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Stress reduction mechanisms during photopolymerization of functionally graded polymer nanocomposite coatings

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ABSTRACT

From the experimental analysis of the photocuring process in terms of reaction kinetics as well as modulus and shrinkage build-up, the residual stresses arising during the photopolymerization of functionally graded composite coatings based on an acrylate matrix and Fe_3O_4@SiO_2 core@shell nanoparticles are evaluated through a Finite Element Modeling approach. Owing to the monotonous variation of volume fraction of the constituent phases that influences the local conversion of the polymeric matrix, these coatings are able to decrease the residual stresses at the coating/substrate interface by as much as ≈25% compared to those encountered in composites with homogeneous compositions, and by as much as ≈40% compared to those arising in the pure polymer. The influence of substrate stiffness, nanoparticle stiffness and conversion degree of the polymer matrix was also analyzed, providing further information for the optimization of the stress reduction mechanism in graded nanocomposite coatings.

1. Introduction

In the last years, the study of many bio-composites has elucidated how their mechanical performance tightly relates to the hierarchical organization of their constitutive elements. These elements operate at different levels and in a synergistic fashion, forming complex and non-uniform macroscopic architectures that perform extremely well under the loading conditions to which they are mostly subjected [1–4]. Beyond doubt, bio-composites take full advantage not only of the intrinsic properties of the single components, but also of their spatial distribution in the global structure. The application of this concept to the design of artificial materials would most probably solve many of the problems currently arising both at the manufacturing stage and during lifetime.

It has already been largely shown how properly designed metal-ceramic functionally graded coatings, which provide an artificial approach to the smooth interfacial transitions of bio-composites, can eliminate the stress discontinuity encountered in classical laminated materials by providing a monotonous variation of volume fraction of constituent phases [5–7]. On the contrary, less attention has been paid to functionally graded polymer-based materials [8], even though they could find applications in many technologies currently using thin layers of dissimilar materials in order to achieve functional requirements [9]. The most important areas include electronic packaging [10] as well as coatings for either oxidation [11], corrosion [12] or abrasion protection [13]. Indeed, in all the above-mentioned applications the dissimilar nature of the constituents poses issues in terms of the mechanical integrity and reliability of the whole structure. Failure phenomena of the protective coating include surface cracking, delamination, buckling and spalling [14–16]. All these damage mechanisms arise from the different material properties and from the residual stresses developed during processing within the coating, as well as at the coating/substrate interface. In a previous article, we proposed and studied a novel synthetic strategy for functionally graded polymer nanocomposites based on the motion of magnetic core–shell nanoparticles (Fe_3O_4@SiO_2) in a photocurable resin under the application of an external magnetic field gradient, prior to curing [17]. These graded nanocomposites showed to be able to reduce the interfacial stresses resulting from thermal loads [8]. In this work, the residual stresses arising during the photopolymerization process of these graded nanocomposites are evaluated for different gradient morphologies as well as for their homogeneous counterparts. Attention was paid to the influence of the local

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concentration of the magnetic particles on the decreased photoconversion state of the polymer owing to the light absorption of the particles, and resulting decreased stiffness of the composite. This is made possible by the experimental analysis of the curing kinetics and of the mechanical properties build-up during the photocuring process, and by adapting a Finite Element coupling model [18], usually employed for thermoset resins, to the chemistry and the mechanics of our photocurable material. As a result, it is shown how properly designed functionally graded polymer nanocomposites can reduce by up to ≈40% the interfacial stresses between the polymeric structure and the substrate, therefore minimizing delamination-related problems already at the manufacturing stage.

2. Experimental

2.1. Materials

Iron (III) acetyacetonate (Fe(acac)3, 99+%) and benzyl ether (99%) were purchased from Acros. Oleylamine (Tech.70%), polyoxyethylene(5)nonylphenyl ether (Igepal CO-520), ethanol (≥99.5%) and the epoxy embedding medium kit were purchased from Aldrich. Cyclohexane (p.A.) was purchased from Applichem. Ammonia solution (25% min) and tetraethyl orthosilicate (TEOS, ≥99%) were purchased from VWR and Merck, respectively. The hyperbranched polyester acrylated oligomer (HBP, commercial name CN2302) was purchased from Sartomer, whereas the photoinitiator (Lucirin TPO) was purchased from BASF.

2.2. Synthesis of Fe_3O_4@SiO_2 nanoparticles

The synthetic procedure for Fe_3O_4@SiO_2 nanoparticles has been reported in previous publications [17,19]. Briefly, Fe_3O_4 NPs were synthesized dissolving $Fe(acac)_3$ in a mixture of benzyl ether and oleylamine. The solution was heated to 260 °C and aged at this temperature for 1 h. After that, ethanol was added to precipitate the nanocrystals, which were then separated by centrifugation and dispersed in cyclohexane. In a typical synthesis of Fe_3O_4@SiO_2 NPs, the dispersion of oleylamine-coated Fe_3O_4 NPs in cyclohexane was added to cyclohexane and mixed with Igepal CO-520. The pH was adjusted to 10 through the addition of ammonium hydroxide and the formation of a transparent brown microemulsion was ensured with the aid of a sonicator. Then, TEOS was added and the reaction was stirred at room temperature for 48 h.

2.3. Preparation of nanocomposites

Photoinitiator was dissolved in the HBP in the desired proportion at 65 °C and stirred for 15 min. Nanocomposites containing core–shell nanoparticles were prepared mixing a certain amount of dried Fe_3O_4@SiO_2 NPs in the HBP and promoting their dispersion with the addition of a small amount of hexane. The mixture was then stirred for one hour at room temperature and sonicated for another hour. The solvent was hence evaporated under vacuum until no more weight variation of the suspension was detected. The effective nanoparticles content of the different formulations was calculated starting from the weight residual as from thermal analyses and converting it to particle volume % through the densities of the constituents [19]. The studied nanocomposites contained either 4 or 12 vol.% of nanoparticles.

2.4. Methods

The heat of the photopolymerization reactions was measured by means of differential scanning calorimetry (DSC Q100, TA Instruments), modified with a photo-DSC set up. A UV lamp with a 200 W mercury bulb (OmniCure, 2000, Exfo, Canada) was connected to the DSC cell by means of an optical fiber. The cell was sealed with a quartz window that let the UV light pass onto the open aluminum sample pans. The sample space was flushed with nitrogen and the reaction was considered completed when it was no longer possible to detect a change in heat flux. The heat of polymerization was recorded as a function of time and the double bond conversion x was calculated according to Hoyle [20] from the total heat of reaction calculated by integrating the exotherm:

$$x = \frac{H_{HBP}}{H_{100\%}} = \frac{H_{total}/m_{HBP}}{[AG] \cdot \Delta H_{AG}} \quad (1)$$

where H_{HBP} is the heat of reaction per gram of HBP, H_{total} the measured heat of reaction per gram of sample, $H_{100\%}$ the theoretical heat for 100% double bond conversion of the HBP, m_{HBP} the weight fraction of HBP, $[AG]$ the concentration of acrylate groups in the HBP, and ΔH_{AG} is the energy of the acrylate double bond equal to 86.31 kJ mol^{-1} [21].

Dynamic mechanical analysis (DMA Q800, TA Instruments) of HBP at different final conversions was performed at 0.1 Hz, at a constant strain of 0.5% and at room temperature. Samples ~3 mm wide and ~0.2 mm thick were obtained by photopolymerization under nitrogen with the same OmniCure 2000 UV lamp used for the photoDSC experiments. A constant final thickness was ensured by carrying out the polymerization between two quartz plates maintained at a relative distance of ~0.2 mm by polymer spacers.

Polymerization shrinkage during photopolymerization was monitored real-time using a Michelson interferometer, following the method proposed by de Boer [22]. A detailed description of the measurement method and of the set-up employed is reported elsewhere [23]. A 100 μm thick layer of sample was spread on a laboratory glass using a doctor blade. The reaction chamber was flushed with nitrogen and the onset of illumination was synchronized with the data acquisition by sending an electrical signal to the acquisition system while switching on the UV lamp. A typical sampling frequency was 200 Hz. The linear shrinkage S_L was calculated according to the following equations:

$$S_L = \frac{N_{MM}\Delta h_c}{h_{c,fi} + N_{MM}\Delta h_c} \quad (2)$$

$$\Delta h_c = \frac{\lambda}{4n_c(t)} = \frac{635\ \text{nm}}{4n_c} \quad (3)$$

where N_{MM} is the number of maxima and minima of the interference signal, Δh_c is the thickness change between a maximum and a minimum, $h_{c,fi}$ is the final thickness of the coating, λ is the wavelength of the laser, n_c is the refractive index of the coating, and t is the time. The refractive index was given by the supplier (n_c = 1.473) and the final thickness of the sample was measured with a digital caliper (Pro-Max, Fowler). Light intensities were always checked with a Solatell SolaCheck® UV spectrometer.

Curing degrees of the samples prepared for DMA, interferometer and DSC tests were compared between each other by means of Fourier Transform Infrared Analysis, which were acquired using a Perkin Elmer Spectrum One MIR (600–4000 cm^{-1}) with an ATR accessory. The spectra were acquired with 32 scans and a resolution of 4 cm^{-1}.

3. Experimental characterization

3.1. Mechanical properties and chemical shrinkage

In order to be able to correlate the chemistry and the mechanics of the photopolymerization process with the development of the residual stresses, the reaction kinetics and the evolution of the modulus and of the shrinkage during the whole reaction was taken into account. While the kinetics were studied by means of