



In-situ photocrosslinkable nanohybrid elastomer based on polybutadiene/polyhedral oligomeric silsesquioxane



Seyed Amin Mirmohammadi ^{a,*}, Mehdi Nekoomanesh-Haghighi ^{a,*}, Somayyeh Mohammadian Gezaz ^b, Naeimeh Bahri-Laleh ^a, Mohammad Atai ^c

^a Department of Polymerization Engineering, Iran Polymer and Petrochemical Institute (IPPI), P. O. Box: 14965/115, Tehran, Iran

^b Department of Chemical Engineering, Payame Noor University (PNU), P. O. Box: 19395-3697, Tehran, Iran

^c Department of Polymer Science, Iran Polymer and Petrochemical Institute (IPPI), P. O. Box: 14965/115, Tehran, Iran

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ABSTRACT

Hydroxyl functionalized nano-sized POSS or ethyleneglycol as diol monomers was incorporated to hydroxyl-terminated polybutadiene (HTPBD) chain in the presence of fumaryl chloride as extender. Blue light photocrosslinking system based on camphorquinone (photoinitiator) and dimethylaminoethyl methacrylate (accelerator) was applied to cure these two synthesized fumarate based macromers. Self-crosslinkability of unsaturated macromers and also crosslinking in presence of a reactive diluent were investigated in absence and presence of 1,4-butanediol dimethacrylate, respectively. Finally, photocured samples were characterized by XRD, SEM, equilibrium swelling study, TGA, DMTA, AFM and cell culture. The results showed that incorporation of POSS nanoparticle into the polymer matrix with a perfect distribution and dispersion can enhance thermal stability, mechanical and biocompatibility properties which can prove a good potential of this in-situ photocrosslinkable nanohybrid in medical applications.

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1. Introduction

One of the interesting research areas in the field of block copolymers is synthesis of polymeric nanocomposite while one of the comonomers is a reactive nanoparticle [1,2]. Particularly, the use of polyhedral oligomeric silsesquioxanes (POSS) nanoparticle has been considered as an attractive and effective way in preparation of nanohybrids at the molecular level. The T₈-POSS cubic type nanoparticles have an empirical formula (RSiO_{1.5})_n composed of Si—O chemical bonds with an inorganic Si₈O₁₂ structured cage-like skeleton and the diameter of 1–3 nm in size. These nanocages have been surrounded by several R groups, bonded to the Si atoms, which can be either unreactive organic groups on the corners (to enhance solubility or miscibility in conventional solvents or organic matrixes) or reactive groups (for polymerization purposes) [3–6].

Those surrounded by the reactive R groups can be classified into mono- and multi-functional comonomers in polymerization reactions. Chemical incorporation of POSS into the polymer backbone with an ideal dispersion has dramatic enhancements on nanocomposite properties including increases in glass transition temperature (T_g), thermal

stability, oxidation resistance, mechanical properties, surface hardness, biocompatibility, wear resistance, as well as reductions in flammability and viscosity [4,7,8].

POSS has been prosperously incorporated into numerous common polymers, such as polyethylene, polypropylene, polybutadiene, polystyrene, polycaprolactone, polynorbornene, polyacrylate, epoxide resin, nylon, etc., to obtain different kinds of polymer/POSS nanohybrids with improved properties [4,9]. Elastomeric based nanocomposites like polybutadiene (PB)/POSS should be crosslinked to transform from soft plastic-like materials into elastic ones by forming a three dimensional structure nanohybrids and achieve ultimate enhancements. To crosslink saturated elastomers (such as ethylene propylene rubber) or unsaturated ones (such as PB) numerous approaches have been developed thus far including sulfur systems, peroxides, urethane crosslinkers and so on [10–13]. But, in some special technologies (such as coating) or applications (such as in-vivo implantation) different processes like photoinitiating systems are needed for in-situ crosslinking of resins [3, 14–18].

Among them, the best system which acquires almost all of indispensable criteria such as obtainable homogenous network throughout the sample, lower shrinkage and temperature rising during the crosslinking reaction, commercially available and has no toxic, inflammatory, allergic, carcinogenic or mutagenic reactions is a system based

* Corresponding authors.

E-mail addresses: mirmohammadi.sa@gmail.com (S.A. Mirmohammadi), m.nekoomanesh@ippi.ac.ir (M. Nekoomanesh-Haghighi).

on camphorquinone (CQ) as a photoinitiator and various amines as accelerators [19–22].

In this work, we have fabricated a new injectable and in-situ photocrosslinkable elastomeric nanohybrid based on PB, POSS and fumaric acid. This highly viscous fumarate based nanohybrid resin is biocompatible, customizable and features a robust and easy toward implementation of blue light (λ : 450–500 nm) curing process. By virtue of the mentioned principles, this in-situ crosslinked resin has a great potential to be examined and used in the extensive applications such as medical electronics, sealing and tubing industries, and also medical device coating technologies (for example introducer sheaths, several cardiovascular and urology catheters, guidewires and short-term implanted devices) to provide the ultimate protection and durability specially for metallic devices. According to our best survey, fabrication of 3-dimensional in-situ photocrosslinked fumarate based PB/POSS nanocomposite by CQ-amine and blue light system has not been reported till now.

2. Experimental

2.1. Materials

trans-Cyclohexanediol isobutyl POSS (POSS diol) was purchased from Hybrid Plastics Co. (Hattiesburg, Mississippi, USA) and used as received. Anhydrous hydroxyl terminated polybutadiene (HTPB) (M_n : 4900 gmol^{-1} and *PDI*: 2.83) were obtained from Iran Polymer and Petrochemical Institute (IPPI) (Tehran, Iran). Ethylene glycol (EG), 2-dimethylaminoethyl methacrylate (DMAEMA), 1,4-butanediol dimethacrylate (BDM), calcium hydride, potassium carbonate (K_2CO_3), dichloromethane (DCM), methanol, acetone, *n*-dodecane, cyclohexane, carbon tetrachloride (CCl_4), toluene and tetrahydrofuran (THF) were purchased from Merck Chemicals Co., Germany. EG were dried over calcium hydride for 48 h and distilled under reduced pressure. Anhydrous K_2CO_3 was grinded into a fine powder before application and kept desiccated before any further application. Anhydrous DCM was obtained by distillation after reflux for 1 h in the presence of calcium hydride. Fumaryl chloride (FuCl) was purchased from Sigma Aldrich Co., USA, and purified by distillation at 161 °C under ambient pressure. All other reagents were used as received without further purification.

2.2. Methods

2.2.1. Polyesterifications

The synthesis procedure of polyesters i.e. linear polybutadiene fumarate based on EG, HTPB and FuCl (EG-PBF) and its nanohybrid counterpart composed of POSS diol, HTPB and FuCl (POSS-PBF) is adopted from our recent works [3,23]. POSS diol nanoparticles and EG as diol comonomers were separately used for polyesterification reaction of HTPB. In a typical batch, EG or POSS diol (0.52 mmol) and HTPB (0.58 mmol) were dissolved in 50 mL of anhydrous DCM and charged into a three-necked glass reactor equipped with magnetic stirrer. The mixture was kept stirred for 1 h in an oil bath. Potassium carbonate powder was added to the reaction mixture in 5:1 M ratio respective to the diol-comonomers. The FuCl (0.99:1 M ratio respective to the diols) was separately dissolved in 50 mL anhydrous DCM and added dropwise (in about 30 min) to stirred diol-comonomers/DCM/ K_2CO_3 suspensions while the reaction mixtures were maintained at boiling temperature of DCM (39 °C). Both of the reactions (containing POSS diol or EG) were performed under reflux condensation and nitrogen atmosphere.

After adding all FuCl-DCM solution the reaction mixture was allowed to stir for an additional 12 h. Upon completion of the reaction, the organic phase was washed with water and centrifuged at 6000 rpm for 45 min (hamic CF 15RX, Tokyo, Japan) to remove all particulate matters also aqueous soluble residues like K_2CO_3 . For better purification, the residue was dissolved in small amounts of DCM, and then

dropped into an excess volume of acetone/methanol (90% v/v) mixture (as a non-solvent) to precipitate the macromers. The purification stages were repeated several times to obtain a pure, transparent mass of polymer. The resulting macromers were vacuum-dried at 35 °C for 24 h and stored at –20 °C for further use.

2.2.2. Synthesis of photocrosslinked networks

The macromers were crosslinked by visible light irradiation at blue region (λ : 450–500 nm) in the presence of CQ and DMAEMA as a photoinitiator-accelerator system. Therefore, an appropriate amount of viscous macromer was mixed with BDM (10% w/w) on a glassy petri-dish by a spatula. DMAEMA (2% w/w to macromer) and a corresponding amount of CQ (1:1 w/w to DMAEMA) was added to the mixture. The specimens were then cured for 200 s using a blue LED source with an irradiation circa of 550 $\text{mW}\cdot\text{cm}^{-2}$ (Optilux 501, Kerr. Co., California, USA) at room temperature. To investigate self-crosslinking property of the macromers, the same procedure was also applied without adding BDM to the mixtures. In this case, the initiator and accelerator were only dissolved in the viscous macromers.

2.2.3. Characterizations

2.2.3.1. Gel permeation chromatography (GPC). The number-average molecular weight (M_n) and polydispersity index (*PDI*) of the copolymers were determined using an Agilent 1100 GPC on an Aquagel column (Agilent Technologies, Santa Clara, CA, USA) of 7.5 mm \times 300 mm (ID \times L) with the flow rate of 1 mLmin^{-1} at 23 °C equipped with a refractive index detector according to ASTM D 6579–06. Low polydispersity polystyrene standard samples were used for calibration.

2.2.3.2. X-ray diffraction (XRD) and scanning electron microscopy (SEM). The prepared films were identified by a D5000 X-ray diffractometer instrument (Siemens, Frankfurt, Germany) over the scan speed of 1.2 ° min^{-1} and the range of 5 to 65°. The sample dimensions were 20 \times 5 and thickness of 2 mm.

The structure and morphologies of the samples were studied using a VEGA SEM instrument (TESCAN, Brno, Czech republic) with an accelerating voltage of 20 kV after sputter-coated with gold.

2.2.3.3. Equilibrium swelling studies. Crosslink density of the networks was determined using equilibrium swelling data according to the Flory-Rehner equation [21,24]. The equilibrium degree of swelling (Q), which is the reciprocal of volume fraction of polymer in swollen state (V_p), was calculated based on the swelling data of the samples in various solvents using the following equations:

$$V_p = \frac{W_p/d_p}{W_p/d_p + W_s/d_s}, \quad Q = \frac{1}{V_p} \quad (1, 2)$$

where, W_p , W_s , d_p and d_s stand for dry weight of polymer, weight of solvent taken up at equilibrium swelling, polymer density and solvent density, respectively. In order to determine the values for solubility parameter (δ) of the photocrosslinked samples, Q was plotted against δ for different solvents. From the plot it was found that cyclohexane has maximum values of Q for the photocrosslinked samples. Average molecular weights between crosslinks (M_c) were also determined in cyclohexane as solvent at 25 °C according to the Flory-Rehner equation:

$$M_c = - \frac{\vartheta_s d_p \left(V_p^{\frac{1}{3}} - \frac{V_p}{2} \right)}{\ln(1 - V_p) + V_p + \chi_{12} V_p^2} \quad (3)$$

where, v_s and χ_{12} are molar volume of solvent and polymer-solvent interaction parameter, respectively. The χ_{12} parameter was calculated

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