Synthesis and characterization of some composites with bioactive properties on the basis of vinyl ester resins

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Abstract: Vinyl ester resins are unsaturated polyesters, widely used as matrix for high performance composite materials. The paper presents the synthesis and characterization of some vinyl ester resin/hydroxyapatite bioactive compositions using an unsaturated copolyester based on turpentine oil as reactive diluent. The vinyl ester oligomer /unsaturated copolyester/hydroxyapatite structural complex was characterized from the morphological point of view, water absorption, density measurements and volume contraction. The water uptake is dependent on the concentration in vinyl ester resin. The increase of the vinyl ester resin content in the bioactive composite leads to the increase of the density, respectively to a significant decrease of the volume contraction

Keywords: vinyl ester resin, turpentine oil, hydroxyapatite

Introduction

Vinyl ester resins are epoxidic monomers chemically modified by addition of some α,β -unsaturated acids (acrylic, metacrylic, crotonic or cynamic) to oxirane group. The most known vinyl ester resins are those obtained using bisphenol-A as the raw material. The main features of the vinyl ester resins are as follows: resistance to water and chemical compounds, thermal and electrical stability, reduced content of the volatile materials evolved during manufacture, mechanical resistance and decreased contraction to the strength tensing [1]. Presently, synthesis and manipulation of the vinyl ester resins are of major interest, being recognized as materials with various applications, such as: obtaining of composites for manufacturing of pipes, tanks, filter devices, sewerage pipelines, dental materials, photo-crosslinking inks etc [2, 3]. The vinyl ester networks show good mechanical properties and temperature resistance, which are higher to other types of polymers. That is why they are preferred as matrix to achieve advanced composite materials [4-6]. The composite materials with vinyl ester matrix extended their applicability area, from the special domains, such as aeronautic, naval or autovehicle constructions towards biomedical science [7].

The properties of the vinyl ester resins are dependent on their chemical nature, molecular mass and cross-linking degree. The high initial viscosities (1000-80000 poise), which are characteristic to the vinyl ester oligomers, require dilution before cross-linking. In practice, the compounds which react with the vinyl ester oligomers found in the network structure are used as reactive diluents. One of the most used reactive diluent for this kind of resins is styrene [8]. Due to its high volatility and toxicity, styrene is not indicated as reactive diluent for the vinyl ester networks, when their biomedical applications are endorsed [9]. In the most frequent cases the vinyl

ester resins, intended to biomedical applications, are diluted with dimetacrylates [10-12]. The possibility of the turpentine use as reactive diluents with low toxicity level for vinyl ester oligomers on the basis of bisphenol A was reported by Matasa and Balaban [13].

In a previous paper [14] we reported the synthesis and the characterization of an unsaturated copolymer, obtained as result of the reaction between turpentine oil, maleic anhydride and glycerol. It was noted that the synthesized unsaturated polyester can act as a reactive diluent for the vinyl ester resins based on bisphenol A [15]. In recent years the composite materials based on the organic polymers and hydroxyapatite were widely studied with the goal to use as biomaterials [16, 17]. This work reports the synthesis and the characterization of some bioactive compositions on the basis of vinyl ester resins and hydroxyapatite, in presence of the unsaturated copolyester from turpentine oil, maleic anhydride and glycerol, used as reactive diluent.

Results and discussion

Generally, vinyl ester polymeric matrices are obtained as a result of the cross-linking of the corresponding oligomers. In the present work the vinyl ester oligomer was obtained using the reaction between Ropoxid 501 epoxidic resin and acrylic acid, as shown in Scheme 1.

Scheme 1. Synthesis of vinyl ester oligomer.

The synthesized vinyl ester oligomer was characterized by FT-IR and $^1\text{H-NMR}$ spectroscopy. Figure 1 shows the IR spectrum of the vinyl ester oligomer. The spectrum in Fig. 1 presents bands, which are characteristic to the valence vibrations of OH functions at 3320 cm^{-1} , the signals specific to the valence vibration of C-H bonds (-CH, -CH₂ and -CH₃ atom groups) at 2969 , 2929 and 2871 cm^{-1} , the vibrations which are characteristic to the aromatic ring at 1889 , 1591 , 1467 , 1090 and 750 cm^{-1} , the bands specific to the double bond at 1635 , 940 and 894 cm^{-1} , the signals which are specific to the etheric function (1712 cm^{-1}) as well as the signals characteristic to the carbonyl group (-C-O, C-O-C and C-CO-O bonds) at 1293 , 1224 and 1160 cm^{-1} .

Fig. 1. FT-IR spectrum of vinyl ester oligomer.

Fig. 2. ¹H-NMR spectrum of vinyl ester oligomer.

The ¹H-NMR spectrum (Figure 2) confirms the structure of the vinyl ester oligomer by the signals at 1.0-1.1 ppm, which are characteristic to CH₃ group from propylidene structure (A), the signals in the range 2.1-2.7 ppm, for the protons of the hydroxyl group (B), the multiplet at 3.5-4.3 ppm, due to the protons resulted from the opening

of the epoxidic group (C), the specific signals placed in the interval between 5.7 and 6.2 ppm for the protons attached to the double bond, respectively the signals which are characteristic to the aromatic structure (F) in the interval 6.7-7.1 ppm.

The unsaturated copolyester, with the structure shown in Figure 3, was characterized by FT-IR spectroscopy. The FT-IR spectrum of the copolymer (Figure 4) shows bands characteristic to the valence vibration of the OH groups at 3378 cm^{-1} , respectively for the carbonyl group at 1727 cm^{-1} . The bands at 1636 , 918 and 760 cm^{-1} characterize the double bond from the maleic structure. The other bands specific to the synthesized unsaturated copolymer are localized at 2877 cm^{-1} (CH_2 group) and 2819 cm^{-1} (CH_3 group), respectively.

Fig. 3. Structure of unsaturated copolymer.

Fig. 4. FT-IR spectrum of unsaturated polyester.

The vinyl ester oligomer/unsaturated polyester composite films were exposed to UV radiation, when polymeric networks were obtained. The glass transition temperatures

(T_g s) of the networks, determined using DSC technique, increase together with increase of the vinyl ester resin content in the network, as can be seen in Figure 5.

Fig. 5. Dependence of T_g on vinyl ester content.

Simultaneously, it was noted that the increase of the vinyl ester resin content in network leads to the increase of the gel fraction in the network (Figure 6), while the swollen indexes, determined both in the solvents and in distilled water, decrease. The increase of the gel fraction and the decrease of the swollen coefficients, are due to the increase of the cross-linking density of the network with increase of the oligomer content in the network.

Fig. 6. Dependence of gel fraction on vinyl ester content: (■) methyl chloride solvent; (●) methyl ethyl ketone solvent.

The dimensional distribution of the synthesized hydroxyapatite particles, as a function of their size, is shown in Figure 7.

Fig. 7. Dimensional distribution of hydroxyapatite particles: (a) ultrasonated hydroxyapatite and (b) water dispersed hydroxyapatite.

Figure 7 shows that the synthesized hydroxyapatite is characterized by the presence of particles with dimensions in the range between 1.26 and 158.5 ppm. In this range, the particles with dimension of 19.8 μm constitute the major fraction, representing 83% from the whole analyzed hydroxyapatite particles.

The polymeric matrix/hydroxyapatite structural complex was characterized from the morphological point of view, taking into consideration the water uptake, density and volume contraction. Figure 8 shows some micrographs characteristic to the studied composites, using electronic microscopy (x 4200). Analysis of the micrographs shows a uniform distribution of the hydroxyapatite particles (darkness zones) in the polymer matrix.

Fig. 8. SEM of hydroxyapatite dispersed in: (a) vinyl ester matrix, (b) vinyl ester matrix with 40 % unsaturated copolyester and (c) vinyl ester resin with 60 % unsaturated copolyester.

The water uptake was gravimetrically measured, immersing some blocks of the composite material (3x3x3 mm dimensions) into the distilled water. The study was carried out at the room temperature ($22 \pm 1^\circ\text{C}$), the samples being daily weighed until the water absorption reached the equilibrium (2 month). The results obtained taking into consideration the compositions with 40 % hydroxyapatite are listed in Table 1.

The data presented in Table 1 shows that the water uptake of the composite materials depends on the concentration of the unsaturated copolyester to a great extent. The increase of the copolymer concentration leads to the increase of the quantity of the water uptake. Simultaneously, introduction of hydroxyapatite into the polymer matrix increases the content of the water uptake with one up to two percentages, as against the standard sample. The density of the composite material (ρ) was measured at 25 °C, using the picnometric method.

Tab.1. Water uptake of the composites with 40 % hydroxyapatite.

Sample	Hydroxyapatite (%)	Water uptake (%)
1	40	6.28
2	40	5.82
3	40	5.07
4	40	5.00
5	40	4.48

The sample mass (around 1 g) was evaluated by its maintenance both in air (a) and in water (b), while the density (ρ) was calculated using Eq. (1):

$$\rho = \frac{a}{a - b} \rho_0 \quad (1)$$

where, ρ_0 means the water density at 25 °C.

The volume contraction was evaluated using Eq. (2):

$$\text{Volume contraction (\%)} = \frac{\frac{1}{\rho_n} - \frac{1}{\rho_{in}}}{\frac{1}{\rho_n}} \cdot 100 \quad (2)$$

where, ρ_n means the density of the uncross-linked composite, while ρ_{in} – the cross-linked composite (network) density.

Tab. 2. Variation of the volume contraction respectively of the density, before and after photo-crosslinking) for the composites with 40 % hydroxyapatite.

Sample	ρ (g cm ⁻³)		Volume contraction
	Before photo-crosslinking	After photo-crosslinking	(%)
1	1.641	1.724	4.76
2	1.685	1.767	4.72
3	1.692	1.735	2.54
4	1.691	1.737	2.71
5	1.685	1.702	1.01

The data referring both to the density and to the volume contraction, which were obtained for the composites with 40% hydroxyapatite, before and after photo-crosslinking, are listed in Table 2.

A slight increase in the density of the composites after photo-crosslinking can be noted. Also, an increase of the composites density can be observed together with increase of the content of the vinyl ester component. The increase of the vinyl ester component leads to an important decrease of the volume contraction.

Conclusions

The bioactive composites based on vinyl ester resin and hydroxyapatite were synthesized and characterized from a morphological point of view, water uptake, density and volume contraction measurements. The unsaturated copolyester obtained in reaction between turpentine oil, maleic anhydride and glycerol was used as reactive diluent for the synthesized bioactive complex. The composite films of vinyl ester oligomer/unsaturated polyester/hydroxyapatite, which were characterized by SEM microscopy, showed the presence of a uniform distribution of the hydroxyapatite particles in the polymer matrix (vinyl ester resin). The water uptake is dependent on the concentration in vinyl ester resin. The increase of the vinyl ester resin content in the bioactive composite leads to the increase of the density, as well as to a significant reduction of the volume contraction.

Experimental part

Synthesis of vinyl ester oligomer

The vinyl ester oligomer was synthesized starting from 364 g (1 mol) epoxy resin Ropoxid 501 (Polycolor S.A., Bucharest) and 144 g (2 mol) acrylic acid. The reaction mixture of the two components was heated on the oil bath at 60 °C, and stirred under inert protective layer (nitrogen), using a glass bulb with 1000 ml capacity. After half an hour stirring 4 g catalyst (tetrabutylammonium chloride) was introduced into the reaction vessel together with 0.8 g thermal polymerization inhibitor (hydroquinone). The temperature in the reaction vessel was raised to 110 °C, the reaction mass being kept at this temperature 4 hours, under stirring. After cooling, 483 g (0.95 mol) reaction product was obtained, yield 95 % and an esterification degree of 99%.

Synthesis of unsaturated copolyester

Synthesis of the unsaturated copolyester was previously reported [12], starting from turpentine oil, maleic anhydride and glycerol (1:2:1 molar ratio), in the presence of phosphoric acid.

Preparation of vinyl ester resin/unsaturated copolyester composites

The synthesized unsaturated copolyester, as solution in acetone, was mixed with variable quantities of vinyl ester resin (Table 3) and with photoinitiator [bis(2,4,6-trimethyl-benzoyl)-phenylphosphin oxide]. The photoinitiator was added as a mass proportion of 25% reported to the mass of that two used monomers. After that a homogeneous solution was obtained, acetone was removed by evaporation. The obtained product was solved in dimethylformamide and a solution with 40% concentration resulted; the solution was then used to make films.

Tab. 3. Polymeric compositions synthesized on the basis of vinyl ester resin and unsaturated copolyester.

Sample	Vinyl ester oligomer (%)	Unsaturated copolyester (%)
1	0	100
2	20	80
3	40	60
4	60	40
5	100	0

Synthesis of hydroxyapatite

Hydroxyapatite, as particles with micrometric dimensions, was synthesized with a yield of 95% using wet precipitation method [18]. A water suspension of calcium hydroperoxide and phosphoric acid were the starting materials, which react according to the following chemical reaction:

A suspension containing 10.6 g (0.1492 mol) $\text{Ca}(\text{OH})_2$ powder was heated in a water bath under vigorous stirring, temperature 50-55 °C and time 1 h. 135 ml (0.6 mol) H_3PO_4 solution was then added dropwise and the reaction mixture was stirred for other 3 h. After the end of the reaction, a maturation stage was performed maintaining the content of the reaction vessel to the room temperature for 72 h. After maturation, the precipitated hydroxyapatite was separated by filtration under vacuum, and dried in an oven at 110 °C for 3 h.

Preparation of polymeric matrix/hydroxyapatite composites

The vinyl ester resin/unsaturated copolyester/reactive diluent (polymeric matrix)/hydroxyapatite composites were obtained following some successive stages, as follows: (1) vigorous mixing of the vinyl ester resin/unsaturated copolymer complex with hydroxyapatite, in presence of the initiator, (2) overnight maintenance of the mixture in an oven to remove the included air, (3) films deposition on the glass plates, (4) films exposure to a UV lamp and (5) characterization of the obtained composite material.

Measurements

The FT-IR (Fourier transform-infrared spectroscopy) spectra were recorded with a FT-IR Spectrometer **Bruker** Vertex 70 type at a resolution of 4 cm^{-1} and 128 scans. The peak surfaces were used to evaluate the IR intensity, which were expressed in absorbance. The ^1H -NMR (Nuclear Magnetic Resonance) spectra were obtained using a JEOL-JNMC 60-HL apparatus, the spectra being recorded at 55 °C from CDCl_3 + TMS. The UV irradiation were performed with a medium pressure mercury lamp, type HQE-40, having a polychrome emission spectrum, and a power of 30 W/m^2 . The samples, as films, were mounted on a rotational device, which was positioned at a distance of 5.5 cm from the lamp. The mounted films were withdrawn from the device at different times and analyzed by FT-IR spectroscopy. The SEM (Scanning Electron Microscopy) measurements were carried out with a TESLA BS

301 type apparatus, at a tension $U=80\text{kV}$. The samples were covered with carbon/palladium, using the replica method. The thermal characterization by DSC (differential scanning calorimetry) was carried out in purified nitrogen, using a calorimeter 12E METTLER type, at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ and temperatures between 20 and $400\text{ }^{\circ}\text{C}$. The apparatus sensibility was $50\mu\text{V}$. The T_g measurement was performed taking into consideration the whole domain of compositions. The T_g values were considered as the modulation points from alignment of the base line in the glass transition region.

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