

PREPARATION OF NEW PHOTOPOLYMERIZABLE HYBRID NANOCOMPOSITES BASED ON URETHANE MACROMERS AND Fe₃O₄ NANOPARTICLES

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Abstract

In this work, a photopolymerizable urethane monomer of oligomer type with flexible spacers consisting of polytetrahydrofuran was used in tandem with commercial photoreactive monomers in the preparation of polymeric hybrid nanocomposites reinforced with Fe₃O₄ nanoparticles taken in variable proportions (between 0.05 and 0.5 wt. %). For the prepared experimental formulations, particular characteristics such as photoreactivity, surface and mechanical properties, as well as the magnetization profiles were investigated by specific measurements. Through the incorporation of magnetite nanoparticles before UV-curing of monomer mixtures the maximum tensile strength increased, whereas the elongation at break decreased. This study describes the possibility to prepare magnetic coatings able to be deposited onto the surfaces of various materials.

1. Introduction

In recent years, the UV-curing of (meth)acrylate monomers or oligomers in the presence of a suitable photoinitiator is well known to guarantee the building up of polymer thermoset matrixes through a fast, energy efficient and environmental friendly process. These particular features recommend its large applicability in various fields such as stereolithography, electronics, optics or dentistry [1-3]. On the other side, the development of hybrid nanocomposites was progressively explored, since the dispersion of nanosized inorganic particles (e. g. clay, silica, hydroxyapatite, metals and metal oxides) into a polymer matrix open the possibility to generate new types of nanostructured materials (nanodevices) with designed surface and structural properties, such as flexibility, hardness, thermal/chemical stability or optical/magnetic characteristics [4-6]. Usually, metal nanoparticles display a high affinity to agglomerate or aggregate, and therefore the employment of polymeric materials as stabilizers caused the adsorption of polymers onto the surface of metal nanoparticles. This arrangement confers some protective steric repulsion that acts as a wall against the interaction between the particles, assuring their good dispersion in the organic matrix. Many investigations were performed on systems containing magnetite nanoparticles, taking into account their potentially valuable electronic, magnetic, and catalytic features deriving from their composition, chemical structure, nanoscopic size and shape [7,8]. Commonly, the magnetite-containing hybrid materials have been achieved through the sol-gel method

combined with the photopolymerization process, and also by the physical mixing of iron oxide nanoparticles with the organic partners, depending on the targeted applicability field.

The present work describes the results obtained in the preparation of new hybrid nanocomposites using photopolymerizable urethane monomer of oligomer type with flexible spacer of polytetrahydrofuran as organic matrix for magnetic nanoparticles. Subsequently, some photoreactive experimental mixtures incorporating Fe₃O₄ nanoparticles in proportions between 0.05 and 0.5 wt. % were obtained by using the oligodimethacrylate taken in combination with other methacrylates functionalized with specific groups (carboxyl, phosphate). The photopolymerization parameters (the time to reach the maximum polymerization heat (t_{max}), double bond conversion and rate of polymerization), mechanical characteristics, distribution of magnetite nanoparticles inside the photopolymerized matrix as well as the magnetization profiles were evaluated through adequate methods (photoDSC, TEM, mechanical and magnetization determinations) in order to select the most versatile composition for targeted applications.

2. Results and discussions

The chemical structures of the photopolymerizable monomers included in this study are graphically represented in Figure 1. They consist of an urethane dimethacrylate oligomer DMAU-1 with polytetrahydrofuran soft segment ($M_n = 1000$) previously synthesized in our group [9], and three commercially available monomers, namely triethylene glycol dimethacrylate (TEGDMA), ethylene glycol methacrylate phosphate (EGMP) and methacrylic acid (MA). The magnetite nanopowder with particle size between 50-100 nm was purchased from Sigma Aldrich Chemical Co. and was used without additional modifications.

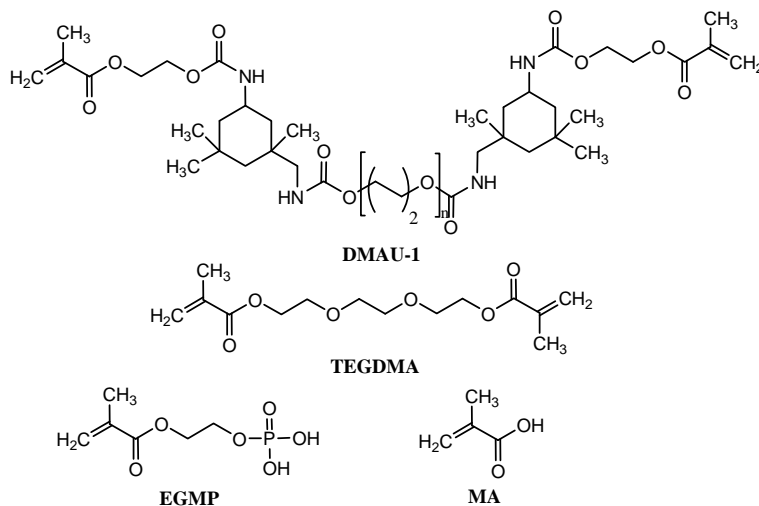


Figure 1. Structures of the monomers used in the study.

The given monomers were mixed in various gravimetric ratios to prepare some experimental formulations according to the mass percentages included in Table 1. To follow the photopolymerization and photocrosslinking reactions occurred in the case of photosensitive materials the photoDSC method was used, since the knowledge of curing degree for this type of materials is essential from the applicative point of view. Consequently, this method allows a fast evaluation of the most important parameters characterizing the curing kinetics of the photopolymerizable systems which are the rate at the peak maximum (R_{max}^P) and the degree

of double bond conversion (DC). The photopolymerizations of our experimental formulations were performed with a low light intensity of 4.5 mW/cm² and in the presence of 1 wt. % Irgacure 819 taken as photoinitiator.

Formulation	DMAU-1 (wt. %)	TEGDMA (wt. %)	EGMP (wt. %)	MA (wt. %)	Fe ₃ O ₄ NPs (wt. %)
1	60	10	30	-	0.05
2	60	10	30	-	0.1
3	60	10	30	-	0.5
4	60	10	-	30	0.05
5	60	10	-	30	0.1
6	60	10	-	30	0.5

Table 1. Composition (wt.%) of the experimental formulations (1-6).

As can be observed from the graphical representation of the polymerization rates given in Figure 2a, the photochemical polymerization of monomer mixtures occurs fast so the maximum polymerization rates (R_{max}^p) were attained after about 4-5 seconds of UV irradiation. Regarding the values of the maximum polymerization rates, the reactivity of the formulations is decreasing with the increase in the amount of magnetite nanoparticles, behaviour that can be attributed to a restriction effect exerted by the metallic nanoparticles on the mobility of the active radicals, while the formulations with phosphate units (1-3) are more reactive than those containing carboxyl groups (4-6). The conversion degree calculated for our photopolymerizable composites after 2 minutes of irradiation (Figure 2b) varied between 80 and 67 % for the hybrid formulations based on EGMP, whereas this parameter ranged between 78 and 69 % in the materials comprising MA monomer.

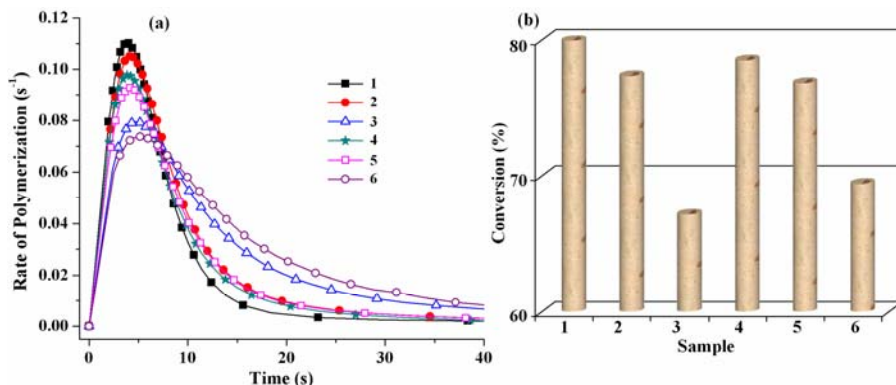


Figure 2. PhotoDSC rate profiles for the 1-6 formulations containing magnetite nanoparticles (a) and double bond conversion for the hybrid materials after 2 minutes of UV irradiation (b).

The distribution of magnetite particles inside the polymeric matrix was investigated by transmission electron microscopy (TEM), a method that allows the obtaining of information about the shapes and sizes of the particles. Figure 3a shows the TEM image of spherical magnetite particles dispersed in the formulation 3. It seems that the particles are not agglomerated in the resulting hybrid composite, possible due to the stabilizing effect exerted by the photocrosslinked polymeric network.

The mechanical parameters were measured on photopolymerized composite films for which we have determined the maximum tensile strength and elongation at break (Figure 3b). It might be observed that the growing of magnetite amount into the hybrid composites caused an

increase of the maximum tensile stress coupled with a decrease of the elongation at break, attributed principally to the reinforcing outcome created by the higher number of magnetite nanoparticles that restrict the molecular motion of polymer chains. On the other hand, the elongation at break and the maximum tensile strength are lower for the hybrid composites including MA monomer units, comparatively to those comprising EGMP derivative.

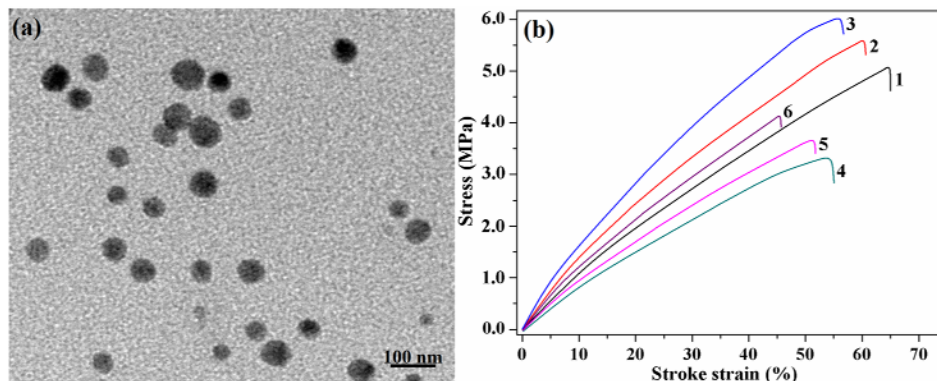


Figure 3. TEM image of 3 hybrid composite containing 0.5 wt. % magnetite nanoparticles (a) and stress-strain curves for the hybrid composite films with different magnetite percentages (b).

The magnetization curves of the photocured films obtained in the presence of 0.05, 0.1 and 0.5 wt. % magnetite nanoparticles (samples 1, 2, 3 and 6, respectively), measured at room temperature are reported in Figure 4a. The recorded magnetic hysteresis loops suggests a ferromagnetic behavior, characteristic for magnetite nanoparticles with sizes larger than 10 nm. Also, the saturation magnetization (M_s) values clearly increased with the enhancement in the magnetite content from an M_s of 18.3 emu/g for sample 1 to an M_s of 37.2 emu/g for sample 3. The saturation magnetization of Fe_3O_4 particles is slightly influenced by the presence of phosphate or carboxyl units in the formulation (M_s of 37.2 emu/g for the phosphate sample and of 33.1 emu/g for the carboxyl sample, respectively), denoting that there are some chemical interactions between the magnetite nanoparticles and the organic matrix.

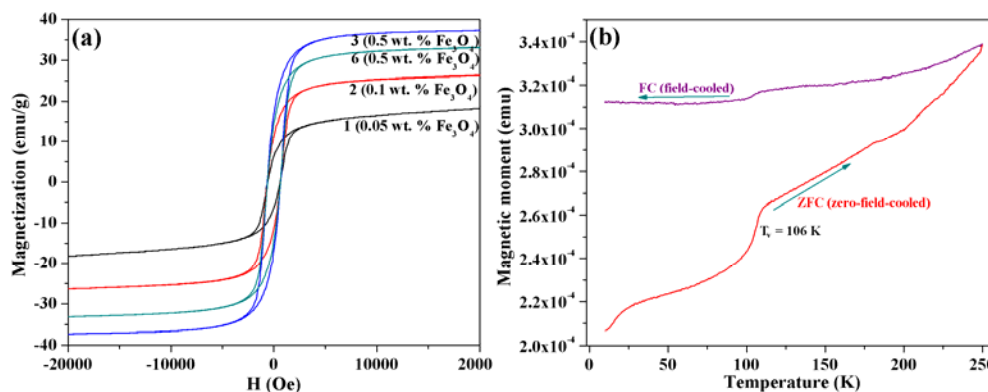


Figure 4. Room temperature magnetization curves of some hybrid composite films (a) and FC/ZFC curves (b) measured on the cured film 3.

Analysing the investigated samples it can appreciate that these show a ferromagnetic behavior, attributable to the large diameter of the magnetite nanoparticles (the superparamagnetism is characteristic to the magnetite samples with dimensions under 10 nm). This compartment is evidenced from the ZFC (zero-field-cooled) and FC (field-cooled) curves (Figure 4b)

recorded for sample 3, where no blocking temperature (T_b) can be noticed, only the Verwey transition temperature ($T_v = 106$ K) was observed.

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