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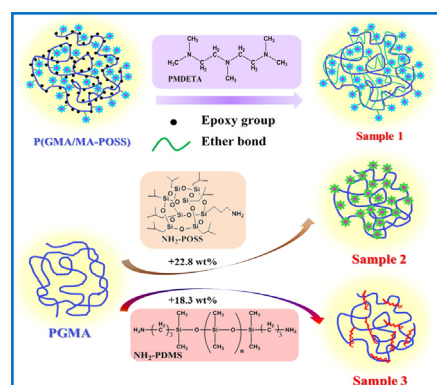
## Cage and linear structured polysiloxane/epoxy hybrids for coatings: Surface property and film permeability



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## GRAPHICAL ABSTRACT



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## ABSTRACT

Three polysiloxane/epoxy hybrids obtained by evolving cage- or linear-structured polysiloxane into poly glycidyl methacrylate (PGMA) matrix are compared used as coatings. One is the cage-structured hybrid of P(GMA/MA-POSS) copolymer obtained by GMA and methacrylisobutyl polyhedral oligomeric silsesquioxane (MA-POSS) via free radical polymerization, the other two are PGMA/NH<sub>2</sub>-POSS and PGMA/NH<sub>2</sub>-PDMS hybrids by cage-structured aminopropylsilybutyl POSS (NH<sub>2</sub>-POSS) or linear-structured diamino terminated poly(dimethylsiloxane) (NH<sub>2</sub>-PDMS) to cure PGMA. The effect of MA-POSS, NH<sub>2</sub>-POSS and NH<sub>2</sub>-PDMS on polysiloxane/epoxy hybrid films is characterized according to their surface morphology, transparency, permeability, adhesive strength and thermo-mechanical properties. Due to caged POSS tending to agglomerate onto the film surface, P(GMA/MA-POSS) and PGMA/NH<sub>2</sub>-POSS films exhibit much more heterogeneous surfaces than PGMA/NH<sub>2</sub>-PDMS film, but the well-compatibility between epoxy matrix and MA-POSS has provided P(GMA/MA-POSS) film with much higher transmittance (98%) than PGMA/NH<sub>2</sub>-POSS film (24%), PGMA/NH<sub>2</sub>-PDMS film (27%) and traditional epoxy resin film (5%). The introduction of polysiloxane into epoxy matrix is confirmed to create hybrids with strong adhesive strength (526–1113 N) and high thermostability ( $T_g = 262\text{--}282\text{ }^\circ\text{C}$ ), especially the cage-structured P(GMA/MA-POSS) hybrid (1113 N and 282 °C), but the flexible PDMS improves PGMA/NH<sub>2</sub>-PDMS hybrid with much higher storage modulus (519 MPa) than PGMA/NH<sub>2</sub>-POSS (271 MPa), which suggests that PDMS is advantage in improving the film stiffness than POSS cages. However, cage-structured P(GMA/MA-POSS) and PGMA/NH<sub>2</sub>-POSS indicate higher permeability than PGMA/NH<sub>2</sub>-PDMS and traditional epoxy resin. Comparatively, the cage-structured P(GMA/MA-POSS) hybrid is the best coating in transparency,

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permeability, adhesive strength and thermostability, but linear-structured PGMA/NH<sub>2</sub>-PDMS hybrid behaviors the best coating in mechanical property.

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## 1. Introduction

Epoxy resin has attracted great attention in strong adhesive strength, easy processing and super solvent resistance. However, epoxy resin is difficult to meet the requirement of high transparency and permeability when it is used as protective coatings. In this case, introducing polysiloxane into epoxy matrix to obtain polysiloxane/epoxy hybrids is an effective approach in tailoring surface properties of epoxy-based coatings [1]. Therefore, the polysiloxane of cage-structured polysiloxanes of polyhedral oligomeric silsesquioxanes (POSS) and linear-structured polysiloxane of polydimethylsiloxane (PDMS) are involved into epoxy matrix for organic-inorganic hybrids used as promising materials for surface coating [2–5].

The cage-structured POSS is normally considered to be a kind of monodisperse silica (1–2 nm) with cube inorganic core of (SiO<sub>1.5</sub>)<sub>n</sub> (n = 8, 10 or 12) and the organic shell attached organic groups to give potential synthesis by covalent bonding [6–11]. When the substituent of POSS is polymerizable or reactive group, it can be incorporated into a suitable polymer backbone by (co)polymerization or functionalization reactions (e.g., grafting, initiation, and termination), thus providing an opportunity to design and build materials that have a well-defined composition and dimension to show nanophase behavior (nanocomposites) [12]. The dramatic effect of POSS on the copolymer properties will lead to the increased properties in glass transition temperature, decomposition temperature, oxygen permeability, resistance to chemicals, mechanical strength, and the reduced properties in flammability and heat evolution, enhanced miscibility, and modified properties [13]. While, the linear-structured PDMS is composed of an inorganic backbone of  $-(Si-O-Si)_n-$  and organic substituents in the side chains to endow with the possibility of chemical synthesis [4]. PDMS can be easily introduced into composite films by mixing nanoparticles or other nanostructures [14,15], and can be patterned on its surface or inner structures [16,17]. Therefore, introducing POSS or PDMS into epoxy matrix could provide the targeted materials with high thermal stability, ultraviolet resistance and weatherability by inorganic (SiO<sub>1.5</sub>)<sub>n</sub> in POSS or  $-(Si-O-Si)_n-$  in PDMS [18,19], with strong adhesive strength by the formation of POSS- or PDMS-anchored structures in the cured epoxy network [20], and with transparency and permeability by cage structured NH<sub>2</sub>-POSS and favourable flexibility of NH<sub>2</sub>-PDMS. According to this consideration, we attempt to obtain polysiloxane/epoxy hybrids using cage-structured aminopropylsilyl POSS (NH<sub>2</sub>-POSS) and linear-structured diamino terminated PDMS (NH<sub>2</sub>-PDMS) as curing agents in epoxide ring-opening reaction of epoxy resin, and using methacrylisobutyl POSS (MA-POSS) bearing functional group of CH<sub>2</sub>=CH- as monomer to polymerize with epoxy for obtaining polysiloxane/epoxy hybrid copolymer.

In order to obtain polysiloxane/epoxy hybrids, glycidyl methacrylate (GMA) is particularly a candidate epoxy ingredient due to its bifunctional groups of an unsaturated group for polymerization with other monomers [21–25] and epoxy group for reacting easily with functional groups like amines, thiols, aldehydes and carboxylates to get acquired high performance in coating applications [26–29], such as PB-g-(MMA-co-St-co-GMA) [30], poly(MDO-co-GMA) [31], P(NiPAAm-co-GMA-co-DBA-co-AA) [22], and aminated PGMA vectors [23,32] or grafted P(GMA-co-EGDMA) [33]. Actually,

the covalently grafted mono- and multi-layered PGMA/poly(tert-butyl acrylate) [34] copolymers as cross-linking materials, or block copolymers of poly(BMA-*b*-GMA) synthesized using reverse atom transfer radical polymerization as coatings [35], are surely improved the thermostability of copolymers [36,37]. But, it is worth noting that, due to the cure nature of GMA, high GMA content will inevitably decrease the film-formation of the copolymers by lumping to unable gain transparency and permeable surface. So far, very few studies have reported the preparation of polysiloxane/epoxy hybrids [28]. It is still not clear that the real effect of different structured polysiloxane on the polysiloxane/epoxy hybrids in their surface properties and film permeability.

In the present work, in order to understand the effect of polysiloxane on the properties of polysiloxane/epoxy hybrids, two different cage-structured polysiloxanes and one linear-structured polysiloxane are evolved into PGMA matrix to obtain polysiloxane/epoxy hybrids for coatings. One is the P(GMA/MA-POSS) copolymer obtained by GMA and MA-POSS via free radical polymerization, the other two are cross-linked PGMA via NH<sub>2</sub>-POSS and NH<sub>2</sub>-PDMS to gain PGMA/NH<sub>2</sub>-POSS and PGMA/NH<sub>2</sub>-PDMS, respectively. The chemical structures of three polysiloxane/epoxy hybrids are characterized. The effect of MA-POSS, NH<sub>2</sub>-POSS and NH<sub>2</sub>-PDMS on surface wettability, transparency, permeability, adhesive strength and thermostability of hybrids films are characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), static contact angle (SCA), UV-Vis, differential scanning calorimetry (DSC), thermogravimetry (TGA), mercury porosimeter and mechanical strength (DMA). The results verify that the obtained polysiloxane/epoxy hybrids could provide great potential applications as transparent and permeable coatings.

## 2. Experimental

### 2.1. Materials

Methacrylisobutyl polyhedral oligomeric silsesquioxane (MA-POSS, 99.9%, C<sub>35</sub>H<sub>74</sub>O<sub>14</sub>Si<sub>8</sub>, Fw = 943.64, powder) and aminopropylsilyl polyhedral oligomeric silsesquioxane (NH<sub>2</sub>-POSS, C<sub>13</sub>H<sub>71</sub>NO<sub>12</sub>Si<sub>8</sub>, Fw = 874.58, powder) were purchased from Hybrid Plastics (USA). Diamino terminated poly(dimethylsiloxane) (NH<sub>2</sub>-PDMS) (amino value 3.0–3.2%, Mn = 900–1000 g/mol, viscosity = 20–30 mPa s) was provided by Gelest (USA). MA-POSS, NH<sub>2</sub>-POSS and NH<sub>2</sub>-PDMS were used as received. Glycidyl methacrylate (GMA, 97%, C<sub>7</sub>H<sub>10</sub>O<sub>3</sub>, Fw = 142.15) and azobisisobutyronitrile (AIBN, C<sub>8</sub>H<sub>12</sub>N<sub>4</sub>, Fw = 164.21) were provided by Aladdin. Commercial epoxy resin E-51 was with epoxy value of 0.48–0.54 eq/100 g, viscosity ≤2500 mPa s (40 °C). N,N,N',N'-pentamethyl-diethylenetriamine (PMDETA, 97%, supplied by Aldrich) and triethylamine (TEA, C<sub>6</sub>H<sub>15</sub>N, 97%, supplied by Aldrich) were used without further purification. Chloroform (CHCl<sub>3</sub>) and dibutylketone were stirred over CaH<sub>2</sub> for 12 h at room temperature and then distilled under reduced pressure prior to use.

### 2.2. Synthesis of P(GMA/MA-POSS)

The preparation of P(GMA/MA-POSS) was performed by free radical polymerization according to our previous paper [38], as

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