



Photopolymerization of keratin-based thiol-ene coatings



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ABSTRACT

Keratin extracted from wool by sulphitolysis, up to a content of 15 wt/wt% was used as a natural reinforcing agent for cross-linked polymers obtained by photopolymerization of thiol-ene systems.

The keratin-based photocured coatings obtained show significant improvement in terms of thermal stability, crosslinking density, T_g values and mechanical properties.

Moreover, a clear increase of the biodegradability of the starting thiol-ene polymer matrix was induced by the presence of the keratin biopolymer as reinforcement.

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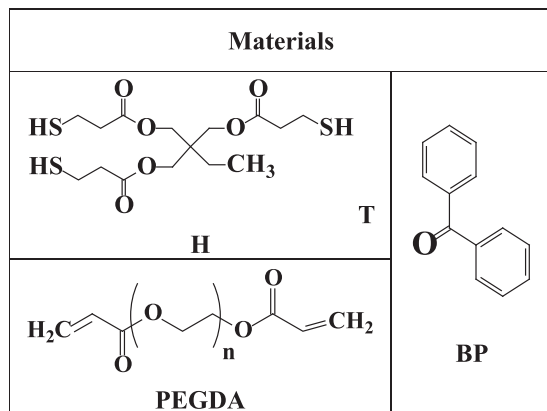
1. Introduction

In the last years, there is a growing interest on bio-based polymers from renewable sources due to the urgency to develop novel eco-friendly materials able to replace or substitute the oil-based materials [1,2]. Products from renewable resources can be considered green and sustainable if they have recycling capability, biodegradability, commercial viability and environmental acceptability [1]. Sustainability is a complex problem and several parameters must be considered, including the raw materials from which the biopolymer is generated, the energy consumed and the life cycle assessment analysis from production to ultimate disposal or recycle. Bio-based polymers containing natural reinforcements can represent a new generation of value-added environmentally friendly coatings. Natural fibers, as actual and potential reinforcement for bio-composites, offer many advantages, such as low cost, high availability, biodegradability, good strength and good thermal properties [3,4]. Keratin is an abundant natural polymer, present in hair, nails, wool, claws, horns and feathers among other natural sources. It's a polymer with a fascinating structure displaying properties suitable for meeting the remarkable demand for biocompatible products. Keratin is a durable and insoluble protein, chemically inert, thus suited to stand severe environmental conditions [4–6]. A distinctive feature of keratin is its relatively high sulphur content due to the presence of sulphur containing amino acids namely cystine and methionine; inter and intra molecular disulphide bonds are present and give rise to a compact

three-dimensional fibrous structure that confers to keratin a high stability and high resistance to chemical and enzymatic attacks [4]. Disulphide bonds make keratin more attractive for the preparation of novel polymer coatings based on thiol-ene chemistry by using the UV curing technique. Photopolymerization plays an important role in the field of coatings and can be considered an environmentally friendly technique due to the solvent free process usually carried out at room temperature [7]. It assures high curing rates in a very short time and low energy consumption. A wide variety of polymers can be photo-chemically polymerized, on many kinds of substrates and for any coating applications [7,8]. In the frame of UV-induced polymers, thiol-ene systems are particularly interesting because they have the desirable features of a “click” reaction, being highly efficient, simple to execute with no side products. Polymerization proceeds rapidly to high yield and allows the preparation of new photocured materials with peculiar final properties. In fact thiol-ene systems assure a fast formation of a uniform cross-linked polymer network with high polymerization rates, low shrinkage, reduced oxygen inhibition and good adhesion, also without photoinitiator [9–12]. Our research group has proposed in previous works different approaches for obtaining hybrid photo-cured thiol-ene coatings, including the in situ synthesis of silica nanoparticles within the thiol-ene matrix by sol-gel process [13], the in situ generation of silver particles by photo-reduction [14] and the simple addition of different silicates into the polymeric matrix, without any kind of previous modification or functionalization [15]. The final coatings showed enhanced properties, such as thermal stability, chemical resistance, mechanical and surface properties, as a result of synergistic reactions between the components: they are overall attributed to the uniform distribution of the inorganic particles into the photocured cross-linked matrices and

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Table 1
Chemical structure of the materials employed for the preparation of keratin-based coatings.



to the interactions between the filler and the polymer [13–15]. Following this research line, in this work we describe the preparation and characterization of new thiol-ene coatings reinforced by keratin extracted from wool fibers. We show that also using organic reinforcing agents, enhancement of the final properties is obtained, especially in terms of thermal stability and thermo-mechanical properties. Added value comes from the biodegradability improvement of the material upon addition of the natural protein instead of inorganic fillers.

2. Experimental

2.1. Materials

Trimethylolpropane tris(mercaptopropionate) kindly given by Bruno Bock (Marschacht, Germany) (TH) and polyethylene glycol diacrylate (PEGDA, $M_n = 700$) from Aldrich, were used as photoreactive monomers. Benzophenone (BP), purchased from Aldrich, was chosen as a radical UV photoinitiator. The chemical structures of the thiol-ene monomers and of the photoinitiator employed are reported in Table 1.

Trypsin from porcine pancreas, catalog no. T7409 and phosphate buffered saline solution (PBS), used for biodegradability tests, were purchased from Sigma–Aldrich.

2.2. Preparation of keratin

Keratin was obtained from wool by means of sulphitolysis followed by purification and regeneration by dialysis and freeze-drying, as previously reported [16,17].

The disulphide bonds of cystine are broken by sulphite ions in cysteine and cysteine-S-sulphonate residues; urea was used as a protein denaturing agent able to break the hydrogen bonds.

2.3. Preparation of the photocured composites

TH and PEGDA were mixed in equimolar ratio; BP was added at 1 wt/wt%. Different amounts of keratin up to a content of 15 wt/wt% were dispersed within the thiol-ene formulation by mechanical stirring. All the liquid formulations were coated onto a glass substrate by means of a wire-wound applicator and photocured for 2 min in nitrogen atmosphere by using a medium pressure mercury lamp (Helios Italquartz, Italy), with a radiation intensity of 28 mW/cm² over the sample. The light intensity was measured by means of an EIT radiometer. Photocured films 100 μm thick were obtained.

2.4. Characterization techniques

The kinetics of the photopolymerization reaction was determined by real time spectroscopy, using a Thermo-Nicolet 5700 FT-IR spectrometer.

The liquid formulations were exposed simultaneously to the UV beam, which induces the polymerization, and to the IR beam which analyzes in situ the extent of the reaction. A medium pressure mercury lamp (Hamamatsu) equipped with an optical guide was used to start the photopolymerization, with a light intensity on the surface of the sample of about 30 mW/cm². Conversion was calculated monitoring the decrease of the area of the absorption band of the reactive functionality (thiol SH band at 2570 cm⁻¹ and acrylate C=C band at 1640 cm⁻¹) with time. The area was normalized by a constant signal in the spectra (carbonyl C=O peak at 1730 cm⁻¹). Percent conversion is given by the following equation:

$$\text{Conversion\%} = \left(1 - \frac{\text{peak ratio at time}}{\text{peak ratio at } t = 0} \right) \times 100 \quad (1)$$

ATR-FT-IR spectra were collected by means of the same spectrophotometer Thermo-Nicolet 5700 equipped with a single reflection, monolithic diamond, ATR Accessory (Golden Gate).

Gel content of the film was determined by measuring the weight loss after 24 h extraction with chloroform at room temperature, according to the standard test ASTM D2765-84.

Differential Scanning Calorimetry analyses (DSC) were performed with a Mettler-Toledo DSC1 STARe System in the range between –80° and 350°C with a heating rate of 10°C/min in nitrogen atmosphere.

Thermal gravimetric analysis (TGA) was performed with a Mettler TGA/SDTA 851 instrument at a heating rate of 10°C/min in air, in the temperature range 25–800°C.

Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in the tensile configuration. Specimens of 4 mm × 2 mm and 100 μm thicknesses were analyzed. Storage (E') and loss (E'') moduli, as well as $\tan \delta$ (E''/E') were measured as a function of temperature between –60°C and 60°C.

The morphology of the coatings was investigated by scanning electron microscopy (SEM) after metallization of the samples. The SEM instrument (PEI PHILIPS–Quanta inspect 200 LV) was operated at 15 kV in an ultrahigh vacuum (10⁻⁷ bar).

For the in vitro biodegradability tests, the thiol-ene coatings were incubated at 37°C in a solution (6 mL) containing 0.5 mg/mL of trypsin in PBS. The trypsin solutions were changed and collected every day. At the designated time points, samples were washed with distilled water, dried in an oven at 50°C overnight and weighted in order to estimate the weight reduction.

3. Results and discussion

The aim of this work is the preparation of novel coatings by photopolymerizing thiol-ene systems in the presence of keratin as natural reinforcing agent.

Keratin was extracted from waste wool fibers by sulphitolysis, in the presence of urea as denaturing agent. During this process cystine disulphide bonds are cleaved by sulfite to give cysteine thiols (reduced keratin) and cysteine-S-sulphonate residues (known as Bunte salts).

As reported in literature [17,18], the keratin extraction method, which uses the sulphitolysis reaction, does not degrade the protein. In fact, the extracted protein is made of keratins of the intermediate filaments (KIF), having molecular weights of 60 and 45 kDa (also known as low sulphur content keratins) and keratin associated proteins (KAPs) of the inter-macrofibrillar matrix, having molecular weights in the 28–11 kDa range (also known as high sulphur

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