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Critical examination of chemically modified hybrid thermosets: Synthesis, characterization and mechanical behavior in the plateau regime of polyaminosiloxane-nitrile-DGEBA

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Poly(3-aminopropylmethylsiloxane) has been modified with acrylonitrile via aza Michael addition and a broad range of modified oligomers have been prepared with CN:NH_2 ratio ranging between 0.1 and 1. NMR and FTnIR analysis reveals that acrylonitrile modification proceeds without formation of tertiary amines. Modified oligomers have been characterized by DSC and analysis of Tg reveals that the adducts are self-associated probably due to weak hydrogen bonding and dipole interactions. The modified oligomers with a modification degree higher than 0.4 were miscible with DGEBA. The low and high temperature relaxations of the cured thermosets have been measured by DMTA. In addition to the commonly observed β_2 relaxation, a new β_1 process linked by an isosbestic point to β_2 has been found. β_1 is attributed to an extended segment comprising the pendant propionitrile group as well as the aminopropyl segment that connects tertiary amines to the polysiloxane backbone. Elastic modulus as well as the α relaxation can be tuned from high Tg and high rubbery modulus to low Tg and high damping thermosets changing the nitrile content. The experimental network structure obtained from elastic measurements and the Tg were related through well established structure-property relations.

1. Introduction

The structure and properties of epoxy/siloxane reactive blends is currently an open question in the field of advanced thermosetting materials. Both components are immiscible and phase segregation limits the morphology and phase composition, size and distribution. Several efforts to improve the compatibility by introducing reactive groups in the silicon-based component have been compiled in a recent review [1]. Common approaches include the functionalization of the inorganic siloxane backbone with reactive functional end-groups [2] (epoxy, amine, acrylate or isocyanate), the synthesis of siloxane block copolymers with a resin compatible segment [3] or the introduction of pendant reactive groups [4]. This last solution was adopted by our group in earlier reports on the synthesis of poly(3-aminopropylmethyl siloxane) (PAMS) and its curing with DGEBA based epoxy resins [5,6].

Crosslinking agents for epoxy resins based on polyfunctional aminosiloxanes render very interesting polymer–polymer hybrid systems in which structure changes dramatically with both chemical conversion [5,6] and polymerization protocol [7]. They belong to the class of hybrid thermosetting blends and present a number of distinctive features. Contrary to conventional thermosets, a phase separated system consisting of PAMS spherical domains surrounded by the continuous epoxy matrix is formed upon mixing both reactants. In spite of their thermodynamic incompatibility, both components begin to react and, depending on the specific epoxy precursor and curing protocol, homogeneous (at the micron scale) or partially homogeneous thermosetting polymers are formed [7,8]. Another distinctive characteristic is related with their modification. They can be modified by physical mixing with conventional toughening agents, such as butadiene homo- and copolymers yielding a fine morphology [8]; but if a small amount of PMMA is used, a polymer with an extremely high affinity for the epoxy precursor, an *aphron*-like morphology is obtained in which the reactant mixture self organizes into polyhedral aphrons excluding the PMMA towards the interphase [9].

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However, the most interesting feature is probably concerned with their high functionality which, at the same time, increases the Young's modulus in the rubbery state, increases hydrophobicity [10] and switches gelation towards lower conversion fixing the final morphology well before limiting conversion. This high functionality can be tuned reacting some of the pendant amino groups with molecules that may impart specific properties while the remaining provide enough crosslinking density to give high performance thermosets. An earlier successful attempt was done reacting some amino groups with 2,3-Epoxypropyl phenyl ether [11] aiming to delay gel conversion and to increase miscibility with DGEBA. However, the Tg and viscosity of the modified oligomers notably increased due to the bulkiness of the pendant group limiting the suitability of this approach.

In this work, we present a new alternative for modification of PAMS using the well-known aza-Michael addition reaction of aliphatic primary amines to acrylonitrile [12], which, as we will show, proceeds extremely well in this particular case yielding modified PAMS oligomers with highly polar cyano groups. Firstly we will present the synthesis and characterization of these adducts demonstrating the absence of double additions, i.e. the modified oligomers contain a controlled ratio between primary and secondary amines. Next, the adducts will be used to prepare a broad range of organo-inorganic thermosets differing in the amount of nitrile groups, i.e., different crosslinking densities, finding that for CN:NH_2 ratios higher than 0.4, homogeneous systems at the micron scale are formed. The paper then focuses on the analysis and critical interpretation of the low and high temperature relaxations and in their elastic behavior. The high T relaxations will be explained using the concentration of elastically active network chains obtained from elastic measurements.

2. Experimental part

2.1. Materials

Diglycidyl ether of bisphenol-A (DGEBA, $M = 377$ g mol^{-1}, $n = 0.14$) and acrylonitrile (AN, 99% purity) were purchased from Sigma–Aldrich. 3-aminopropylmethyldiethoxysilane (APDES) was purchased from ABCR Gmbh (97% purity) and used without further purification.

2.2. Synthesis and characterization of poly(3-aminopropylmethylsiloxane) precursor

Poly(3-aminopropylmethylsiloxane) (PAMS) was synthesized form APDES by hydrolysis and condensation in aqueous solution according to methods already reported [5,6,13]. Molar mass and cyclics content were measured by MALDI-TOFF spectrometry (4700 Proteomics Analyzer, Applied Biosystems) with external calibration. Spectra were taken in reflector mode focusing on 1500 uma. Sample was dissolved in dicholoromethane (1 mg mL^{-1}). Matrix solution was prepared with 2,5-dihydroxybenzoic acid (10 mg mL^{-1}) in ethanol: dichloromethane (25:75). Sample and matrix solutions were mixed (1:10 ratio) and 0.5 μL aliquot was deposited onto the MALDI sample holder. Results show that PAMS consists of a mixture of linear and cyclic oligomers; cyclics amount 40.6% in number with number and weight average molar masses of $M_n(C) = 744$ g mol^{-1} and $M_w(C) = 926$ g mol^{-1}. The number and weight average molar masses of the linear fraction are $M_n(L) = 1250$ g mol^{-1} and $M_w(C) = 1508$ g mol^{-1}. The average molar masses of the sample are $M_n = 1036$ g mol^{-1} and $M_w = 1343$ g mol^{-1}. The number and weight average polymerization degrees are $x_n = 8.74$, $x_w = 11.35$. Consequently, the average monomer molecular weight is 118.52 g mol^{-1}.

2.3. Synthesis and characterization of PAMS-acrylonitrile adducts

PAMS-acrylonitrile adducts were synthesized via aza-Michael addition reaction (Scheme 1). Nine adducts were prepared with varying CN:NH_2 ratio from 10% to 100%. Samples were designed as Ax, where x is the nominal percentage of AN (Table S1 Supplementary material). In a typical experiment, adequate amounts of AN where added dropwise over 4 g of pure PAMS at room temperature (23 °C) in a 25 mL double necked round flask continuously purged with a small N_2 stream and with slight agitation. Temperature was measured all along the reaction (Fig. S1 Supplementary material); although reaction was completed in less than 20 min, agitation and N_2 stream were maintained for 2 h and then the reaction mixture was vacuum distilled to remove AN traces and stored at −4 °C in vacuum. Adducts characterization was done by FTIR (Perkin Elmer, GX2000) in both the medium (4000–400 cm^{-1}) and near ranges (7500–4000 cm^{-1}) (four scans, 4 cm^{-1}), and by ^{1}H NMR (AVANCE DPX-300). ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz), δ (*ppm*): C1 (0.47, m; 2H), C2 (1.44, m; 2H), C3 (2,61, m; 2H), C4 (2.44, t(br); 2H), C5 (2.83, t; 2H).

2.4. Curing of adducts with DGEBA

For DMTA measurements, the following method was used to prepare specimens. Stoichiometric amounts of DGEBA and adducts were thoroughly mixed, vacuum degassed and introduced in a steel mold which was previously treated with a releasing agent (Frekote®). The mold was designed to obtain 25 × 10 × 2 mm^3 specimens. Mold was heated up to 120 °C in an oven for 2 h followed by a postcuring treatment at 140 °C for 30 min. This curing protocol ensured full conversion as it was verified by the absence of residual heat in DSC and by the absence of residual epoxy and amine bands by FTIR. Samples were designated as ThAx.

Cured specimens were characterized by dynamic mechanical thermal analysis (DMTA, TA Instruments, Q 800, bending mode, 1, 10 and 30 Hz, 2 °C min^{-1}). The high temperature relaxation, T_α, was measured at the maximum in *tan δ* at 1 Hz. Moduli data in the elastomeric state were obtained at $T = T_\alpha + 50\ K$.

Density measurements of the cured specimens were carried out in an He pycnometer (Micrometritics, AccPyc 1330) at 35.1 °C with a typical standard deviation of 2 kg m^{-3}. For calculation of the concentration of elastically active chains from modulus values at Tg + 50K, density data were corrected at that temperature using typical data for the linear thermal expansion coefficient, α_L, below (50 10^{-6} K^{-1}) and above (170 10^{-6} K^{-1}) glass transition temperature for epoxy resins cured with amines [14], through the use of the following relation $\rho(T) = \rho(T_0)/[1 + 3\alpha_L \Delta T]$. This correction decreased density data in 3–4%, one order of magnitude higher than typical standard deviation of the measurement.

3. Results and discussion

3.1. Synthesis and characterization of the adducts

The aza-Michael reaction is a well-known method to conjugate amines to α,β unsaturated nitriles [15]. It usually requires basic conditions [16], such as the medium provided by the pure PAMS used here, and high conversions are usually achieved at moderate temperatures. The method used here does not use any solvent since PAMS is a low viscosity liquid in which AN readily dissolves, and we have found that the reaction is highly exothermic reaching almost completeness in a short period of time, typically less than 20 *min* (see Fig. S1 Supplementary material). The two main parameters of the synthesized adducts that are needed to characterize the starting monomers for the network formation with epoxy resin are the