

Polymer–Ceramic Nanocomposites: Interfacial Bonding Agents

Organic–inorganic composites represent a special class of materials with properties intermediate between organic polymers and inorganic ceramics (see *Polymer–Nonsilica Ceramic Nanocomposites*; *Polymer–Silica Nanocomposites*). The primary goal of preparing such composites is to achieve combinations of properties from both components. One successful approach for preparing organic–inorganic composites has been the *in situ* polymerization of metal alkoxides within organic polymer matrices via sol–gel process. This process is based on hydrolysis of metal alkoxides to produce metal hydroxides followed by polycondensation of the hydroxyl groups to form a three-dimensional network.

Unfortunately, incompatibility of two phases most often tends to result in undesirable phase separation. Thus, the interactions between the organic phase and the inorganic phase is paramount in constraining phase separation. The possible interactions between the organic phase and the inorganic phase can be achieved through hydrogen bonding, employing organic polymers with hydroxy or alkoxy terminating chains which can participate in the hydrolysis reaction used to generate ceramic, or bonding the dissimilar phases with the use of a bonding agent (O'Reilly and Coltrain 1996).

1. Interfacial Bonding

Bonding of organic polymers to inorganic surfaces with the primary goal of preparing composites with high strength-to-weight ratio has long been known (Plueddemann 1991). In this approach, two dissimilar phases are held together by use of a coupling agent, also known as a bonding agent. This bonding agent, in general, can undergo hydrolysis with the sol–gel precursor forming the inorganic network, at the same time it can react with the organic polymer. Improved interfacial bonding between phases retards phase separation, giving materials with enhanced properties. Thus, the overall quality of the composites can be improved by the use of bonding agents, especially under high-humidity and high-temperature conditions. Silanes are most widely used as coupling agents (Plueddemann 1991). However, other coupling agents such as organotitanates, phosphorous-containing compounds, and chromium coordination complexes are also used.

2. Silane Coupling Agents

Silane coupling agents play an important role in the preparation of composites from organic polymers and inorganic fillers such as glass, minerals, and metals.

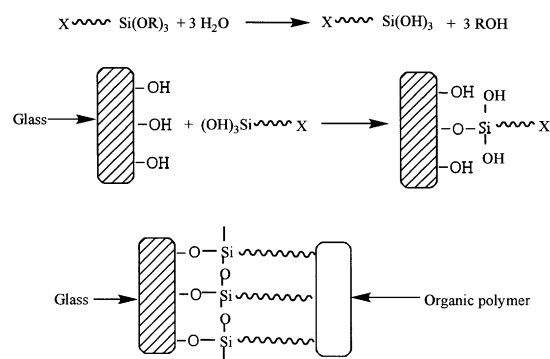


Figure 1

Improved interfacial bonding by a silane coupling agent.

The general structure of silane coupling agents are $(RO)_3\text{-Si-R'-X}$, where X is an organofunctional group, R' is a small alkylene linkage, and RO is a hydrolyzable group such as an alkoxy group (Pape 1996). The organofunctional group and the alkoxy group can form strong bonds with the polymer matrix and with the filler particles, respectively. The number of hydroxy groups resulting from the hydrolysis of alkoxy groups can be controlled by adjusting the rates of hydrolysis and condensation of the silane coupling agent to achieve optimal bonding effects (Premachandra *et al.* 1998). Figure 1 illustrates the mechanism of a silane coupling agent to improve the interfacial bonding between two phases.

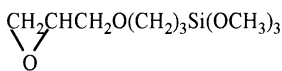
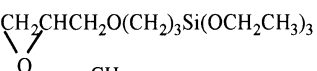
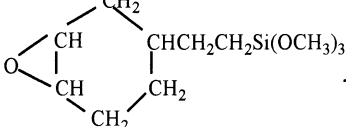
Organic groups such as vinyl, allyl, amino, methacryloxy, and epoxy groups, in general, react favorably with polymers (Stepek and Daoust 1983). Some commercially available silane coupling agents which can be utilized for different polymer systems are given in Table 1 (Stepek and Daoust 1983, Pape 1996).

3. Bonding in High-temperature Polymer–ceramic Composites

High-performance high-temperature polymers, in general, are difficult to treat in the usual sol–gel technique (see *Ceramic-modified High-temperature Polymers*). Because of their intractability, the processing is difficult, and their unreactivity often causes poor bonding between the organic polymer and the inorganic ceramic phase, resulting in undesirable phase separation. Therefore, improvements in bonding between the phases is critical in high-temperature polymers to achieve the desired properties.

Coupling agents used for high-temperature polymers should be of high thermal stability comparable with the polymer. Aromatic silanes, in general, have much better thermal stability and oxidative resistance than aliphatic silanes. However, the aromatic silanes lack the high degree of reactivity which is required to

Table 1 Some commercially available silane coupling agents for different polymer systems.

Coupling agent	Structure	Polymers
γ -Aminopropyltrimethoxysilane	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	PE, PP, PMMA, PC, PA, PUR, polysulfones, polysulfides, epoxies melamine resins, phenoplasts
<i>N</i> - β -(Aminoethyl)- γ -aminopropyltrimethoxysilane	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$	
γ -Glycidoxypentyltrimethoxysilane		PE, PP, PA, PC, PS, ABS, PVC, PUR, polysulfides, polyesters, epoxies phenoplasts, melamine resins
γ -Glycidoxypentyltriethoxysilane		
β -(3,4-Epoxy cyclohexyl)ethyltrimethoxysilane		
γ -Mercaptopropyltrimethoxysilane	$\text{HSCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$	PS, PVC, PPO, polysulfones, polysulfides, EPDM, SBR, NR, PUR, polymercaptans, epoxies
β -Mercaptoethyltriethoxysilane	$\text{HSCH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	
Vinyltriethoxysilane	$\text{CH}_2=\text{CHSi}(\text{OC}_2\text{H}_5)_3$	PE, PP, PVC, SBR, EPM, EPDM, epoxies
Vinyl-tris(β -methoxyethoxy)silane	$\text{CH}_2=\text{CHSi}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$	

function as coupling agents. High-temperature polymer composites have been prepared using some high-temperature polymers, including aromatic polyamides (Wang *et al.* 1993, Ahmad *et al.* 1997), polyimides (Morikawa *et al.* 1992, Wang *et al.* 1994), and some poly(benzoxazoles) (Premachandra *et al.* 1996), and poly(benzobisthiazoles) (Premachandra *et al.* 1996, Premachandra *et al.* 1999), with proper bonding between phases achieved by use of bonding agents.

3.1 Polyimide–ceramic Composites

Polyimide-silica hybrid materials prepared without using a bonding agent were transparent only up to a 8 wt.% of silica content (Morikawa *et al.* 1992). Scanning electron microscopy results demonstrated silica particles with diameters of approximately 5 μm in such films. However, increasing the chemical bonding between phases by using a bonding agent, specifically aminophenyltrimethoxysilane (APT MOS), increased dramatically the transparency of the materials was and the silica particle sizes were reduced (Wang *et al.* 1994). Thermal analysis showed no apparent decrease in thermal decomposition temp-

erature by using APT MOS. Polyimide–silica hybrid materials prepared without a bonding agent showed an increase in the modulus but a decrease in the tensile strength. However, the improved bonding between the two phases increased both the modulus and tensile strength. The hardness measurements of hybrid materials with bonding between phases also showed an increase relative to the pure polymer whereas the hardness in hybrid materials prepared without the bonding agent decreased, as was the case for the tensile strength.

3.2 Polyamide–ceramic Composites

Poly(phenylene terephthalamide) have been used to prepare composites, in some instances, with improved interfacial bonding achieved by bonding agents. The composites prepared with the bonding agent APT MOS showed enhancements in the tensile strength and modulus with increases in the amount of the inorganic phase, silica (Wang *et al.* 1993, Ahmad *et al.* 1997). Composites prepared without the bonding agent, however, showed decreases in the tensile strength on incorporation of filler (Ahmad *et al.* 1997). Using a nonlinear polyamide with a large number of chain ends able to react with the inorganic network

could increase the binding between two phases. The improvements in the tensile strength in this case were significant compared to the pure polyamide, which, however, showed a decrease in the tensile strength compared to the corresponding linear polyamide. The transparencies in both systems, linear and branched polyamides, in which the two phases were chemically bonded were improved compared to those composites prepared with no bonding agent.

3.3 Poly(benzoxazole)–ceramic Composites

Poly(benzoxazoles) (PBOs), in general, are intractable and insoluble in most organic solvents, causing difficulties when fabricating them into useful objects. By introducing specific functional groups and preparing functionalized copolymers, these polymers can be made somewhat more tractable. Hydroxy-functionalized copolymers of PBOs (HPBOs) which are soluble in tetrahydrofuran (THF) have been used to prepare composites using silica as the inorganic phase (Premachandra *et al.* 1996). HPBO–silica composites prepared without bonding could be redissolved in THF but the composites prepared with a bonding agent, specifically isocyanatopropyltriethoxysilane, were insoluble in THF. In addition, the transparencies of hybrid films were improved compared to those without the bonding agent. Substantial improvements in the tensile modulus and tensile strength for the composites could be achieved when a bonding agent is used.

3.4 Poly(benzothiazole)–ceramic Composites

Highly transparent hybrid materials prepared from sulfo-functionalized poly(benzothiazoles) (SPBTs) and silica have been reported (Premachandra *et al.* 1996). The insolubility of the resulting films in methanol suggests sufficient bonding between the polymer and silica phase. Substantial increases in mechanical and thermal properties were exhibited by the SPBT–silica composites compared to the pure polymer.

4. Summary

The improved interfacial bonding between phases can be achieved by using suitable bonding agents in the preparation of organic–inorganic composites. Thus,

the macroscopic phase separation which is often a problem in the preparation of such composites can be suppressed. Improved interfacial bonding exerts a profound effect on the morphology of the resulting hybrid materials: it tends to suppress the agglomeration of ceramic particles, resulting in reduced particle sizes, thus increasing the surface area which can interact with the polymer. This allows the ceramic particles to interact with the polymer backbone at a molecular level, resulting in substantial reinforcement of the hybrid material.

See also: Ceramic-modified High-temperature Polymers; Polymer–Nonsilica Ceramic Nanocomposites; Polymer–Silica Nanocomposites

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C. Kumudinie

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