



Preparation and properties of photopolymerized hybrid composites with covalently attached magnetite nanoparticles



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HIGHLIGHTS

- Magnetite/polymer hybrid composites were prepared by UV photopolymerization.
- The magnetite nanoparticles were functionalized with methacrylate double bonds.
- Castor oil diacrylates with acid groups improved the dispersion of Fe₃O₄ particles.
- Thin elastomeric coatings with ferromagnetic behavior can be easily yielded.

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ABSTRACT

Using magnetite nanoparticles (50–100 nm) containing methacrylic groups (MNPs-MA or shortly, M) as inorganic phase into a mixture of photopolymerizable monomers with and without acid moieties in structure, a series of hybrid nanocomposites were prepared and characterized by FTIR, TEM, SEM-EDX analysis, and magnetization studies. For this purpose, two diacrylates based on castor oil triglyceride functionalized with carboxyl (CO-DAC) or phosphate (CO-DAP) groups were synthesized and incorporated in formulations besides urethane dimethacrylate (DMUO-1) and triethylene glycol dimethacrylate. Kinetic data obtained for photopolymerization in the presence of Irgacure 819, revealed that the maximum polymerization rate (R_{\max}^p) and the conversion degree (DC) are dependent on the monomer structure and the formulation composition. For instance, the inclusion of 0.1 wt.% M had as result a slight decrease of R_{\max}^p from 0.088 s⁻¹ (F1/30 wt.% CO-DAP) to 0.075 s⁻¹ (F1-0.1 M), the highest value being found in the non-acid F3 formulation (0.1155 s⁻¹). When the amount of nanoparticles increased to 1.0 wt.%, the R_{\max}^p , DC, gel content and mechanical characteristics of the hybrid films were influenced in a different manner. TEM and SEM-EDX analysis confirm a good dispersion of nanoparticles in the organic matrix containing CO-DAC or CO-DAP monomer units, compared to the effect of crowded structure observed in the composite with no acid groups. Specifically, the magnetic hysteresis (M_s) loops indicated a ferromagnetic behavior for these composites, for which the saturation magnetization amplified with increasing amount of nanoparticles in the sample (from 37.85 emu/g for F1-0.1 M to 45.31 emu/g for F1-1.0 M).

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1. Introduction

Photoinitiated polymerizations are among the most frequently investigated processes due to their extensive application in the obtaining of UV-curable coatings, printing inks, photoresists, and microelectronics [1–3]. The *in situ* crosslinking photopolymerization of solvent free curable (meth)acrylic systems is very attractive

since the procedure involves the use of UV light for the building up of polymeric crosslinked networks through a fast and environmentally friendly manner with low energy consumption and no emission of volatile organic compounds [4,5]. Moreover, the chemical composition of the monomer mixtures able to photopolymerize is virtually unlimited, ranging from monomers originating from natural to synthetic sources, so the intelligent combinations of monomers may ensure the optimization of polymer networks performances. Of particular interest is the conception of polymer matrixes with a variety of reactive functional groups that by

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specific interactions (electrostatic, dispersive, van der Waals, hydrogen or covalent bonds) interconnect with biomolecules or inorganic nanoparticles [6,7].

In recent years, the development of polymer nanocomposites enclosing inorganic materials has drawn considerable attention especially due to their potential applications in nanoscience and nanotechnologies [8–10]. The main reason for this growing trend concerning polymer/inorganic functional materials derives from their superior properties compared to pure constituents, anticipated flexibility, lower costs, and large applicability in diverse industrial and biomedical fields. Up to now, various inorganic nanoparticles such as metals [11] and metal oxides [12], clays [13], carbon nanotubes [14], silica [15] or hydroxyapatite [16] have been incorporated into polymer matrixes leading to micro/nano-filled materials with distinctive features. The central issues still remain to be addressed in achieving polymer/nanoparticles composites are referring to a rigorous control of the particle size/shape, positional stability and their uniform distribution within the formed polymer network, given the importance of these parameters on the physico-chemical properties of such nanomaterials, as well as the inherent immiscibility between the inorganic and organic phase.

In the frame of the modern researches related to innovative materials, the polymer/magnetite nanoparticles (Fe_3O_4 NPs) hybrid composites have been developed for uses in high density data storage, magnetic resonance imaging, catalysis, sensor, pigments, biomedical and environmental applications, etc. [17–22]. The function of Fe_3O_4 NPs was emphasized by the demonstration that the special properties of the above materials can be magnetically tuned under the action of an external magnetic field. For an enhanced compatibility between phases, Fe_3O_4 NPs need to be chemically modified with organic molecules, often of trialkoxysilane type, to form covalent siloxane bonds on the nanoparticles surface [23]. A direct consequence of the silane groups and reactive sequences (polymerization initiators, double bonds, photoisomerizable sequences) [24–26] is that they improve the chemical interaction inside the hybrid material avoiding the agglomeration of micro/nanoparticles.

The purpose of this work is to extend our research focused on the development of novel photopolymerizable hybrid composites containing small amounts of inorganic nanoparticles (silver, gold)

[27–29] to the synthesis of hybrid composites with magnetite nanoparticles. Knowing that usually metal nanoparticles show a high affinity to agglomerate or aggregate, the choice of the organic polymeric template to hinder the interactions between NPs is essential. Thus, by replacing of some photopolymerizable monomers structures with the other ones bearing carboxyl and phosphate functional groups and the incorporation of magnetite nanoparticles functionalized with photoreactive methacrylate units, new hybrid materials with various magnetite loadings were prepared via UV polymerization. Additionally, the presence of methacrylate functions on the surface of magnetite nanoparticles might enhance the physico-chemical stabilization of Fe_3O_4 NPs leading to versatile hybrid composite coatings.

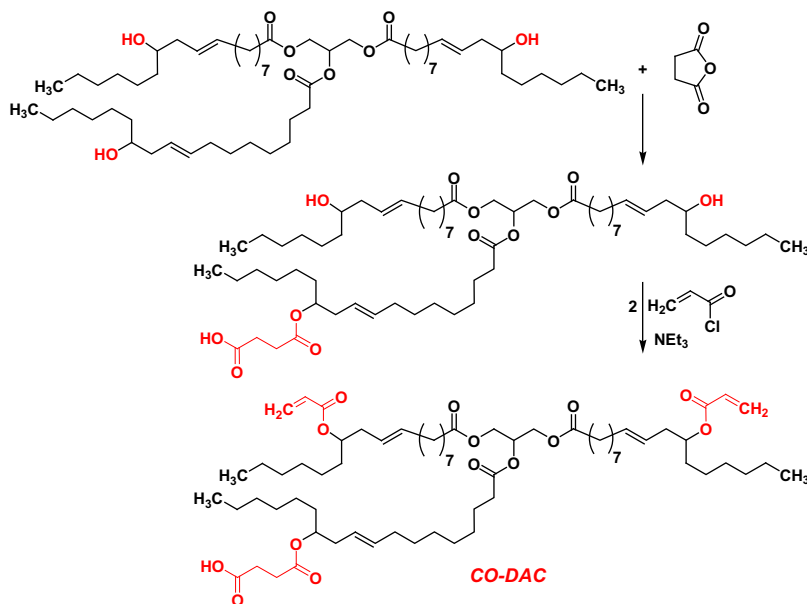
2. Experimental

2.1. Materials

Polyethylene glycol ($M_w = 1000$ g/mol), castor oil (CO), isophorone diisocyanate (IPDI), 2-hydroxyethyl methacrylate (HEMA), acryloyl chloride (AcCl), phosphorus oxychloride (POCl_3), succinic anhydride, triethylamine (TEA), dibutyltin dilaurate, 3-(trimethoxysilyl)propyl methacrylate, triethylene glycol dimethacrylate (TEGDMA), butylated hydroxytoluene (BHT) and Irgacure 819 were purchased from Sigma Aldrich Chemical Co. (Taufkirchen, Germany) and used without further purification. Polytetrahydrofuran (PTHF, $M_n = 1000$ g/mol) was purchased from BASF (Ludwigshafen, Germany). Magnetite nanopowder, 50–100 nm particle size (according to TEM analysis), 97% trace metals basis was purchased from Sigma Aldrich Chemical Co.

2.2. Intermediates and monomers synthesis

For the preparation of castor oil diacrylate with carboxyl group (CO-DAC) (Scheme 1), 5 g (5.36 mmol) castor oil were dissolved in 50 mL tetrahydrofuran and 0.536 g (5.36 mmol) succinic anhydride were added, the system temperature being raised at 60 °C for 6 h. After that, the reaction vessel was cooled to 0 °C and 1.49 mL (10.72 mmol) triethylamine were added. The acryloyl chloride (0.9 mL, 10.72 mmol) was dropwise added so the temperature does not exceed 0 °C. After all acryloyl chloride was added, the reaction



Scheme 1. Synthetic route for the obtaining of CO-DAC carboxyl diacrylate monomer.

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