total conversion of the monomers reached 83 %. The MMA-MA copolymer synthesized was purified by precipitation and subsequent re-precipitation in hexane; afterwards it was dried till constant weight at room temperature under reduced pressure. The chemical composition of the MMA-MA was calculated from the results of reverse potentiometric titration of -COOH groups and elemental analyses.

2.2.2. Synthesis of macrophotoinitiator (MPI) on the basis of poly(methyl methacrylate-co-maleic anhydride) by tethering of benzoin fragments

Tethering of benzoin molecules to the polymer carrier occurred as the polymer modification reaction *via* acylation mechanism of alcohol (Bz) by anhydride (MMA-MA) in the presence of 4-dodecylbenzenesulfonic acid as catalyst. The process was carried out in a sealed glass tube in *o*-xylene as solvent at elevated temperatures. MPI synthesized was purified by precipitation and subsequent re-precipitation in toluene; afterwards it was dried till constant weight at room temperature under reduced pressure in darkness.

2.3. IR-Spectroscopy

IR-spectra of the solid polymer films of initial MMA-MA copolymer and MPI applied on KBr plates were recorded on the Specord M-80 spectrophotometer (VEB Carl Zeiss Jena, Germany) within a range of 3700–600 cm⁻¹.

2.4. UV-Spectroscopy

UV-spectra of Bz, MMA-MA copolymer, and MPI in ethanol solutions placed into quartz cuvettes with 1 mm path length were recorded on the Specord M-400 spectrophotometer (VEB Carl Zeiss Jena, Germany) within a range of 230–260 nm.

2.5. MPI Adsorption

Adsorption of MPI at the surface of inorganic particles (TiO₂ or HA) was investigated in ethyl acetate solutions at various MPI concentrations and adsorption time, under continuous stirring at room temperature. Ratio of the adsorbent to solution was kept constant as 1 to 5. The amounts of MPI adsorbed were estimated using thermogravimetric analysis.

2.6. Curing of Photopolymer Composites

Curing activity of MPI was characterized as the content of gel-fraction and surface hardness of the coating photo-cured on glass slides. For that the freshly mixed photopolymer composition was applied onto glass slides and then exposed to UV-irradiation of high-pressure mercury quartz lamp DRT-400 at 10 cm distance for various irradiation times.

The curing degree of photocomposition after exposition to UV-irradiation was characterized by content of gel-fraction [15]. The samples of photo-cured coating were peeled off from glass slides, grinded, placed into pre-weighed envelopes made of stainless steel fine wire

mesh, and extracted with acetone in the Soxhlet apparatus for 12 h. After the extraction cycles, the samples were rinsed in acetone and dried till constant weight at room temperature under reduced pressure. The gel-fraction was calculated as the percentage ratio of the final weight of the sample to its initial weight.

Surface hardness of the coatings obtained on glass slides was determined in accordance with ISO 1522 Standard [16] using the M-3 pendulum apparatus.

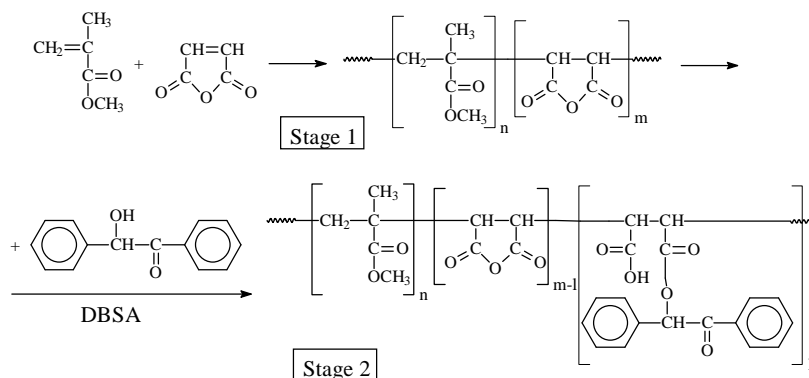
3. Results and Discussion

Synthesis of MPI was realized in two stages shown in Scheme 1. At the first stage a copolymer of methyl methacrylate and maleic anhydride (MMA-MA) was synthesized via their conventional radical copolymerization in accordance with the procedure described above (Section 2.2.1). The purified MMA-MA copolymer had the following characteristics: mole fractions of units $n = 0.507$ and $m = 0.493$ (calculated from results of elemental analysis and reverse potentiometric titration of $-\text{COOH}$ groups); intrinsic viscosity $[\eta] = 0.02$ dl/g (acetone, 298 K).

At the second stage, macrophotoinitiator was obtained by tethering of the benzoin units to MMA-MA macromolecules as described above (Section 2.2.2). This is a typical polymer modification reaction realized *via*

interaction of anhydride moieties of MMA-MA copolymer with hydroxyl functionality of benzoin that resulted in formation of benzoin monomaleate (BzMa) units. The process was carried out in *o*-xylene as a solvent at elevated temperatures and catalyzed by DBSA. Depending on the conditions of this polymer modification reaction (ratio of Bz to MA units in copolymer, amount of solvent added, concentration of DBSA, temperature and reaction time) various amount of Bz units ($l = 0.03$ – 0.25 in Scheme 1) might be tethered to polymer carrier. Particularly for this investigation MPI was synthesized under the following conditions: ratio of Bz to MA units 1 to 5; initial Bz concentration in the system – 3.84 mol/l; DBSA concentration – 3.75 mol/l; temperature – 403 K; and reaction time – 8 h. The purified MPI had the following characteristics: mole fractions of units $n = 0.507$, $(m - l) = 0.343$, $l = 0.150$ (calculated from results of elemental analysis, reverse potentiometric titration of acid groups, and UV-spectroscopy); intrinsic viscosity $[\eta] = 0.096$ dl/g (acetone, 298K).

To confirm the presence of the benzoin fragments in the MPI structure, IR-spectra (Fig. 1) and UV-spectra (Fig. 2) were recorded for both the initial MMA-MA copolymer and MPI on its basis. The most representative absorption bands in IR-spectra taken from Fig. 1 and corresponding chemical bounds and fragments in the structures of the investigated polymers were gathered and summarized in Table 1.



Scheme 1. Synthesis of macrophotoinitiators *via* benzoin tethering to copolymers of maleic anhydride

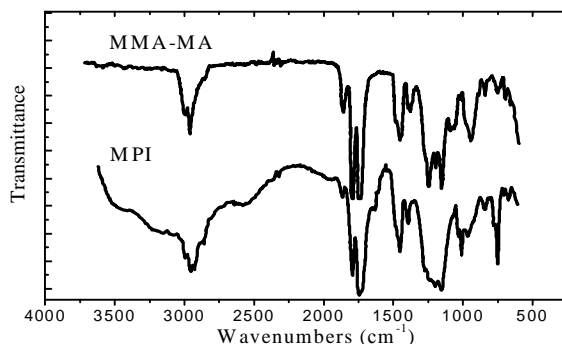


Fig. 1. IR-spectra of MMA-MA and MPI (thin films on KBr plates)

Table 1

Interpretation of IR spectra of MMA-MA copolymer and MPI

Absorption band wavenumbers, cm^{-1}		Bond and vibration mode	Corresponding unit
MMA-MA	MPI		
2830	2830	C–H stretch in $-\text{OCH}_3$	MMA
1736	1736	C=O stretch in ester	MMA
1250	1250, 1235	C–O stretch in ester	MMA
1852, 1780	1848, 1780	C=O stretch in anhydride	MA
-	1606, 1580	C=C stretch in aromatic ring	BzMa
-	3080	C–H stretch in aromatic ring	BzMa
-	1700	C=O stretch in aromatic ketone	BzMa
-	3300-2500	O–H stretch in acid	BzMa
-	950	O–H bend in acid	BzMa

Comparing IR-spectra of MMA-MA and MPI one could mark some similar absorption bands in both spectra. Those are the following characteristic bands: at 1852 and 1784 cm^{-1} assigned to C=O stretch in anhydride cycles of the MA units; 1736 cm^{-1} and 1250 cm^{-1} assigned to vibration of C=O and C–O bonds, respectively, in ester group of the MMA units; 2830 cm^{-1} assigned to C–H stretch of $-\text{OCH}_3$ groups in the MMA units. That evidences that only a part of anhydride cycles in MMA-MA copolymer was opened under conditions of polymer modification reaction, while another big part of anhydride cycles was left unreacted.

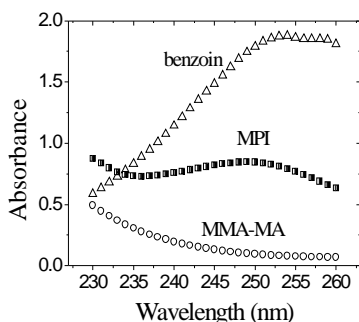


Fig. 2. UV-spectra of the MMA-MA copolymer ($C = 0.17$ wt %), MPI ($C = 0.17$ wt %) and benzoin ($C = 0.046$ wt %) in ethanol

Besides this in IR-spectrum of MPI the new absorption bands appeared which were not present in spectrum of initial MMA-MA copolymer. These new bands appeared certainly because of benzoin tethering and formation of the benzoin monomaleate units, thus confirming the suggested scheme of reaction (Scheme 1, stage 2). Functional groups of BzMa units in the structure of MPI were well recognizable in its IR spectrum due to the presence of the following bands: 1606, 1580 and 3080 cm^{-1} being characteristic of aromatic ring; 1700 cm^{-1} assigned to C=O stretch in aromatic ketone; and strong absorption in the ranges of 3300-2500 and 950 cm^{-1}

assigned to stretch and bend vibration of $-\text{OH}$ groups in monomaleate moieties.

UV-spectrum (Fig. 2) gave strong evidence of the presence of the benzoin moieties in the MPI macromolecules. Both benzoin and MPI demonstrated absorption peaks at $I_{max} = 254$ nm caused by $\pi \rightarrow \pi^*$ electron transition in aromatic ketones, while the initial MMA-MA copolymer had no recognizable absorption in this area. The absorbance values at wavelength 254 nm were used for estimation of the content of Bz tethered in the MPI structure.

Thus MPI synthesized are polyfunctional macro-initiators which macromolecules bear the photoinitiating benzoin fragments and highly reactive and polar carboxylic and anhydride groups. Due to such combination MPI was supposed to be an effective surface modifier of diverse mineral fillers. Surface modification of two fillers, namely rutile Titanium dioxide and nano hydroxyapatite *via* immobilization at their surface of MPI was studied in this investigation. TiO_2 is widely used as a pigment and inert filler in many polymer formulations. Lately a lot of attention is paid to hydroxyapatites and specially to nano hydroxyapatites because of their promising application in medicine.

Immobilization of MPI at the surface of these fillers was achieved through its adsorption from solution in ethyl acetate. Fig. 3 illustrates the main regularities of MPI adsorption at the surfaces of TiO_2 and $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Amount of MPI adsorbed depended on the initial MPI concentration in an ethyl acetate solution and adsorption time. However, in both cases the adsorption values reached plateaus at MPI concentration of about 5 wt % and exposure for 1 h, that was the optimal conditions for MPI immobilization on these fillers. Besides, some features in adsorption processes at these fillers' surfaces were clearly seen, which might be explained by the difference in types of their interactions with MPI. While in the MPI adsorption at TiO_2 surface physical adsorption owing to low reactivity of this adsorbent dominated, in

case of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ the MPI chemisorption can dominate with the formation of ionic interface bonds between adsorbent and adsorbate. In spite of this difference, a high affinity of the MPI macromolecules towards both adsorbents was observed that allowed to immobilize MPI at the surfaces of both of these filler successfully.

Photopolymer composites are promising materials, which have wide application, especially in paints, varnishes and other similar formulations, in diverse lithographic processes, electronics production, medicine (*e.g.* as filling materials), and so on. Formulations of such compositions usually include polymerizable oligomers, monomers and photoinitiators for their curing. They can also include a considerable quantity of the mineral fillers introduced for improving strength and abrasive resistance of cured compositions. In predominant cases physico-mechanical properties of the composite materials essentially depend on interfacial interactions of filler with polymer matrix. A prosperous way to improving interfacial interaction is surface modification of mineral fillers by compounds capable of chemical interaction with the matrix polymer. In our case MPI can play a role of such surface modifier because its photoinitiating centres

should facilitate chemical grafting of the matrix polymer to the filler surface in the process of composite curing.

The most important characteristics of any photopolymer compositions are kinetics of their curing and surface hardness of the cured composition. Both these parameters are affected by many factors; however activity of the photoinitiator used plays here an important role.

In this study we assessed activity of the MPI synthesized and MPI immobilized at the filler surface in comparison with non-bounded virgin benzoin. This assessment was performed by controlling two parameters, namely the content of gel-fraction and surface hardness of the cured compositions. The formulations of the photopolymer compositions were based on the mixture of unsaturated polyester resin PE-246 and triethylene glycol diacrylate TGM-3 (60 wt % and 40 wt %, respectively) and included also 2 wt % of paraffin* and 2 wt % of aerosil A-200. Each of the following photoinitiators was exploited for curing the composition: benzoin (2.6 wt %), MPI (2.0 wt %), MPI immobilized on TiO_2 particles (2.5 wt %) or MPI immobilized on HA nanoparticles (2.5 wt %). The curing features of the aforementioned compositions initiated by these photoinitiators are demonstrated in Fig. 4.

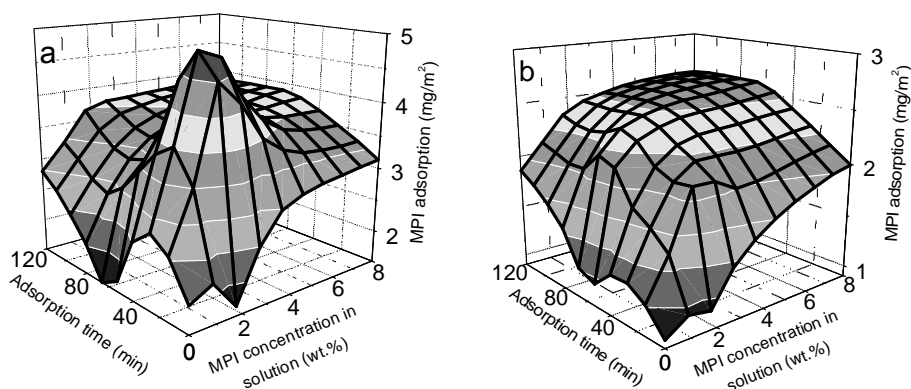


Fig. 3. MPI adsorption from ethyl acetate solutions at surfaces of dispersed TiO_2 (a) and $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (b) vs adsorption time and MPI concentration in solution

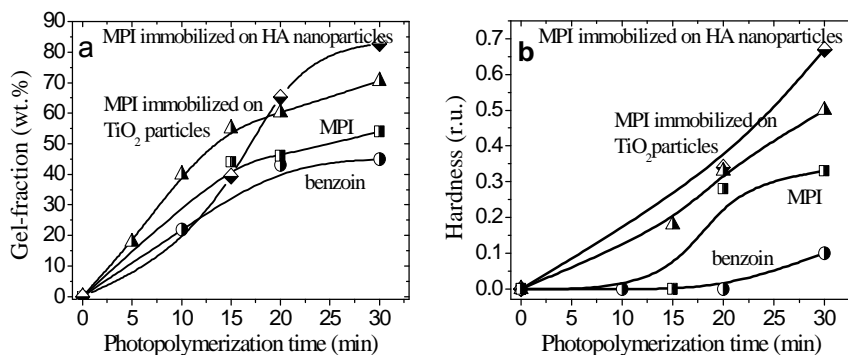
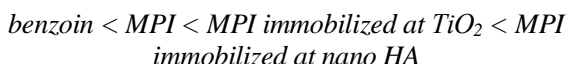


Fig. 4. Plots of gel-fraction content (a) and hardness (b) of the cured photocomposition vs irradiation time

* Paraffin is usually added to photopolymer compositions to prevent inhibition of the process by air oxygen.

From analysis of the plot presented the gel-fraction content versus irradiation time (Fig. 4a) it can be concluded that activity of the investigated photoinitiators increases as follows:



This means that tethering of Bz with polymer carrier brought about enhancing of its photoactivity. Further enhancement was achieved when MPI was immobilized at the surface of dispersed fillers.

The most important result achieved in this investigation was an essential improvement of the surface hardness of the cured photocompositions in the presence of MPI and especially in the presence of immobilized MPI if compared with non-bounded initial benzoin (Fig. 4b).

4. Conclusions

Applying a polymer modification reaction the novel macrophotoinitiator was obtained by tethering of benzoin to polymer carriers poly(methyl methacrylate-co-maleic anhydride). This macrophotoinitiator had high affinity towards diverse mineral surfaces and could be easily adsorbed at the surfaces of dispersed fillers, particularly at TiO₂ pigment or nano Ca₁₀(PO₄)₆(OH)₂. An essential improvement in the properties of photopolymer compositions was shown when macrophotoinitiator itself, and especially after its adsorption at the filler surface, was used instead of non-bounded benzoin.

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СИНТЕЗ І ЗАСТОСУВАННЯ МАКРОФОТОІНІЦІАТОРІВ, ОТРИМАНИХ ПРИЩЕПЛЕННЯМ БЕНЗОЇНУ ДО КОПОЛІМЕРІВ МАЛЕЇНОВОГО АНГІДРИДУ

Анотація. Розроблено новий підхід до синтезу макрофотоініціаторів (МФІ) на основі бензоїну, що ґрунтується на прищепленні фрагментів бензоїну до кополімерів метилметакрилату та малеїнового ангідриду. Цей процес відбувається як полімераналогічна реакція при взаємодії ангідридних груп в полімерній структурі з гідроксильною групою бензоїну і, як наслідок, утворення фрагментів бензоїн мономалеїнату. Хімічна структура МФІ та вміст прищеплених фрагментів бензоїну визначався за допомогою ІЧ- та УФ-спектроскопії. Встановлено, що синтезований МФІ має високу спорідненість до мінеральних наповнювачів, а саме TiO₂ і nano Ca₁₀(PO₄)₆(OH)₂, що дало можливість іммобілізувати МФІ на їх поверхні. Встановлено, що фотоініціююча активність зростає в порядку: бензоїн < МФІ < МФІ, іммобілізований на TiO₂ < МФІ, іммобілізований на nano Ca₁₀(PO₄)₆(OH)₂. МФІ іммобілізовані на поверхні наповнювачів, є багатообіцяючими ініціаторами для різноманітних полімерних композицій.

Ключові слова: макрофотоініціатор, бензоїн, фотоініціювання, фотоструктурування, діоксид титану, nano гідроксипатит, полі(метилметакрилат-ко-малеїновий ангідрид).