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GLASSES, ORGANIC–;INORGANIC HYBRIDS

Organic glasses are amorphous structures with relatively low glass-transition temperatures, T_g, ie, $<400°C$. Their applications are limited to additives such as dyes, stains, and processing aids for foods, polymers, metals, etc. High molecular weight organic glasses, ie, polymers, are generally associated with plastics. Typically, organic polymer glasses possess low modulae owing to the low bond energy associated with carbon–carbon bonds. However, a wide variety of properties can be engineered into these materials by variations in processing, additives, and second-phase reinforcement. Inorganic glasses, on the other hand, which are high energy oxide structures that are useful at elevated temperatures ($>400°C$) have high modulae. Traditionally, a glass can be defined as an inorganic product of fusion which has cooled to a rigid condition without crystallizing. However, this definition has become somewhat obsolete. Low temperature synthetic routes, such as the sol–gel process, have been developed which allow the production of high purity, multicomponent inorganic glasses at temperatures significantly less than those required for traditional fusion, ie, much less than 1000°C.

The search for new high performance materials has spurred the development of composites combining high modulus/high thermal stability inorganic glasses and low modulus/low thermal stability polymeric glasses. Research has resulted in a novel class of amorphous polymer–glass composites referred to as organic–inorganic hybrids or inorganic–organic hybrids, depending on the component with the highest volume fraction. These materials are synthesized in a variety of ways but ultimately exhibit near-molecular-level mixing of the matrix and the filler. Hence the term hybrid. Typically, this high degree of mixing results in transparent materials which exhibit significant increases in thermomechanical properties owing to extensive interaction between the polymeric and inorganic phases. However, the relatively high volume fraction of polymer included in these materials normally limits their service temperatures to well below 400°C. One route to promoting mixed, interactive phases is the sol–gel processing of metal alkoxides, which allows the development of an inorganic, oxygen-bridging network during composite consolidation and promotes the formation of polymeric inorganic glasses with a morphology, and consequently a resultant polymer–glass interface, that is a function of the traditional sol–gel processing variables and other controllable factors. In essence, this approach results in materials that can be broadly defined as amorphous, interpenetrating network structures.

Numerous combinations of polymers–oligomers and oxide glasses have been mixed in the attempt to create hybrid composites. Similarly, variations such as end capping the polymer with functional groups prior to sol–gel processing and also the *in situ* precipitation of the inorganic glass into an existing polymer film have been tried. It has been demonstrated that variables other than the traditional sol–gel processing variables of the water-to-alkoxy ratio, acid-to-alkoxy ratio, reaction medium, and catalyst exist. For example, the molecular weight of the polymer, its ability to stabilize the developing inorganic network, and the miscibility of the solvent used to dissolve the polymer and the alkoxysilane monomer used are of paramount importance. These new factors control the solubility between the organic and inorganic materials developing networks and hence the degree of mixing between the components, which ultimately governs composite properties. This article addresses material systems, processing considerations, and the properties of these transparent (unless otherwise specified), hybrid organic–inorganic glasses.

1. Organic–Inorganic Glass Systems

Many polymers and oligomers have been utilized in the synthesis of these hybrids, including poly(alkenes, acrylates, ethers, esters, amides, imides, and dienes). Some novel inorganic precursors have been used, such as clay. The use of metal alkoxides including methoxides, ethoxides, isopropoxides, as well as phenyl and other organically substituted derivatives of silicon, titanium, zirconium, and aluminum, have been reported. The research concerning the sol–gel processing of silica and its gel-to-glass transition far outweighs that done on the other alkoxides. The systems presented more or less follow the chronological development of hybrid amorphous composites.

1.1. Polydimethyl Siloxane

The development of organic–inorganic networks began in the early to mid-1980s using polydimethylsiloxane (PDMS) oligomers. This polymer was chosen because of the close structural similarity between the siloxane chains and the expected sol–gel-derived silica. Hence, it is also an ideal organic–inorganic glass. Similar synthetic approaches were employed independently by two groups. One approach focused on improving the mechanical properties of PDMS by using the sol–gel processing of metal alkoxides to generate inorganic "fillers" (silica, titania, alumina, and zirconia) within the PDMS network during or after the development of a cross-linked PDMS network (1–9). In all cases, the hybrids generated by either the simultaneous curing and filling or the precipitation of the inorganic component within an existing swollen network (*in situ* precipitation) showed significantly better reinforcement than the network containing fumed silica, an alternate reinforcing agent. Electron microscopy of the hybrids synthesized using the *in situ* precipitated silica shows that the inorganic phase does not agglomerate into large particles within the original PDMS network (2, 4). Rather, most particles fall in the range of 20 to 30 nm and are very finely dispersed. Small-angle x-ray scattering (saxs) experiments of these reinforced networks demonstrated that under strongly basic conditions and large excesses of water, uniformly dense nonfractal particles resulted (6). Conversely, under acidic or neutral conditions, more polymeric structures resulted. The thermal stability of *in situ* filled PDMS networks was also studied using thermogravimetric analysis (tga), and it was demonstrated that this type of reinforcement enhances the thermoxidative stability of ordinary PDMS and fumed silica-reinforced PDMS (9). This reference also provides an excellent review of the different types of sol–gel-derived reinforcement studied (9).

In another approach, PDMS oligomers were used as the polymeric component and sol–gel-derived silica was used as the reinforcing phase. The materials that were developed were termed ceramers to denote the contributions of both the ceramic, inorganic glass and the polymeric, organic glass (10–12). As the name implies, the sol–gel glasses contained more inorganic than organic material. The intent was to engineer glasses with controllable flexibility and optical properties, rather than reinforcement of rubbery systems. This research examined the effect of silanol-terminated PDMS (as a function of wt %) upon the mechanical properties of these sol–gel-derived glasses. The principle means of characterization were mechanical tensile testing, dynamic mechanical spectrometry (dms), and small-angle x-ray scattering. Dms provided new insights, such as the degree of silica-siloxane interaction, into the structure–property behavior of these mixed-phase glasses. The effects of varying the acid (catalyst) concentration employed, the amount of water and tetraethoxysilane [78-10-4] (TEOS) added, and the molecular weight of the PDMS used were reported (10–12). These results indicate that the extent of hydrolysis and condensation the network undergoes is a function of the amount of water added. Therefore, in all likelihood there are residual ethoxy groups that may still be present even after the inorganic–organic network has gelled. Similarly, the simultaneous hydrolysis and condensation of all alkoxysilanes may result in preferential reactions between inorganic TEOS monomer and itself (and the silanol-terminated PDMS and itself), thereby affecting network morphology. Lastly, the degree of solubility between the oligomers, the metal alkoxides, and any solvents added greatly affects morphology and the degree of phase separation present upon final consolidation.

“Rubbery ORMOSILs” have been prepared using PDMS and TEOS (13, 14). An ORMOSIL is an organically modified silicate. Traditionally, such materials are comprised of organosilanes which, as the name implies, possess one or more organic pendent groups on the tetrafunctional silicon atom. When the materials react via the sol–gel process, these pendent groups remain in the structure and impart flexibility to the resulting hybrid. These materials have been thoroughly studied and a good review of this work is available (15).

Other PDMS–silica-based hybrids have been reported (16, 17) and related to the ceramer hybrids (10–12, 17). Using differential scanning calorimetry, dynamic mechanical analysis, and saxs, the microstructure of these PDMS hybrids was determined to be microphase-separated, in that the polysilicate domains (of ca 3 nm in diameter) behave as network cross-link junctions dispersed within the PDMS oligomer-rich phase. The distance between these domains increases from 5.1 to 15.4 nm as the molecular weight of the PDMS chains increases from 850 to 1950, respectively. Phase separation was due to thermodynamic incompatibility between the siloxane backbone, the siloxane end-caps, and the hard segments (urethane–urea linkages) used to cap the PDMS chains with multifunctional alkoxysilanes. Hence, a three-phase system exists. Additionally, hydrogenated polybutadiene (H-PBD) based hybrids were also synthesized and studied. However, these H-PBD based hybrids could be considered two-phase systems because of good miscibility between the polybutadiene backbone and urethane–urea linkages (17).

1.2. Poly(tetramethylene oxide)

It was hypothesized that the tendency of the PDMS and inorganic glass to phase-separate may be due to the immiscibility of the PDMS with the water added for hydrolysis and generated during condensation (18). Therefore, new polymer systems were sought which have better miscibility with water. Poly(tetramethylene oxide) (PTMO) was chosen for precisely this reason. However, the lack of the siloxane backbone to compatibilize the organic polymer and inorganic glass was a concern. Previously, silanol-terminated PDMS was all that was necessary to react with the *in situ* generated silica. To improve the compatibility of the PTMO with silica, the oligomers were end-capped with isocyanatopropyltriethoxysilane, thereby boosting the polymer functionality to 6. Similarly, it was assumed that the reactivities of the ethoxy groups on the TEOS and the PTMO end caps would be the same, thereby eliminating any preferential condensations, as discussed above in the case of PDMS systems. With these concerns addressed, work was begun on the new hybrids focusing on the variables of oligomer molecular weight and functionality, TEOS content, other inorganic constituents, gel age, acid concentration and type (organic vs inorganic), and processing temperatures and methods (18–33). By using characterization techniques such as saxs, dms, mechanical tensile testing, infrared (ir) spectroscopy and nuclear magnetic resonance (nmr), the structure–property relations of this class of hybrids were determined. In particular, saxs still revealed the presence of microphase-separation within the transparent hybrids. However, the mechanical and dynamic mechanical properties were greatly enhanced, confirming a high degree of mixing, and overall the PTMO-based systems were much better than those of the PDMS hybrids.

It was expected that the mixed region, the diffuse glass–polymer interface, would be responsible for many of the composites properties. Therefore, more recently, methods of modifying the microstructure of these hybrids *in situ* have been examined (34, 35). It was found that by using a strongly basic solution of ethylamine and water, the solubility of silica at high pH could be used to selectively modify the interface between the organic and inorganic phases. Essentially, syneresis and ripening of the polysilicate domains just like that experienced for traditional sol–gel-derived inorganic glasses aged at high pH could be induced, resulting in phase separation. This modification resulted in systematic changes in the strength of the hybrid. Additionally, this process has been used in the synthesis of organic–inorganic hybrid *interpenetrating networks (IPN)*. By controlling the degree of interaction (and hence PTMO restriction), the ethylamine procedure was used to control the equilibrium mass uptake of various vinylic monomers absorbed by the original hybrid network. Subsequent γ-radiation-induced polymerization of this absorbed monomer resulted in the formation of an IPN. Indeed, the properties of the new IPN were a function of the preirradiation, ethylamine exposure processing. These new materials were synthesized using methacrylic acid (MAA), *N*-vinylpyrrolidinone (NVP) and cyclohexyl methacrylate (CHMA) monomers. In particular, the PMAA and poly(*N*-vinylpyrrolidinone) (PVP) IPN exhibited hydrogel-like behavior. This approach opens new potential applications for these hybrid glasses.

1.3. Nitrile Rubber

Vulcanized rubber sheets of NBR and montmorillonite clay intercalated with Hycar ATBN, a butadiene acrylonitrile copolymer have been synthesized (36). These rubber hybrids show enhanced reinforcement (up to four times as large) relative to both carbon black-reinforced and pure NBR. Additionally, these hybrids are more easily processed than carbon black-filled rubbers.

1.4. Nylon-6

Nylon-6–clay nanometer composites using montmorillonite clay intercalated with 12-aminolauric acid have been produced (37, 38). When mixed with ϵ-caprolactam and polymerized at 100°C for 30 min, a nylon clay–hybrid (NCH) was produced. Transmission electron microscopy (tem) and x-ray diffraction of the NCH confirm both the intercalation and molecular level of mixing between the two phases. The benefits of such materials over ordinary nylon-6 or nonmolecularly mixed, clay-reinforced nylon-6 include increased heat distortion temperature, elastic modulus, tensile strength, and dynamic elastic modulus throughout the -150 to 250°C temperature range.

1.5. Poly(ethylene oxide)

The synthesis and subsequent hydrolysis and condensation of alkoxysilane-terminated macromonomers have been studied (39, 40). Using ^{29}Si-nmr and size-exclusion chromatography (sec) the evolution of the silicate structures on the alkoxysilane-terminated poly(ethylene oxide) (PEO) macromonomers of controlled functionality was observed. Also, the effect of vitrification upon the network cross-link density of the developing inorganic–organic hybrid using percolation and mean-field theory was considered.

The successful synthesis of a transparent *solid polymer electrolyte (SPE)* based on PEO and alkoxysilanes has been reported (41). The material possessed good mechanical properties and high electrical conductivity (around 1.8×10^{-5} S/cm at 25°C) dependent on the organic–inorganic ratio and PEO chain length.

1.6. Poly(ethyloxazoline)

A transparent, inorganic–organic glassy material composed of a 50:50 volume ratio of SiO_2 to poly(ethyloxazoline) has been synthesized (42). The two components are not covalently bonded, as is usually the intent of other researchers. The report cites no evidence of any second-phase behavior using saxs, differential scanning calorimetry (dsc), tem, and swelling in water and THF. This morphology is expected to give rise to composites with different properties than those hybrids utilizing covalent bonding.

1.7. Poly(2-methyl-2-oxazoline)

Polymers containing strong electron-donor groups can be incorporated and well-dispersed into an evolving inorganic glass (43, 44). These hybrids can function as precursors for porous silica glass of controllable pore size generated by hybrid pyrolysis.

1.8. Poly(vinyl acetate)

The dielectric and mechanical spectra of hybrids produced by mixing a poly(vinyl acetate)–THF solution with TEOS, followed by the addition of HCl have been investigated (45). Mixtures were made which were believed to be 0, 5, 10, 15, and 20 wt % SiO_2, respectively. These composites were transparent and Fourier transform infrared spectroscopy (ftir) revealed hydrogen bonding between the silicate network and carbonyl units of the poly(vinyl acetate) (PVAc). No shift in the T_g of the composites from that of the pure PVAc was observed. Similarly, the activation energies were calculated and shown to be independent of SiO_2 loading. However, the breadth of the tan δ-associated T_g relaxations did increase with increased filler. Dynamic mechanical and dielectric studies suggested a "microheterogeneous" environment within the hybrid.

Transparent, homogeneous hybrids using a 50:50 PVAc-to-TEOS mixture and an acid-catalyzed reaction have been produced and characterized by dsc and dms (46). Dsc indicated only a slight increase in the T_g of the hybrid with incorporation of silica. Dynamic mechanical tan δ responses indicate a strong interaction between the organic and inorganic phases and, hence, well-dispersed phases that lead to high modulus rubbery plateaus.

1.9. Poly(p-phenylene vinylene)

An organic–inorganic hybrid of poly(*p*-phenylene vinylene) (PPV) has been made utilizing a very ingenious approach (47). By mixing a sulfonium polyelectrolyte precursor for PPV and tetramethoxysilane (TMOS) together and subsequently polymerizing the organic precursor via thermolysis, a hybrid network was formed. The catalyst required for the polymerization of the TMOS was supplied as a by-product of the thermolysis. The polymer-doped glass exhibited improved optical quality over that of pure PPV. Similarly, initial studies showed that the hybrid has promise as a waveguide material, although the sol–gel processing of the TMOS may result in a shortening of the conjugation length in the PPV. This is important for future nonlinear optical applications.

1.10. Poly(N-vinylpyrrolidinone)

Transparent, well-dispersed organic–inorganic hybrids can be produced by the sol–gel processing of a metal alkoxide in the presence of an amide carbonyl group by utilizing hydrogen bonding between the silanol group of silica and the carbonyl (43, 44, 48). By using atomic-force microscopy and BET analysis, it was demonstrated that the hybrid possesses a very dense microstructure exhibiting little porosity, ie, the silica domains in this material have much less pore volume than pure sol–gel-derived silica. Hydrogen bonding was confirmed by ftir and cross-polarized, magic angle spinning ^{13}C-nmr. A good review of this work as well as of sol–gel-derived silica hybrids and their uses is available (44).

It has also been found that polymers possessing functional groups such as amines and pyridines are soluble in pregelled sol solutions, especially, poly(2-vinylpyridine) and poly(*N*-vinylpyrrolidinone) (PVP) (49). There, materials were made as part of a study of the synthesis of nonshrinking sol–gel-derived networks (49).

Transparent, homogeneous hybrids using a 50:50 PVP-to-TEOS mixture and an acid-catalyzed reaction have been reported, but only tga data were presented in the way of characterization (46).

1.11. Polymethacrylates

The synthesis of poly(allyl methacrylate) (PAMA) homopolymer- and methyl methacrylate copolymer-containing hybrids using group-transfer polymerization has been reported (50). The allyl methacrylate homopolymers were then functionalized by hydrosilylation of the allylic segments using Speier's catalyst. When mixed with tetrafunctional metal alkoxides in the presence of HCl or methanesulfonic acid and water, transparent, hybrid sol–gel glasses were produced over a wide range of TEOS: triethoxysilyl groups. However, when copolymers of the functionalized PAMA and poly(methyl methacrylate) (PMMA) were used, only the methanesulfonic acid produced transparent hybrid glasses. Similarly, lower fractions of the functionalized PAMA, ie, $\approx 10\%$, tended to produce grainy and opaque materials. The lack of a well-defined T_g for the polymethacrylate using dsc suggested good dispersion of the organic and inorganic phases. Titanium alkoxides were also employed, but met with less success.

1.11.1. Poly(methyl methacrylate)

Extensive work has been done at the Eastman Kodak Corporate Research Labs toward determining the chemical nature of the organic–inorganic interaction and the thermomechanical properties that result from the noncovalently bonded phases interacting within PMMA hybrid glasses (46, 51, 52). The ability to produce well-dispersed networks was attributed to hydrogen bonding between the silanol groups and the carbonyl units in the PMMA (46). Hence, the highly hydrated, "open" polysiloxane chains resulting from the acid-catalyzed sol–gel process were shown to form more homogeneous, transparent hybrids which exhibited enhanced mechanical properties beyond the T_g. Similarly, the mechanical properties were also affected by curing time and temperature (52). Transparency was also a function of the temperature of the substrate the films were cast on, eg, $\geq 30°C$ resulted in films exhibiting no macrophase separation. Base-catalyzed systems, films cast on cooler substrates and polymers incapable of forming hydrogen bonds produced cloudy, poorly dispersed glasses.

The properties of porous, sol–gel-derived glass impregnated with benzoyl peroxide (BPO)-initiated PMMA have been studied. The effect of silane coupling agents was also evaluated (53). It was found that the density, elastic modulus, modulus of rupture, and the compressive strength of the material decreased as the volume fraction of PMMA increased. Conversely, the refractive index increased as the volume fraction PMMA increased. Methacryloxypropyltrimethoxysilane was used as a coupling agent to improve the interaction between the silica glass and the PMMA. The result was an increase in the modulus of rupture as the amount of coupling agent employed increased.

PMMA-impregnated sol–gel-derived silica gels have also been examined (54). Long-wave uv illumination was employed in addition to benzoyl peroxide for PMMA polymerization. This method prohibited the degradation of the silica xerogel from moisture adsorption and desorption. Overall the material behaved more like bulk PMMA than bulk silica, with the exception of hardness.

1.11.2. Poly(n-butyl methacrylate)

Homogeneous, translucent organic–inorganic "alloys" combining poly(*n*-butyl methacrylate) ($M_n = 75,000$) with tetraethyl titanate (TET) and *tert*-butyl titanate (TBT), respectively, have been synthesized (55). The thermal stability of these networks was studied using tga and it was determined that the thermal onset of significant network degradation could be increased by the addition of the titania phase. It was revealed by dsc that crystallization of the amorphous TiO_2 to anatase, in the TET case, occurred at temperatures above the degradation temperature of the polymer. Mechanical reinforcement was also observed by the addition of the titania.

1.12. Poly(arylene ether) Ketone

Transparent hybrids of varying organic contents using triethoxysilane end-capped poly(arylene ether) ketone (PEK) and TEOS have been produced. (56). The T_g dependence on the curing temperature behaved as predicted by the time–temperature transformation behavior for network development (57). Of particular importance was the demonstrated ability of the oligomeric, high T_g PEK to covalently bond to and disperse within the inorganic network, thus producing an optically clear gel. However, as is the case with other hybrids, saxs experiments confirmed the presence of microphase separation. The correlation distance increased as the ratio of PEK:TEOS decreased in a manner similar to that reported for TEOS–PTMO systems.

1.13. Polyimide

Hybrid glassy materials have been made using polyamic acid and TEOS (58). The resulting films consist of noncovalently bonded polyimide–silica species. Transparent, organic–inorganic networks result when the wt % silica is less than or equal to 8 (assuming 100% conversion to an oxygen-bridging network). Beyond the 8% limit, only opaque films result. However, all of the 0 to 70 wt % SiO_2-containing films exhibit considerable flexibility.

The process known as transimidization has been employed to functionalize polyimide oligomers, which were subsequently used to produce polyimide–titania hybrids (59). This technique resulted in the successful synthesis of transparent hybrids composed of 18, 37, and 54% titania. The effect of metal alkoxide quantity, as well as the oligomer molecular weight and cure temperature, were evaluated using differential scanning calorimetry (dsc), thermogravimetric analysis (tga) and saxs.

Molecularly mixed composites of montmorillonite clay and polyimide which have a higher resistance to gas permeation and a lower coefficient of thermal expansion than ordinary polyimides have been produced (60). These polyimide hybrids were synthesized using montmorillonite intercalated with the ammonium salt of dodecylamine. When polymerized in the presence of dimethylacetamide and polyamic acid, the resulting dispersion was cast onto glass plates and cured. The cured films were as transparent as polyimide.

1.14. Hydrogenated Polybutadiene

The mechanical properties of alkoxysilane-terminated hydrogenated polybutadiene (H-PBD) macromonomers (and PDMS oligomers) of varying molecular weight cross-linked via the inorganic silicate phase induced by the sol–gel process have been studied (17). Using a point-source x-ray apparatus, saxs investigations were made to determine the morphology of these materials. The data, in conjunction with dynamic mechanical analysis and dsc measurements, allowed development of a qualitative morphological model for this new hybrid system, which the researchers compare to the hybrids synthesized using PDMS oligomers. In particular, the two-phase nature of this hybrid system was demonstrated. Related work is discussed in the section on poly(ethylene oxide) hybrids (40).

1.15. Sodium Poly(4-styrene sulfonate)

The sol–gel processing of TMOS in the presence of sodium poly-4-styrene sulfonate (NaPSS) has been used to synthesize inorganic–organic amorphous complexes (61). These sodium silicate materials were then isothermally crystallized. The processing pH, with respect to the isoelectric point of amorphous silica, was shown to influence the morphology of the initial gel structures. Using x-ray diffraction, the crystallization temperatures were monitored and were found to depend on these initial microstructures. This was explained in terms of the electrostatic interaction between the evolving silicate structures and the NaPSS prior to heat treatment at elevated temperatures.

2. Applications

There are several areas of application for organic–inorganic hybrids.

2.1. Microelectronic Usage

Organically Organically modified ceramics (ORMOCERS) have been developed based on the sol–gel processing of phenyl and vinyl-substituted organosilanes and silica (62). The systems can be cured either thermally or using photopolymerization of the vinyl groups. The properties of these coatings include excellent electrical properties, such as low ϵ and high surface and bulk resistance, even after weathering. Additionally, the materials are stable up to 260°C.

Several coating compositions based on organically substituted silicon and aluminum alkoxides, eg, vinyltrimethoxysilane, aluminum tri-*sec*-butylate, etc, have been developed. After mixing these solutions with photoinitiators, the resulting solutions are spin-coated onto various substrates and can undergo photocuring to produce patterned microelectronic devices (63). Polymerization can be induced using either a high wattage uv light or a frequency-doubled argon laser.

2.2. Abrasion-Resistant Coatings

Melamine, tris(*m*-aminophenyl)phosphine-oxide (TAPO), diethylenetriamine (DETA), polyethyleneimine (PEI), 4,4-diaminodiphenylsulfone (DDS) and bis(3-aminophenoxy-4-phenyl) phosphine oxide (BAPPO), epoxy resins and other oligomers have all been functionalized using a triethoxysilane coupling agent to produce molecules which can react via the sol–gel process (64–66). These functionalized species may or may not be mixed with additional metal alkoxides. Once the sol–gel process is initiated, but before significant gelation occurs, these sols can be spin-coated onto substrates where they are allowed to finish gelling. Additionally, curing at elevated temperatures may also be employed. The resulting coatings are glasses composed of organic moieties or oligomers covalently bonded via siloxane linkages. These coatings have been shown to significantly enhance the abrasion resistance of a Lexan substrate, and do so with increasing effectiveness as the curing temperature increases (64, 65). Similarly, when additional metal alkoxides such as titanium or zirconium are employed in conjunction with the functionalized moieties, significant increases in the refractive index of the coatings result (64).

The ability of organically modified ceramics based on alumina, zirconia, titania, or silica (and mixtures of each) to function as abrasion-resistant coatings has also been studied (62). For example, polycarbonate, when coated with an epoxy–aluminosilicate system, experiences a significant reduction in the degree of hazing induced by an abrader, as compared to uncoated polycarbonate.

2.3. Thermal–Oxidative-Resistance Coatings

The thermal stability of coatings produced by either covalently or noncovalently incorporating 2,4-dinitroaniline into an inorganic silicate network and coating it onto a sapphire substrate has been examined (67). Although some increase in the thermal stability of the chromophore was observed using uv-vis spectroscopy, the authors conclude that this sol–gel method of chromophore encapsulation does not provide any real thermal or oxidative protection in either the covalently or noncovalently bonded state.

2.4. Nonlinear Optical Devices

A transparent, optically active, sol–gel-derived organic–inorganic glass has been synthesized (68). This hybrid consists of a 2,4-dinitroaminophenylpropyl-triethoxysilane covalently bound to a silicon alkoxide-derived silica network. This hybrid exhibits a strong electric field-induced second harmonic signal and showed no signs of crystallization.

2.5. Hydrogels

A new approach has been taken to produce organic–inorganic hybrid interpenetrating networks using the sol–gel process, as described previously for PTMO, and γ-radiation (69, 70). By swelling existing organic–inorganic networks with either methacrylic acid or *N*-vinylpyrrolidinone and subsequent γ-polymerization of the monomers *in situ*, IPNs which exhibit some degree of hydrogel behavior, ie, the ability to absorb significant amounts of moisture or preferential swelling dependent upon pH, are produced, and they possess the optical transparency of the original gels. Additionally, very significant increases in the strength (up to a factor of 50) and elongation at break, as well as the elastic and dynamic storage modulus were induced.

2.6. Biosensors

Novel biosensors have been created by incorporating several types of biochemically active proteins into the pore structures of sol–gel silica to produce transparent, colored, organic–inorganic glasses (71). The porous structure of the silica matrix enables the transport of small molecules into and out of the sensor at reasonable rates. Additionally, these materials have proved remarkably stable in that the proteins remain within the pores. Using optical spectroscopy (and changes in the color of the glass) to monitor the changes in the protein structures, the ability to remove the copper ion from bovine copper–zinc superoxide dismutase *in situ* by exposing the hybrid to a solution of the chelating reagent EDTA has been shown. Similarly, once removed, the ion can be “reinstalled” and the original color and optical spectrum returned by exposing the material to a solution containing the original metal ion. Also, it was possible to reduce horse heart myoglobin (Mb) to deoxy Mb and subsequently react this with dioxygen or carbon monoxide to make either oxy Mb or carbonyl Mb, respectively. This work has shown that these encapsulated proteins are capable of reversible reactions within the glassy matrix. Similarly, such materials are ideally suited for biosensors.

2.7. Cross-Linking Agents

A review article addresses the use of polyfunctional organosilanes as cross-linking agents for a variety of polyolefins (72). Most techniques employ a grafting initiator, usually an organic peroxide, which is mixed with the polyolefin prior to extrusion. Upon heating, the initiator thermally decomposes to free radicals which abstract hydrogen from the polyolefin backbone, thereby encouraging grafting of the organosilane onto the backbone. Subsequent hydrolysis and condensation of the alkoxysilanes, with or without a catalyst, after polymer processing and shaping induces cross-linking in the preformed product. These methods have the advantage of not requiring treatment at elevated temperatures (eg, above the crystalline melting point) to induce the cross-linking in the final part, as is the case for peroxide-induced cross-linking. Hence, dimensional stability is maintained throughout the cross-linking operation. Traditionally, primarily peroxide and radiation are used to induce cross-linking. However, numerous patents exist regarding this novel organosilane cross-linking method.

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