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Critical role of tetrasilanolphenyl–POSS moieties in competing mechanism of rigid cages and soft segments and its effect on the glass transition temperature of epoxy hybrids

Rui Pan[a,*], Robert Shanks[b], Qiongfen Yang[a], Hong Luo[a]

[a] Chemistry and Material Science College, Sichuan Normal University, Key Laboratory of Special Waste Water Treatment, Chengdu City, Sichuan Province 610066, PR China

[b] School of Science, RMIT University, GPO Box 2476, Melbourne VIC 3001, Australia

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ABSTRACT

Molecular mechanics (MM) and molecular dynamics (MD) simulations were adopted to further investigate the competing mechanism of rigid cages and soft segments in epoxy hybrids with tetrasilanolphenyl polyhedral oligomeric silsesquioxane (TSP–POSS) copolymerized at various moieties. Calculated conformational energy and mean square displacement (MSD) delineated that rigid cage of TSP–POSS unit as an anchoring substituent, inhibited and rigidified polymer chains apparently. The degree of such reinforcement depended on TSP-POSS moieties plays a critical role in determining the final glass transition temperature (Tg) by competing with the effect of epoxy soft segments in bulk structures. At TSP–POSS loading less than 30%·w/w, rigid cages tended to approach mutually and the anchoring effect was strengthened. The restricted mobility and reinforced rigidity of chains led to an improvement of Tg. At TSP–POSS loading over 30%·w/w, increasing rigid cages were fixed by soft segments of epoxy unit and thus, the anchoring effect was weakened and mobility of chains was released to some extent. Additionally, with a steady plasticization mechanism, Tg was slightly decreased in 40%·w/w TSP–POSS embedded in epoxy, which was confirmed by experiments.

1. Introduction

Due to the excellent mechanical strength, perfect chemical resistance and simple processing process, epoxy resins as the important thermosetting resin are widely used as adhesives, coatings and electronic encapsulates [1,2]. Meanwhile, as a kind of good inorganic nanoparticle fillers, polyhedral oligomeric silsesquioxane (POSS) has been received huge attention since the introduction of POSS particles at various moieties into epoxy can lead to apparent improvements in properties including the glass transition temperature, thermal stability, anti-corrosion and flame retardation as well as ablation resistance in coating application [3–6]. Wenchao Zhang and his research group reported that a novel polyhedral oligomeric silsesquioxane containing 9,10-dihydro-9-oxa-10-phosphaphenanthrene–10–oxide was used to improve the flame retardation of diglycidyl ether of bisphenol A epoxy resins, which was apparently depending on the POSS content [7]. Yanli Ma et al. showed that thermo-mechanical property discrepancies with three polysiloxane-epoxy hybrids obtained by dispersing cage- or linear-structured polysiloxane into polyglycidyl methacrylate (PGMA) matrix. The introduction of polysiloxane into an epoxy matrix has achieved high thermal-stability as expected [8]. Jun Kai Herman Teo et al. reported that a novel epoxy-based hybrid composite was successfully synthesized by incorporating 1,2–dimethyl–3–(benzyl–heptaisobutyl–POSS) imidazolium chloride (POSS–IMC) and POSS-IMC-modified clay (POSS–MMT) into a resin based on 3,4–epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate (ECHM) and hexahy-drophthalic anhydride (HHPA) with reduction of thermal expansion coefficient (CTE) [9]. Shree Meenakshi et al. carried on the development of high functionality siloxane based on tetraglycidyl epoxy resin and characterized the structure of nanocomposites, which indicated that modified tetraglycidyl epoxy nanocomposites showed the superior flame retardancy to the unmodified epoxy resin [10]. Magdalena Perchacz et al. reported two types of pre-condensed silica-based precursors with epoxy groups in liquid, which has been verified as novel composites with the enhanced thermoxidative stability [11]. An investigation from Adriana Lungu et al. presented the synthesis of simultaneous interpenetrating polymer networks based on dimethacrylic-epoxy resins with or without polyhedral oligomeric silsesquioxane (POSS), and which was demonstrated the tailored thermal decomposition with various POSS concentration [12]. Ian Hamerton

* Corresponding author.
E-mail address: panrui@sicnu.edu.cn (R. Pan).

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et al. produced a series of nanocomposites of diglycidylether of bisphenol A with POSS, which was validated that the introduction of POSS into the epoxy-anhydride network could increase the glass transition temperature (Tg) and cross–link density in a rigid network apparently [13]. Raimondo et al. compared the effect of dodecaphenyl POSS (DPHPOSS), epoxycyclohexyl POSS (ECPOSS), glycidyl POSS (GPOSS) and triglycidylcyclohexyl POSS (TCPOSS) as different flame retardants embedded into epoxy resin in expection of thermal, fire resistance and electrical conductivity improvement for aeronautic application [14]. Libor Mate jka, et al. presented characteristics of epoxy–POSS hybrid microstructure with POSS bonding as pendicle cages or with POSS scattering in the matrix, which presented discrepancies of thermomechanical property [15]. Suzanne Laik et al. discussed the tendency of fire behaviour observed for different epoxy networks combined with POSS-OH and an aluminium-based additive, which brought significant improvement with a substantial and effective morphology [16]. John M. Misasi, Qifeng Jin and Katrina M. Knauer et al. synthesized a hyper-branched epoxy (HBE) with POSS, that provided the desirable toughness strengthening and sustainable processability [17]. Chung Hwei Su et al. reported polymerization of organic-inorganic TSP–POSS/epoxy at various concentration, and they showed improvement of thermal stability [18].

In addition to the synthesis of POSS-epoxy hybrid composites, increasing research on molecular simulation of POSS embedded into various polymers has emerged to illuminate the contribution of POSS to microstructure of hybrid composites. Evidences from various simulation techniques suggest that there are complex competing changes to ultimate properties of tailored POSS-epoxy composites resulting from sophisticated interactions in bulk structures, such as rigidity and mobility of chains, network packing, chain topology, and plasticization of bulk structures [19–28]. The predominance of interactions from various factors is dependent upon the competing mechanisms in bulk structures as well as different POSS structures. Since the mechanisms have not been clarified sufficiently for various POSS embedded into epoxy networks, it often leads to an elusive modification in synthesis and property estimation for novel POSS-epoxy composites, especially in thermal properties.

According to the research of organic-inorganic TSP-POSS/epoxy hybrids by Chung Hwei Su et al.[18], the thermal stability and oxidation resistance of epoxy resins increased as the content of tetrasilanolphenyl polyhedral oligomeric silsesquioxane (TSP-POSS) components increasing [18]. Nevertheless, no clear trend in glass transition temperatures was discernible in hybrids embedded with various concentration of TSP-POSS due to competing factors depending on characteristics of complex hybrids' structure. Our present modelling and simulations aim to elucidate the competing effect of TSP–POSS rigid cages and soft segments of epoxy unit on the analysis of packing features in hybrids, and provide a complement to the molecular mechanisms of structure and glass transition temperature relationship of organic-inorganic hybrids based on TSP-POSS.

2. Modelling and simulation procedure

The Accelrys Amorphous Cell module and COMPASS force field in Materials Studio software were adopted in our research process, which has been used successfully for the simulation of polymer nanocomposites containing POSS monomers [29–33]. The Van der Waals interactions were set by an atom based method at a cut-off distance of 9.0 Å with coulombic interactions taking into account using the Ewald method. Pressure was controlled by the "Berendesen method", and the temperature was in constraint of the Andersen thermostat NPT in molecular dynamics (MD) simulation process.

The construction of cross-linked networks in TSP-POSS-epoxy composites was performed in the following steps: A single chain consisting of 20 repeating units (shown in Fig. 1) of hybrid composite models with 10, 20, 30 and 40%·w/w moiety of TSP-POSS were constructed, respectively. Then periodic boundary conditions were imposed into construction of an amorphous bulk network by the Amorphous Cell Construction module with an initial density of 1.0 g/cm^3 applied. For each periodic condition, 20 cells with independent configuration were originally generated and the following energy minimization process was undertaken, which were subjected to the smart molecular mechanics (MM) and the molecular dynamics (MD) optimization cycle to relax each cell with 100 ps in NPT. After this equilibration procedure, as the density fluctuation of each system was confirmed less than 0.02 g/cm^3, and five cells with a minimum energy were maintained while the remaining of cells with higher energy were abandoned. Since these optimized cells configurations might be in a localized energy minimum state, an additional annealing procedure from 1200 K to 300 K was imposed on the above selected cells by the Velocity Verlet algorithm to decrease the potential energy. Each cell configuration was set to be saved in every 100 fs. Finally, cells with the highest energy configuration were eliminated and the remaining cells were maintained for further analysis of composites' characteristics [31,33–37].

3. Results and discussion

3.1. Models validation in simulation process

The application of Compass force field for our system was confirmed by reports, in which the structure and energy of epoxy composites were successfully constructed and simulated in processes [31,38–41]. Furthermore, model structures were generated through several cycles of the molecular mechanics (MM) and the molecular dynamics (MD) optimization for optimum equilibration. Table 1 lists the average values of all components of the internal stress tensor in each cell.

All values of the averaged internal stress tensors are close to zero indicating that the generated composite structures were fully relaxed and in an equilibrium state, which verifies the efficiency of our initial construction procedure and the geometry of each cell being suitable for the following analysis.

3.2. Conformational energy analysis of chains' rigidity

For TSP-POSS/epoxy systems we studied, TSP–POSS moiety in each cell was expected to impact upon the rigidity of epoxy chains. The rotational barrier energy height of dihedral angle containing Si–O pair in unit was investigated by using MM to evaluate the rigidity of chains. The dihedral angle containing Si-O pair along the backbone is designated as $\phi 1$ in Fig. 1, which was set from -180° to 180° with an interval of 5°, and the remainder of epoxy chains were allowed to fully relax. The torsional energy was averaged for all possible $\phi 1$ dihedral angles in each TSP–POSS unit. Plots of the finally averaged energy versus torsional angle are shown in Fig. 2. In the energy profile of 10EP, four energy maxima occurred at -148°, -78°, -74° and 95°, and three energy minima occurred at -125°, 50° and 80°. For 20EP, four energy maxima occurred at -178°, -150°, -70° and 22°, and the energy minima occurred at 52°. Energy barriers of torsion in 10EP and 20EP were found to be less than 100 kcal/mol. However, energy barriers in 30EP and 40EP were both over 800 kcal/mol.

A relative low energy barrier often imparts chain flexibility for easier torsion while a high energy barrier elucidates chain rigidity for more difficult torsion. The rigidity of chains of hybrids is in the order: 40EP > 30EP > 20EP > 10EP from energy plots. Thus, rigidity of chains in 30EP and 40EP was reinforced due to the relative higher energy barrier. This result demonstrates that the increasing TSP-POSS moieties can rigidify polymer chains, which is expected to increase Tg of hybrids as regular pattern.