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Polyimide−Ceramic Hybrid Composites by the Sol−Gel Route

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A number of polyimides have gained considerable importance as high-performance polymers during the last 2 decades primarily because of their excellent thermal stability and toughness. Some applications, however, require property enhancements and the desired improvements can often be obtained through incorporation of ceramic-like particles such as silica. Such hybrid inorganic−organic composites are frequently obtained using the in situ generation of the dispersed inorganic phase by the sol−gel technique. A number of studies have now been carried out on the preparation and characterization of such hybrid polyimide composites, and the purpose of this review is to give a brief account of the strategies used for this purpose and to describe some of the properties of the resulting composites.

Introduction

High-performance polymers of the polyimide (PI) type are already widely used in microelectronic industries because of their outstanding characteristics, such as excellent tensile strength and modulus, low thermal expansivity and dielectric constant ϵ, and good resistance to organic solvents.[1−4] Specific examples of their applications are their uses as dielectric layers, α-particle barriers, and insulating layers in multichip semiconductor packaging.[5,6] Some applications, however, such as circuit-printing films and semiconductor coatings, require control or even enhancement of certain properties. More specifically, characteristics such as coefficient of thermal expansion (CTE), mechanical strength, and thermal deflection temperature have to be strictly controlled and even improved. In the case of a pure PI, it is difficult or impossible to adjust its thermo-physical properties, such as thermal expansivity, to those of other constituent layers (which is critical for avoiding debonding upon changes in temperature). PIs are also limited with regard to additional improvements in performance because of limitations inherent in all organic materials, for example, thermal stability. This suggests incorporating inorganic materials such as ceramics to provide enhancements in properties (such as stability, resistance to hostile environments, and mechanical behavior).

One promising approach is to use the sol−gel process, which has been used (i) alone as a chemical route to ceramics of high purity and controlled microstructure, but also (ii) in conjunction with polymeric materials as a method for preparing organic−inorganic hybrid composites.[7−9] The process consists of two steps, the first being the hydrolysis of a metal alkoxide and the second the polycondensation of the hydrolysis products. The method allows one to combine the superior thermal stability, high refractive index, low thermal expansion coefficient, and wide range of permittivity of ceramics with the tremendous toughness, ductility, processability, and crack-deflection properties of polymers.[10−12] PI−ceramic composites made by the sol−gel technique are the subject of this review.

General Approach and Representative Systems

PIs are generally insoluble in organic solvents and are therefore fabricated into products such as films and coatings using a soluble PI precursor, typically polyamic acid (PAA).[13,14] A typical preparation involves mixing solutions of a dianhydride (e.g., pyromellitic anhydride (PMDA), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), or 2,2-bis(3,4-dicarboxy-phenyl)-hexafluoropropane dianhydride (6FDA)] with a diamine [e.g., 4,4′-oxydianiline (ODA)] in a convenient solvent [e.g., dimethylacetamide (DMAC) or *N*-methyl pyrollidone (NMP)]. A metal oxide precursor [e.g., tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS)] is then added and the hydrolysis and polycondensation are carried out, using an appropriate catalyst. The ingredients are then heated to around 300 °C, which eliminates water and generates the desired polyimide. This route is shown in Scheme 1.

Many factors influence the kinetics of hydrolysis and condensation reaction in the sol−gel process. Some important factors are temperature, pH, nature of the solvent, and the type of alkoxide precursors. Hydrolysis precedes the condensation reaction, but depending on the conditions may not go to completion prior to the onset of condensation. The relative rates of the competing hydrolysis and condensation reactions determine the final structure of the hybrid material. The acid-catalyzed reaction provides relatively fast hydrolysis and slow condensation reaction. The slow condensation

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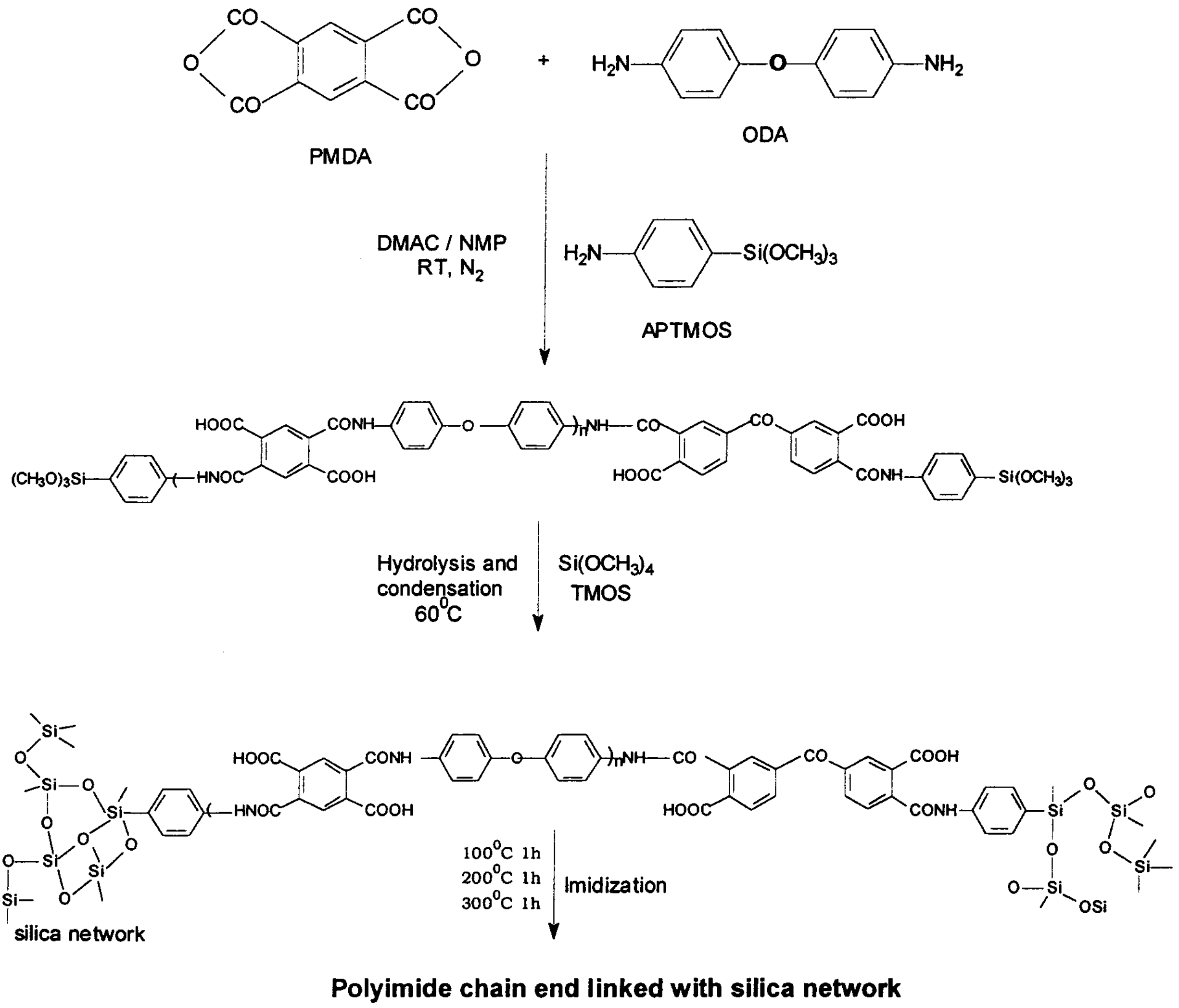
Scheme 1



reaction means slow network formation, thus providing a better environment for greater interpenetration of the phases. The sol−gel reaction in the preparation of PI−silica composites has generally been carried out in acidic media.

The conversion of polyamic acid to polyimide can be followed by FTIR analysis (decrease in carbolic acid absorption at 3400 cm^{-1} and amide carbonyl absorption at 1650 cm^{-1} and an increase in imide carbonyl absorption at 1720 and 1780 cm^{-1}). Moreover, the appearance of absorptions at 1100 and 830 cm^{-1} indicates the formation of silicon−oxygen bonds in the silica network. In addition, ^{29}Si NMR spectroscopy has been used to monitor in detail the condensation reaction leading to the network structure. One conclusion is the fact that mono-hydroxy and di-hydroxy species may still be present with non-hydroxy silicon even after the imidization process.

Figure 1 describes the structures of some of the PIs and silanes discussed in the present paper. The excellent thermal stabilities of the PIs are an advantage in the sol−gel process because the polymer can be heated to the fairly high temperature of 300 °C, which accelerates the polycondensation of the metal oxides used to generate the ceramic phase. The strong hydrogen-bonding interactions expected between the PAA−PI precursor and the hydroxyl groups from the inorganic phase help in suppressing undesirable phase separation. In fact, control of phase separation is critical to obtaining the morphologies that give the best combinations of properties. For example, constraining the phase separation to the point that the inorganic clusters are very small is essential for obtaining good transparency.

Some Attempts at Compatibilization

One way of decreasing the extent of phase separation (increasing the miscibility) is by (i) functionalizing the oligomers or polymer chains at their ends, (ii) selecting polymers with appropriate groups within the repeat units, (iii) including comonomers possessing appropriate functional groups, or (iv) adding a coupling agent that can bond with both the growing inorganic oxide network and the PI chains. Various methods used for effectively introducing inorganic phases into PI matrixes have been discussed by Mark and co-workers,[15,16] Wen and Wilkes,[17] Mascia,[18] Schmidt,[19,20] and Morikawa et al.,[21] among others. Given below is an account of some of the approaches taken.

In some of the earlier studies (before 1990), the incorporation of metal oxides was frequently not very successful, yielding inhomogeneous distributions of particles (markedly higher concentrations at or near the polymer surfaces.[22−32]) In many cases, agglomeration

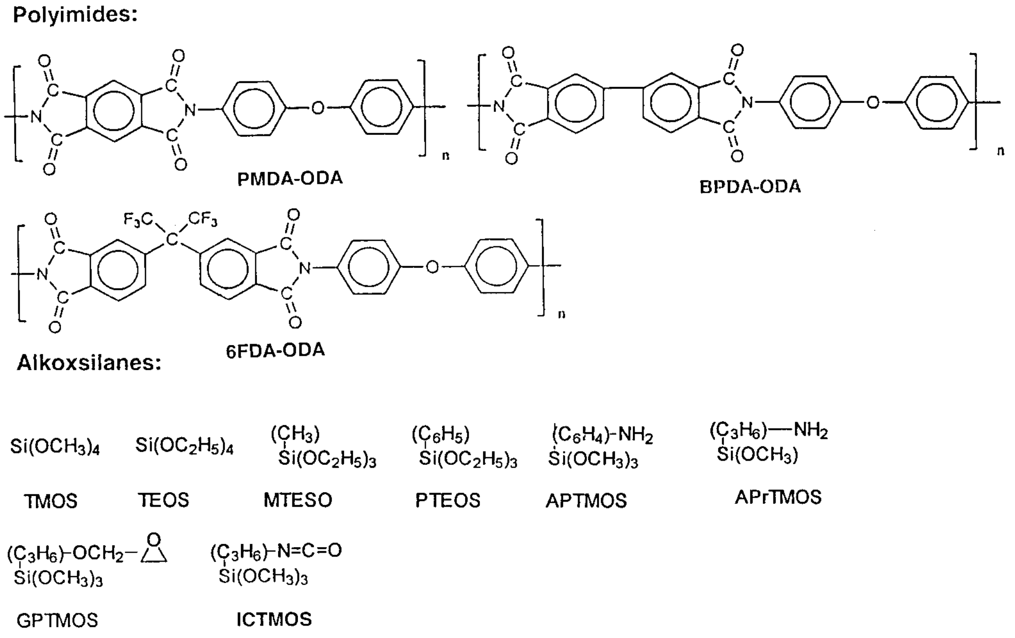


Figure 1. Structures of the polyimides and alkoxysilanes discussed in this review.

of the inorganic particles degraded the properties of the resulting materials. In 1990, however, McGrath and co-workers[33] reported the synthesis of functionalized PI oligomers capable of bonding themselves into sol−gel networks. More specifically, amine-terminated soluble polyimides were prepared by solution imidization techniques. The amine end groups of the PI were quantitatively derivatized to nadimide structures through reaction with *cis*-norborane-2,3 dicarboxylic anhydride. The nadimides were then converted to trimethoxysilane functionalites via hydrosilylation reactions, using chloroplatinic acid as the catalyst. The resulting hexamethoxy-functionalized polyimide oligomers were finally hydrolyzed and condensed with TMOS at elevated temperatures and modest pressures to generate the PI−silicate hybrid composites. Solid state ^{29}Si magic-angle spinning NMR was used to moniter network formation as a function of composition and reaction temperature. The diffusion-controlled reactions in the gel state were found to occur to higher conversions when processing temperatures exceeded the glass transition temperature T_g of the organic polymer. Because only PI oligomers were used in this case, the mechanical properties of the resulting hybrid material were not of particular interest.

The first successful attempt to produce compatibilized PI−silica hybrid composites using high molecular weight polymer was carried out by Sen and co-workers.[34,35] They suggested that the metal alkoxide could be chemically bonded to the precursor PAA through cohydrolysis of carboxylic groups and thus be maintained in isolated packets even at the final stage of the synthetic process (because of the relative rigidity of the polyimide matrix). The coordination of the polyimide carbonyl groups to the metal centers on the surfaces of the particles may also play a role in suppressing cluster mobility, thus preventing significant agglomeration of the metal centers. In the preparation of the hybrid materials, TEOS and titanium tetraethoxide were used with PMDA and ODA. The resulting polymeric mixtures were cast into films, which were then cured at 300 °C. These workers used a site isolation technique that constrained phase separation between the polymer and inorganic clusters to a relatively small scale. This gave hybrid materials which differed in several respects from those obtained in previous studies,[22−32] specifically smaller particle sizes, increased homogeneity, and good optical transparencies even with SiO_2 concentrations as high as 32 wt %. Microscopy results showed 1−1.5-nm metal oxide particles homogeneously dispersed in the polyimide matrix. The thermal decomposition temperature of the TiO_2−PI ceramic polymers ("ceramers") was reported to be 25 °C lower than that of the pure polyimide but for the corresponding PI−SiO_2 ceramers it was increased by 30 °C. The silica-containing polyimides showed an approximate 10 °C increase in T_g, while for TiO_2-based ceramers, T_g was found to decrease. Unfortunately, the mechanical properties and the other thermal characteristics of the hybrid materials were not reported.

Kakimoto and co-workers[36,37] prepared PI hybrid films by the hydrolysis and condensation of TEOS in a solution of PAA. Fairly flexible yellow films were obtained at silica contents up to 70%. Films with less than 8% silica were transparent, whereas films with higher silica contents were opaque. The densities of these films were around 1.65 g cm^{-3}, and silica particles having diameters around 5 μm were observed in the hybrid films by scanning electron microscopy (SEM). At low TEOS contents the T_g's of the hybrid film were found to be lower than that of the parent PI, suggesting that a substantial amount of un-cross-linked siloxane-like oligomeric chains may have remained dissolved in the PI matrix (because of incomplete hydrolysis of the TEOS). In fact, ^{29}Si NMR spectra showed that the silica in the films consisted of non-hydroxy, mono-hydroxy, and di-hydroxy siloxane structures. Their presence would have caused plasticization of the PI or might have even prevented the imidization reaction from going to completion. The densities and elongation moduli of the hybrid films increased with increasing silica content, whereas the tensile strengths and elongations at break of the film decreased. The linear thermal expansion coefficients were found to be in the range 0.3×10^{-3} to 1.3×10^{-3} deg^{-1}, which suggested that the silica in the films had a porous structure.

In later studies,[38,39] these workers introduced functional groups into the PI backbone using alkoxysilylated diamines in place of ODA, and this provided bonding sites for the silica. Various properties of hybrid films prepared using different types and concentrations of pendant alkoxy side chains were reported. Films containing 70% silica were free-standing and tough, and their transparencies increased with increasing ethoxysilyl group content in the polyimide matrix. SEM results showed that the silica particle size was 0.5−1.0 μm, that is, smaller than those in the previous studies,[36,37] and they were more homogeneously distributed. Also, in contrast to the previous results, the tensile strengths of the hybrid films showed no decrease with increasing silica content. Dynamical thermal mechanical analysis (DTMA) showed the motions of the PI chains to become more restricted as the number of bonding sites increased (from increases in the number of ethoxysilyl groups in the PI chains). This was attributed to increased interactions between the organic and inorganic phases. Further refinement of the morphology, however, seemed to be hindered by disadvantages from increasing the number of pendant siloxane groups. This caused the subsequent deterioration of the properties of the PI as a result of increases in chain irregularities, which hinder the packing of the chains.

Iyoku et al.[40] used triethylamine salts of PAA in methanol to obtain fine dispersions of lightly cross-linked siloxane gel in a PI matrix. This was done by including a trifunctional silane, specifically methyltriethoxysilane (MTEOS), and even a difunctional one, dimethyldiethoxysilane. These silanes hydrolyze and condense to silica−siloxane phases that are much softer than silica itself. The same approach was used by Morikawa et al.[41] to produce PI−silica ceramers using TMOS in methanolic solutions of polyamic acid triethylamine salt. In contrast to the results of the previous studies,[36,37] the films that were obtained remained transparent to much higher silica contents (50%). An interconnected globular structure was observed upon etching the hybrid films with hydrazine hydrate to remove the PI phase. Although the films were transparent, the sizes of the globules were fairly large (200 nm), but they were reduced to 70 nm by room-temperature drying of the precursor hybrid solution. A high-pressure polymerization procedure[42,43] used by this group was found to concurrently complete the polymerization reaction of both the inorganic and organic phases. It did not, however, permit full densification of the sol−gel-derived silica, as was originally thought by the authors. This failure was attributed to the lack of PI to act as lubricant for compaction of the silica domains or for its penetration into the silica pores.

The same group studied PI hybrids in which the dispersed phase was really a silica−siloxane material derived from triethoxysilanes, that is, MTEOS or phenyl triethoxysilanes (PTEOS).[44−46] Since the dispersed phases were relatively soft, both the moduli and tensile strengths of the hybrid films decreased. The phenyl or methyl groups on MTEOS or PTEOS acted as compatibilizers and the diameters of the dispersed silica particles were smaller, making the films more transparent than the hybrids containing similar contents of silica but derived from TEOS alone.

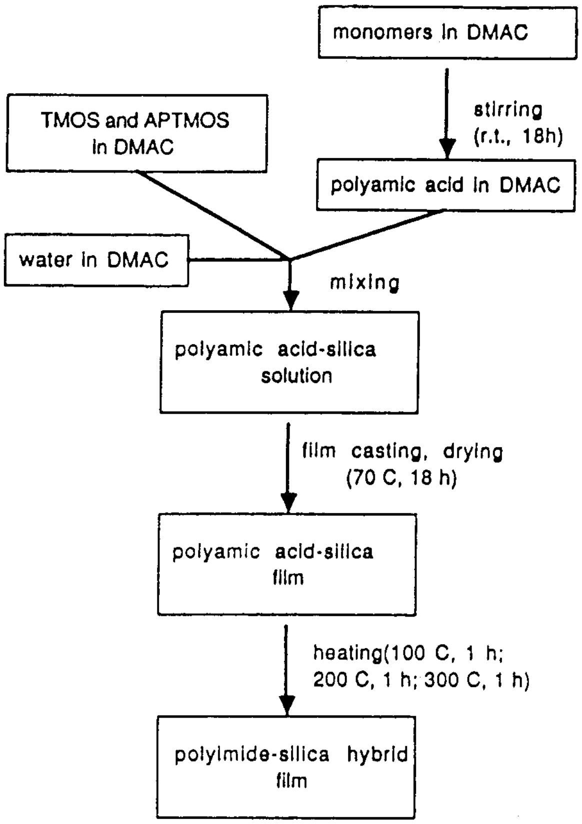


Figure 2. Typical flow sheet diagram used for the preparation of compatibilized PI ceramers. Reprinted with permission from ref 48. Copyright 1994 American Chemical Society.

Illustrative Bonding Agents

Ahmad and co-workers[47,48] prepared bonded polyimide−silica hybrids using organically substituted alkoxysilanes, for example, (aminophenyl)trimethoxysilane (APTMOS), (aminoethylaminomethyl)phenethyltrimethoxysilane, or 1-trimethoxysilyl-2-(*m*,*p*-chloromethyl)phenylethane. The alkoxy ends of these silanes undergo hydrolysis and polycondensation along with TEOS to form silica or polymeric silicates, while the other end groups (such as amino or chloro) provide primary or secondary bonds with the PI chains. These specific aromatic compounds were chosen for their high thermal stabilities, which are comparable to that of the polyimide itself. Another advantage of introducing APTMOS to bond the PI with the silica is the possibility of achieving improved reinforcement of the hybrid material. The general scheme used to prepare such hybrid materials is given in Figure 2. The transparency of the films was considerably improved upon addition of these triethoxysilane bonding agents. SEM results on the hybrid films containing the aminophenylsilane showed that the particles were smaller and more homogeneously distributed and also had rougher surfaces (presumably improving the compatibility of the silica with the polymer). Figure 3 shows some stress−strain curves for the PI−silica hybrids with 10% silica, with and without addition of 0.5% triethoxysilanes. Adding a small amount of these bonding agents was found to improve the moduli and strengths of these hybrid

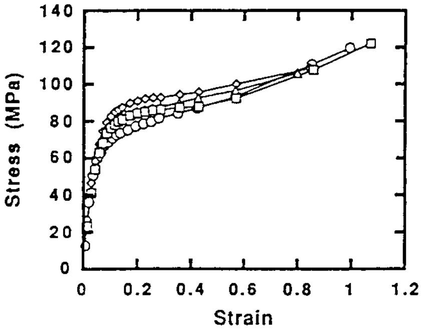


Figure 3. Stress–strain curves in elongation for PI hybrids having 10 wt % silica compatibilized using the coupling agents aminophenyltrimethoxysilane (◇), (aminoethylaminomethyl)phenethyltrimethoxysilane (△), 1-trimethoxysilyl-2-(*m*,*p*-chloromethyl)phenylethane (□) and also without any coupling agent at all (○). Reprinted with permission from ref 48. Copyright 1994 American Chemical Society.

materials, with the APTMOS giving the largest improvements. The reinforcement observed was presumably due to both the improved bonding and the reduction in sizes of the filler particles. This is consistent with the fact that tensile strengths are known[37] to be reduced if there are no bonding sites between the organic polymer and the inorganic phase. This is presumably due to the otherwise weak interactions between these types of polymers and the silica, in which case the silica acts as a nonreactive nonreinforcing filler. It is generally believed[49] that external stress on a plastic composite is transferred from the continuous phase (polymer matrix) to the discontinuous phase (filler). Thus, the ultimate properties of a composite are dependent on the extent of bonding between the two phases, the surface area of the filler, and the arrangements between the filler particles. Increasing the amount of bonding agent, however, did not give very large increases in mechanical strength and reduced the elongation at break. Later, Maryska and co-workers[50] also reported transparent PI–silica hybrid materials with covalently bound phases using APTMOS-terminated PAA. The optical transparencies of the hybrid films were found to increase with the number of bonds between the phases, in agreement with earlier results.[47,48]

Mascia and Kioul[51–53] and Menoyo et al.[54] reported the use of γ-glycidyloxypropyltrimethoxysilane (GPTMOS) and isocyanatopropyltrimethoxysilane (ICTMOS) to “couple” PAA to the silicate network prior to the condensation reactions, leading to the formation of the ceramer. Better compatibility was achieved upon exceeding a critical concentration of coupling agent, with the compatibility increasing linearly with total silica content up to a particular level. A threshold GPTMOS:TEOS molar ratio was determined[54] for the production of transparent ceramers having various silica contents. The effect of this ratio on the compatibility of PI–silica hybrids is shown in Figure 4. In the absence of GPTMOS, the maximum silica contents that allow the formation of compatibilized morphologies is around 8–10% (which corresponds exactly to the level estimated earlier by Morikawa et al.[37]). However, for 25% silica the threshold ratio is 0.35. In fact, this value is related to the ability of the coupling agent to displace the strongly associated DMAC solvent molecules with the PAA units of the polymer chains to develop the required interfacial interactions between the organic and inorganic components. The results of tensile tests carried out on these hybrids are shown in Figure 5. These hybrids exhibited improved mechanical strengths upon introduction of the silica when GPTMOS was used as a compatibilizer.[53] This was attributed to the development of co-continuous phase morphologies leading to efficient stress-transfer mechanisms. Elongations at rupture on the other hand were found to decrease monotonically with increasing amounts of silica.

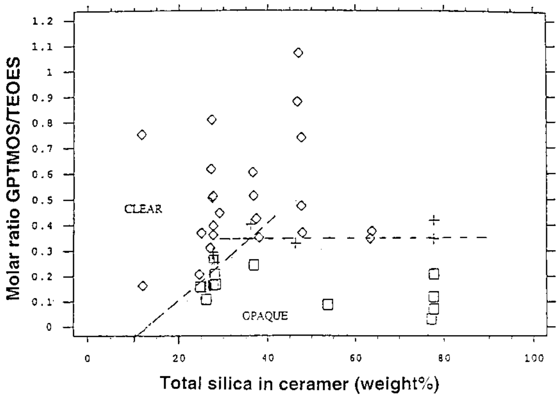


Figure 4. Visual appearances of PI–silica hybrid films having various silica contents. Effects of molar quantities of GPTMOS relative to TEOS; opaque (□), transparent (◇), or hazy (+). Reprinted with permission from ref 54.

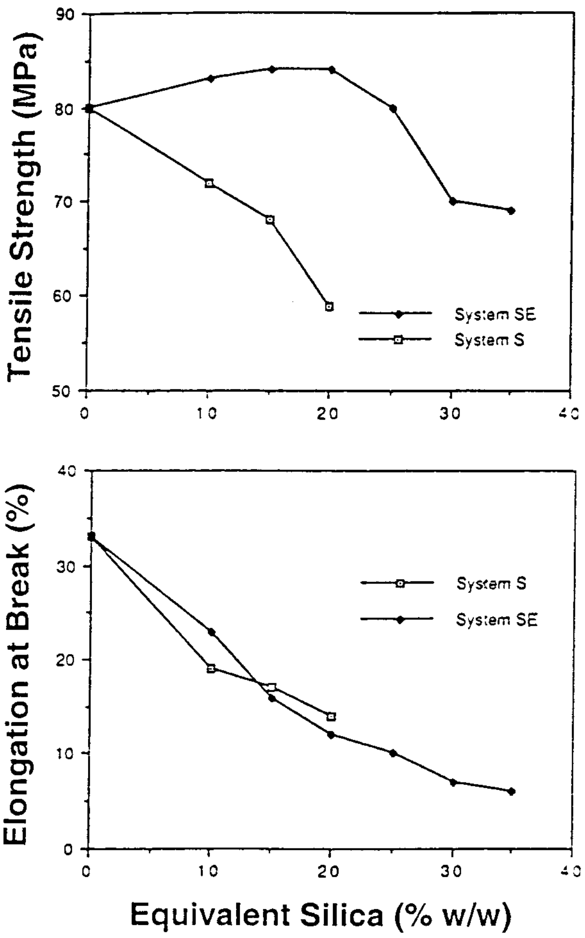


Figure 5. Variation of mechanical properties of noncompatibilized (S) and compatibilized PI-silica hybrids using GPTMOS (SE), as a function of silica content (% w/w). Reprinted with permission from ref 53.

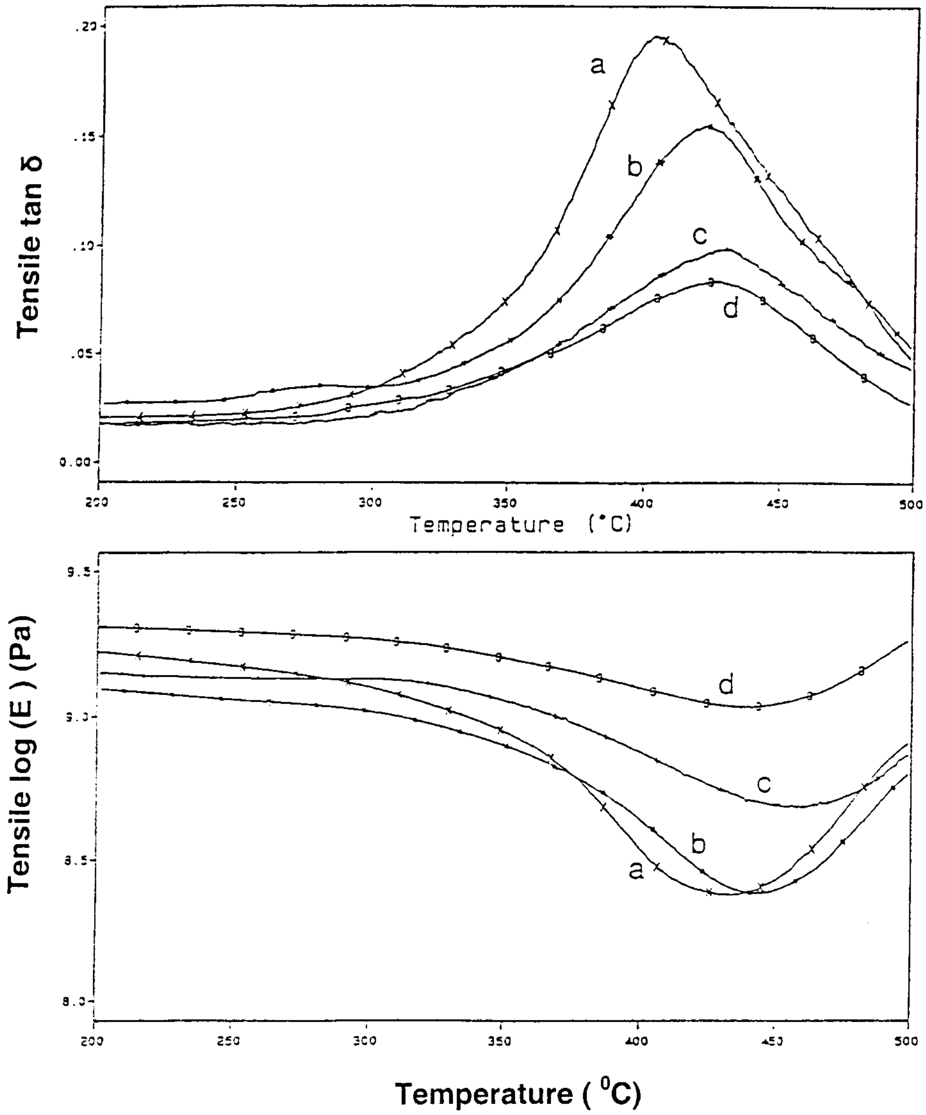


Figure 6. Dynamical thermal mechanical spectra of (a) PI, (b) noncompatibilized PI ceramer with 25% (w/w) silica, (c) compatibilized PI ceramer with 25% silica, and (d) compatibilized PI ceramers with 35% silica. Reprinted with permission from ref 53.

Thermal Stabilities and Aging Effects

The thermal decomposition temperatures of chemically bonded PI ceramers are generally higher than that of the pure PI. For example, TGA thermograms for PI–silica hybrids bonded through aminophenol show a weight loss around 600 °C, mainly from the decomposition of the polymer. Also, as expected, the weight retained around 900 °C is proportional to the silica contents in the sample. The nonchemically bonded silica, however, does not give any improvements in thermal stability.

The effect of thermal aging on the tensile properties of these ceramers was also studied. Polyimide ceramers exhibited approximately 20% increases in tensile strength when aged at 400 °C for 2 h in air. At longer times, however, the pure PI and PI–ceramers having more than 35% silica showed sharp decreases in tensile strength, while ceramers containing 25% silica exhibited a plateau between 2 and 4 h of aging, followed by a sharp decrease in strength above 4 h. Ductility of the polyimide and resulting ceramers was reported to decrease rapidly with increased aging. DTMA results carried out on some of these samples are described in Figure 6. Values of T_g in GPTMOS-compatibilized ceramers having 25% silica were reported[53] to increase by 10–15 °C relative to that for pure PI. There were also relatively large reductions in the tan δ peak (characterizing viscoelastic losses) relative to that for the nonbonded composite. This was attributed to the enhanced compatibility of the two phases because the epoxy group of the GPTMOS apparently reacted with the acid group of the PI precursor, resulting in chemical bonding between the organic and inorganic phases. These results illustrate the role of the interconnected silica-rich particles within the polyimide-rich matrix in depressing α-relaxations. Large reductions[53] in CTE were noted when the morphology of the dispersed silica component changed from particulate in noncompatibilized ceramers to co-continuous in the compatibilized ones. This is shown in Figure 7. The effect became even more pronounced at temperatures above the T_g of the PI, and this change is in accordance with greater suppression of the α-relaxations, as was revealed in the DTMA.

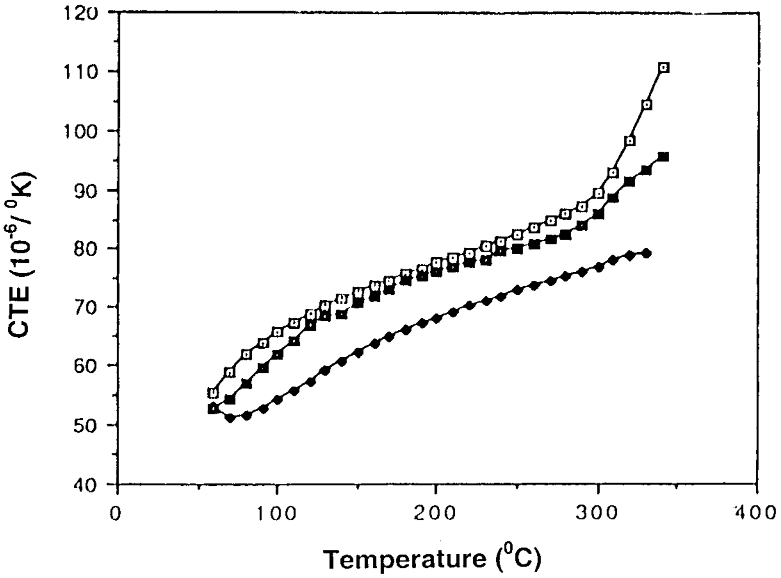


Figure 7. Effects of compatibilization on the coefficients of thermal expansion of PI pure (□), PI ceramer containing 25% (w/w) silica noncompatibilized (■), and 25% silica compatibilized using GPTMOS (◆). Reprinted with permission from ref 53.

Schrotter et al.[55,56] prepared PI–silica hybrids using several aminoalkoxysilanes, including (aminopropyl)-trimethoxysilane (APrTMOS) and APTMOS. The presence of both amino and methoxy side groups enabled chemical bonding between the organic and the inorganic networks, resulting in the formation of homogeneous films. Chen and Iroh[57] also used APrTMOS with the PAA precursor of PIs to develop bonding with the inorganic networks produced though the sol–gel process. The presence of chemical bonds between the PI and silica had pronounced effects on the properties of the hybrid films, especially their mechanical properties. The elongation moduli and ultimate strengths increased and the elongations at break decreased with an increase in silica content. Surface energy results from contact angle measurement showed increasing surface energies with increases in the amount of silica. These hybrids showed no apparent decreases in the thermal decomposition temperature. The microstructure of the materials, however, was drastically different from that of the PI hybrids prepared without any aminoalkoxysilane. In this regard, Rehman[58] recently studied in detail the morphology of PI–hybrids using various types of aminoalkoxysilane as coupling agents. The SEM micrographs (Figure 8) illustrate the vital role of the coupling agent (ICTMOS) in changing the morphology from a typical particle-dispersed microstructure to a finely interpenetrating heterophase network.

Some Applications

Some important applications are high-performance films, coatings, membranes, and so forth[59–64] and other approaches have been used to control the morphologies and properties for these particular uses. Some additional specific examples will now be briefly described, along with some comments on the possible uses of these materials in various industrial applications. In one example, Kim and co-workers[65–67] studied the effects of TEOS content on the dielectric properties of a hybrid film using two types of soluble precursors chemically convertible to PI (specifically PAA and polyamic diethyl ester). The values of the dielectric constant of the composite films monotonically increased with inclusion of silica because of the inherently higher dielectric constant of silica relative to that of the PI. Sigmoidal behavior with sweep frequency variation having no particular effect on ϵ was observed,[65,66] as is illustrated in Figure 9. The composite PI films prepared from the PAA exhibited higher dielectric constants than those from the polyamic diethyl ester. This difference was ascribed to the uniformity in distributed nanometer-sized silica particles in the former composites.

Polyimide–silica hybrid materials for thin film microelectronics were also prepared by Kang and coworkers,[68] who used a sol–gel reaction in *N,N'*-dimethylformamide as solvent. The resulting thin films were transparent up to 50% silica loading, and the moisture gain of these hybrids was less than 0.5%. The dielectric constants of the PI composite having approximately 50 wt % silica were in the range 3.935–3.885. The effect of coupling agent on the dielectric breakdown of polyamide–imide composite films containing silica has been studied by Iida et al.[69] They successfully prepared thin PI–silica films having good electrical and mechanical properties useful for microelectronic applications when γ-aminopropylmethyldiethoxysilane was included as a coupling agent.[70] Similarly, Mukherjee and Wang[71] prepared low-ϵ PI composites with controlled coefficients of thermal expansion. Laminates filled with uniformly distributed aerogel microspheres having voids at nanoscale dimensions were prepared by extrusion impregnation and lamination techniques. The aerogel microspheres had been prepared by a sol–gel technique with supercritical drying of the sol–gel particulates.

Ree et al. also prepared PI nanocomposite films for use in fabrication of microelectronic devices, but in this case by the solution blending of polyamic acid and silica aerogels.[72] Optical and dielectric properties were improved, but the interfacial stress and thermal expansion coefficient were significantly degraded by large disturbances in the polymer chain in-plane orientation caused by the silica aerogels (despite their low thermal expan-

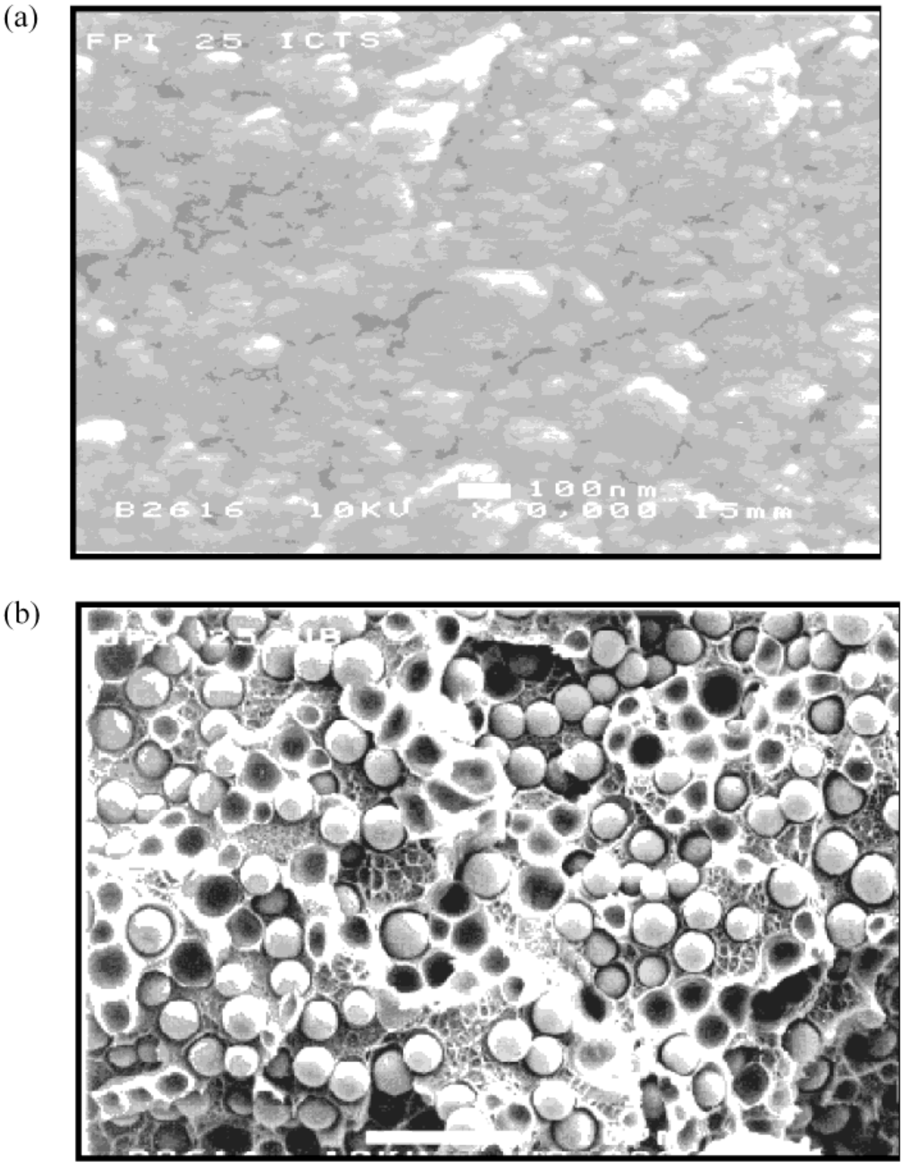


Figure 8. Scanning electron micrographs of fractured surfaces of PI ceramers having 15% w/w silica: (a) compatibilized using ICTMOS; (b) noncompatibilized. Reprinted with permission from ref 58.

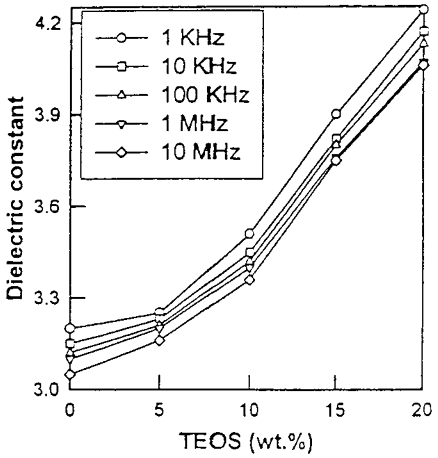


Figure 9. Effects of TEOS content on the dielectric constant of PI–silica composite films at varying sweep frequencies. Reprinted with permission from ref 65.

sivities). This underscores the fact that, in rigid types of polymer composites, the orientation of the polymer chains has a very important effect on physical properties.

As an alternate to the use of hollow microspheres to obtain low-permittivity composites, Zhang et al. developed ceramic substrates having a sandwich structure. This structure consisted of a porous, fiber-reinforced silica core and two thin polymer plates fabricated by sol–gel processing and polymer infiltration.[73] The rheological behavior of an aqueous colloidal SiO_2 sol containing short SiO_2 fibers was studied as a function of particle loading, fiber loading, and gelation time. The short SiO_2 fibers had been introduced to limit drying shrinkage and thus to minimize substrate cracking during drying. After the pseudoplastic sol was tape cast and sintered at 1150 °C, the PI solution was infiltrated into the porous SiO_2 core. The short fiber reinforcement, the PI infiltration, and the surface coating increased the strength and toughness of the PI–ceramic composite. For example, the substrate strength increased from 1.93 to 3.83 MPa after polyimide infiltration. Rheological permittivities ranging from 1.81 to 3.08 could be achieved

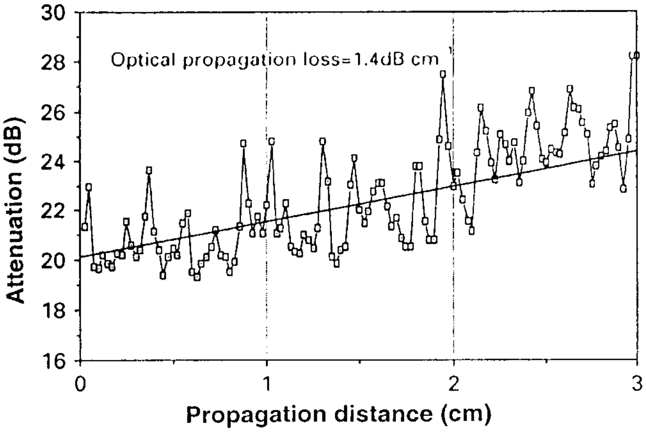


Figure 10. Optical intensity decay in PI–titania hybrid waveguides. Reprinted with permission from ref 76.

using 32–42% SiO_2, 5–50% PI, and 63–8% porosity.

Optical waveguides have also been fabricated from composite materials consisting of sol–gel-processed inorganic materials and polyimides.[74,75] For example, optically transparent composite waveguide materials have been produced by the dispersion of nanosized TiO_2 particles into a fluorinated PI using reverse micellization in the sol–gel approach.[76,77] This method for the synthesis of fine particles has several advantages over conventional methods. It is based on the three-component system hydrocarbon (for example, isooctane)/surfactant (for example, sodium bis(2-ethyl hexyl) sulfosuccinate)/water, and it enables the synthesis of particles of various sizes by variations in the size of the water pool, which serves as a microreactor. This is illustrated by titanium isopropoxide dissolved in isooctane slowly diffusing into the reverse micelles. The hydrolysis and polycondensation reactions take place in the microreactor, resulting in the formation of nanosized TiO_2 particles. In the study cited, these particles were extracted and dispersed in the solid state into a fluorinated PI solution, the approach avoiding the occurrence of various kinds of species such as titanium complexes. The optical propagation loss of these PI composites was measured by observing the optical intensity decay with respect to the propagation distance, using a CCD camera. The intensity decay showing the losses as the slope was found to be 1.4 dB cm^{-1} (4 wt % TiO_2) at 633 nm. This is illustrated in Figure 10. Because the TiO_2 particles produced using this technique were very small, the losses were just equivalent to that of the pure PI. The improved thermal and mechanical properties and low thermal expansion coefficients of such rigid materials can provide a better edge-polishing capability. This gives lower coupling losses, together with the capability of manipulating the refractive index.

Moisture permeation is a serious problem in applications of PIs in the microelectronics industry,[78–81] particularly if the interactions between phases involve hydrogen bonding.[82] It is therefore not surprising that there have been many water and gas permeation studies on PI hybrid materials. For example, Kita et al.[83,84] prepared PI–silica membranes by the sol–gel reaction of TEOS, MTEOS, or PTEOS in solutions of PAA prepared by condensation of an equimolar amount of PMDA, BPDA, or 6FDA with ODA in NMP solvent. (The structures of these substances are given in Figure 1).

Table 1. Water Vapor Permeability at 105 °C for Membranes of PI, PI–Silica Composites, and Silica-Coated PI (Reprinted with Permission from Ref 83)

membrane (silica wt %)	P [10^{-8} cm^3 (STP) cm cm^{-2} s^{-1} cm Hg^{-1}]
Polyimides	
PMDA–ODA	14.8
Kapton-H	4.05
BPDA–ODA	5.53
6FDA–ODA	15.7
Polyimide/Silica Composites	
PMDA–ODA/PTEOS(14)	16.1
PMDA–ODA/PTEOS(29)	23.6
PMDA–ODA/PTEOS(52)	24.1
BPDA–ODA/TEOS(20)	7.81
BPDA–ODA/PTEOS(20)	7.15
6FDA–ODA/TEOS(20)	20.1
6FDA/ODA/TEOS(13)	16.0
Silica-Coated Polyimide	
PMDA–ODA/TEOS–MTEOS	11.7
Kapton-H	2.27

Table 2. Permeability Coefficients at 35 °C for PI–Silica Composite Membranes (Reprinted with Permisson from Reference 83)

	P [10^{-8} cm^3 (STP) cm cm^{-2} s^{-1} Hg^{-1}]					
membrane (silica wt %)	H_2	CO_2	O_2	N_2	CO	CH_4
PMDA–ODA	7.18	2.36	0.604	0.0916	0.172	0.0625
PMDA–ODA/TEOS(20)	7.43	2.22	0.560	0.0823	0.148	0.051
PMDA–ODA/PTEOS(14)	12.4	5.16	1.24	0.218	0.402	0.179
PMDA–ODA/PTEOS(29)	17.8	11.2	2.47	0.504	0.884	0.504
BPDA–ODA	3.54	0.582	0.171	0.0213	0.0413	0.0119
BPDA–ODA/TEOS(20)	3.02	0.521	0.145	0.0186	0.0365	0.0109
6FDA–ODA	40.7	16.7	3.88	0.733	1.16	0.341
6FDA–ODA/TEOS(20)	23.4	6.01	1.72	0.369	0.565	0.240

Although the permeability was dependent on the acid dianhydride moiety in the order 6FDA > PMDA > BPDA, the permeabilities through the PI/silica composite membranes increased for a given dianhydride moiety. It also increased with an increase in silica content, which was attributed to increases in the solubility of water vapor resulting from the presence of hydroxy species on the silica. There was, however, a reduction in the permeability in the case of silica-coated polyimide membranes. Some of these results are shown in Table 1. Increasing the amount of the PTEOS silane also gave an increase in the permeability to water vapor. Gas permeation data for H_2, CO_2, CO, O_2, N_2, CH_4, and H_2O vapor are given in Table 2. A slight reduction in gas permeability was generally observed for composite membranes obtained using TEOS. Additional data would be required, however, to draw any definite conclusions.

On the other hand, Hu et al. prepared nanocomposite membranes from PI and titania and silica components that had higher permeability coefficients and significant improvements in permselectivity.[85] The sorption and permeation of O_2, N_2, H_2, CO_2, and CH_4 in PI–silica hybrid films have also been investigated by Joly et al.[86] Their composite membranes showed higher solubility coefficients and permselectivities than the pure PI ones. Thin PI–silica composite membranes on porous supports have also been prepared[87,88] by coating a hybrid sol on a porous tube consisting of a γ-alumina coating on an α-alumina support. Smoothing of the substrate surface and hybridization of the silica and PAA were both effective for the formation of defect-free and thin microcomposite membranes. After imidization the gas permeation properties were evaluated with He, N_2, and CO_2. The effective thickness of the PI layer in the membrane was less than one-tenth the total thickness, which was 330 nm. These microcomposite membranes showed high permeance, retaining the high permselectivty inherent with PI membranes. The fractions of silica in the composite membrane which optimized the balance between permeance and selectivity were found to be 0.6−0.7.

PI hybrids have also been found to be useful as polymer-based optical materials where the major requirement is that there must be at least a roughly uniaxial ordering of chromophores in the bulk material. Thermodynamic relaxation of the chromophore alignment can be prevented by raising the T_g of the polymeric materials after an electric field poling process. This rigidification has been accomplished by thermal imidization of PAA and sol−gel processing of alkoxysilane-incorporated chromophores. Transparent PI films containing moieties having large nonlinear optical (NLO) coefficients have been prepared by Jeng and co-workers.[89,90] Here, linked alkoxysilane dyes and the PI form a semi-interpenetrating polymer network, resulting in a substantial increase in the α-relaxation temperature and superb thermal stability of the poled ordering. Optically transparent PLZT−PI composite films were prepared by Chariar et al.,[91] where PLZT represents a $(Pb_{1-x},La_x)(Zr_y,Ti_{1-y})O_3$ sol of (8/65/35) composition. It was prepared using stoichiometric quantities of lead acetate, lanthanum acetate, zirconium acetylacetonate, and titanium isopropoxide. The PLZT sol had been added drop by drop to the ammonium salt of PAA with constant stirring to avoid gelation or formation of lumps. The room-temperature dielectric constant of a 20-μm-thick composite film at 1 kHz was approximately 13. The films showed good dielectic properties in general and very encouraging NLO properties. Dalton and coworkers[92−94] have reviewed different techniques for the production of NLO lattices. Topics include the generation of polyimides containing covalently incorporated NLO chromophores and the exploitation of thermosetting systems (including sol−gel processing in which the NLO chromophore is covalently attached to the reacting species).

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