Hybrid Organic-Inorganic Composites Containing Mixed-Oxide Ceramics and High-Temperature Polymers

J. E. Mark[a]

[a] Department of Chemistry and the Polymer Research Center, The University of Cincinnati Cincinnati, Ohio, USA

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J. E. MARK

Department of Chemistry and the Polymer Research Center
The University of Cincinnati
Cincinnati, Ohio 45221-0172, USA

ABSTRACT

The preparation of organic–inorganic composites by in-situ hydrolysis reactions is illustrated using two polymer–ceramic systems. The first consists of elastomeric poly(dimethylsiloxane) as the polymeric phase and silica, titania, or a silica–titania mixed oxide as the ceramic phase. In the second, the polymeric phase is either a polyamide or polyimide of high thermal stability and the ceramic phase is silica.

INTRODUCTION

The composites to be described are prepared using techniques very similar to those used in the new sol–gel approach to ceramics. Organometallics such as silicates, titanates, and aluminates are hydrolyzed in the presence of polymer chains (for example, polysiloxanes and polyimides) that typically contain hydroxyl or amino groups. The functional groups are used to bond the polymer chains onto the silica, titania, or alumina being formed in the hydrolysis, thus forming organic–inorganic composites. When the polymer chains are present in excess, they constitute the continuous phase, with the ceramic-type material appearing as reinforcing particles. When present in smaller amounts, the polymer is dispersed in the continuous ceramic phase to give a polymer-modified ceramic. Under some conditions, bicontinuous systems are obtained. The composites thus prepared are characterized

by electron microscopy, x-ray and neutron scattering intensities, density determinations, and stress–strain and impact-strength measurements.

In some cases the components employed can be derived from naturally-occurring materials, for example cellulose acetate from cellulose [1]. Also, at least in the case of the silica, the ceramic phase can be generated from organosilicon compounds obtained by solubilizing sand in a strongly alkaline medium containing ethylene glycol [2].

SOME COMPOSITES BASED ON POLY(DIMETHYLSILOXANE)

General Aspects

Poly(dimethylsiloxane) (PDMS), $[-Si(CH_3)_2O-]_x$, is the most important and by far the most widely used siloxane polymer, but almost all applications require that these elastomers be reinforced by fillers in order to improve their mechanical properties [3]. For these reasons a novel reinforcement technique which can generate reinforcing particles within an elastomeric matrix has recently been developed [4, 5]. The most important reaction for doing this is the acid- or base-catalyzed hydrolysis and condensation of tetraethoxysilane (TEOS). Silica (SiO_2) is thus generated, as shown by

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \tag{1}$$

Previous studies of such in-situ generated fillers have concentrated on silica because it is the most widely used and most effective filler available. Silica has some disadvantages, however, such as losses in reinforcement at high temperature and decreases in maximum extensibility of the elastomer [4, 6]. For this and other reasons, several other fillers have been in-situ precipitated into PDMS, including titania (TiO_2) [7–9], alumina (Al_2O_3) [10], and zirconia (ZrO_2) [11]. These fillers have also been incorporated in PDMS elastomers by industry in the usual blending technique. Generally speaking, different fillers can offer different advantages in reinforcement applications. For example, although titania provides only mild reinforcement in polysiloxane elastomers, it gives substantial improvements in weather resistance and heat stability. It is thus of considerable interest to try to identify a filler which possesses a combination of such advantages, for example binary fillers such as silica–titania, silica–zirconia, and silica–alumina mixed oxides [12].

Stress–Strain Isotherms

The stress–strain isotherms obtained on some unfilled networks and networks filled with silica–titania mixed oxides were represented as plots of modulus against reciprocal elongation, as suggested by the Mooney–Rivlin equation [13] $[f^*] = 2C_1 + 2C_2\alpha^{-1}$, where $2C_1$ and $2C_2$ are constants independent of elongation α. Typical isotherms are shown in Fig. 1 [14]. It compares the stress–strain isotherms for networks filled with silica, with titania, and with silica–titania mixed oxides. Compared with the silica-filled PDMS networks, the PDMS network containing the mixed-oxide filler had larger extensibilities and had upturns which occurred at higher elongations. The upturns were less pronounced, however, because of the smaller reinforcement provided by the titanium oxide. A filler consisting entirely of
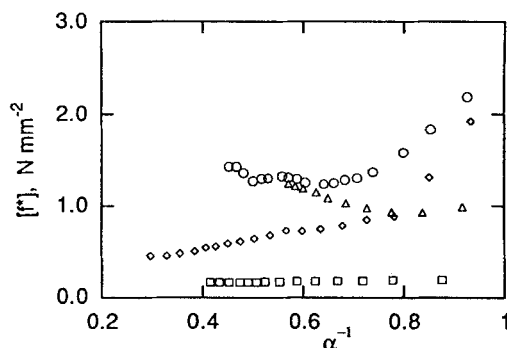
FIG. 1.   Stress–strain isotherms at 24°C for an unfilled PDMS network and PDMS networks filled with various fillers [14]. The quoted M_n of the PDMS utilized was 18,000, and the types and values of the wt% filler were ($\square$) 0.0, ($\lozenge$) 19.5 titania, ($\bigcirc$) 21.4 silica-titania mixed oxides, and ($\triangle$) 22.4 silica.

silica generally increases ultimate strength but decreases maximum extensibility. The present silica–titania mixed-oxide fillers, however, seem to have less of a detrimental effect on the extensibility, and could thus serve as a good compromise in providing the best balance of these two important properties.

Structure

Electron micrographs indicated that the silica–titania mixed oxide particles had an average diameter of several hundred Angstroms, a range of particle sizes that is usually a problem in filler-blended elastomers [4, 5]. The particle size increased as the crosslink density decreased (network "pore size" increased). For example, the average diameter of the particles increased from approximately 200 to 300 Å when the molecular weight M_c between crosslinks in the PDMS network increased from 18,000 to 26,000 g·mol^{-1}. A similar conclusion was reached by Schaefer and coworkers, and is presumably due to the confining effect of the network pores [15].

Thermal Stability

Thermogravimetric analysis (TGA) measurements under nitrogen showed that the samples containing in-situ precipitated fillers all had small weight losses at relatively low temperatures, well below the temperature at which the pure PDMS begins to degrade. This could possibly be due to the loss of organic groups not hydrolyzed from the TEOS [16] or titanium butoxide precursor, and the cleavage of siloxane bonds in the chain caused by OH groups on the surface of the filler. Of particular interest is the onset of pronounced degradation, which is presumably due to the formation of volatile cyclic oligomers. This degradation occurred at relatively low temperatures for unfilled PDMS networks and for PDMS networks mechanically blended with silica and titania. The presence of in-situ mixed oxide filler significantly increased the onset temperature for the degradation.

Since the presence of in-situ precipitated filler retards the depolymerization process, it appears that the hydroxyl groups on the surface of the filler can hydrogen bond with those at the ends of the polymers, resulting in the deactivation of the depolymerization process. Blended silica and titania fillers did not increase the degradation temperature nearly as much as did the in-situ precipitated mixed oxides. It seems that the hydroxyl groups on the surface of these fillers have less ability to deactivate the hydroxyl groups on the PDMS chains.

As in the case of silica–titania fillers, the silica–zirconia mixed oxides also significantly increased the degradation onset temperature. Surprisingly, the presence of silica–alumina mixed oxide actually *decreased* the degradation onset temperature. It would be worthwhile to study the mechanisms of this accelerated degradation.

Adhesion between Phases

Swelling measurements in toluene were carried out at room temperature on portions of unfilled and filled PDMS networks, with several days being allowed for attainment of equilibrium [12, 17]. The extent of swelling was characterized by the volume fraction of rubber in the network at equilibrium swelling. According to Kraus' theory [18], it is possible to distinguish between nonadhering filler and adhering filler by studying the effect of the filler on the extent of swelling. This approach can thus give insight into the reinforcement mechanism. The results obtained indicated that the mixed oxides were of the adhering type. The reinforcement provided by these fillers is also consistent with strong elastomer–filler attachments. Good dispersion and small particle size are also important because the number of attached elastomer chains is proportional to the filler surface available [19].

Impact Strengths

The impact strengths of several samples of this type were determined by both the Charpy impact test and the falling-weight test, with essentially equivalent results [12, 20]. It was found that the higher the molecular weight or the larger the amount of PDMS introduced, the higher the impact strength. Apparently there is phase separation in spite of the fact that the OH-terminated PDMS was successfully incorporated into the SiO_2 network by chemical bonding. The PDMS phase thus generated behaves as an elastomer because its glass transition temperature is far below room temperature. Thus, when the composite is subjected to an impact test, the PDMS component can absorb a great deal of energy and thus delay the growth of cracks and the fracture process. In this way, considerable toughening of the glass can be achieved. Increasing the molecular weight presumably facilitates the phase separation because of the decrease in polymer solubility with an increase in molecular weight. Increasing the amount of PDMS would increase the number or size of the phase-separated domains helping to absorb the impact energy.

The observation of fracture surfaces by scanning electron microscopy for a sample with low PDMS content showed a smooth fracture surface associated with completely brittle failure, with no evidence of effective resistance to either initiation or propagation of cracks. This was found to be independent of the molecular weight of the PDMS. Rather different behavior was shown by samples with high PDMS contents. These samples fractured first in a brittle manner but then with consider-

able ductility. This was shown by the pronounced whitening or shearing in evidence on the electron micrograph [12, 20]. The material had relatively low resistance to crack initiation but good resistance to crack propagation because of the energy-absorbing mechanism introduced by the PDMS.

SOME COMPOSITES BASED ON HIGH-TEMPERATURE POLYMERS

Polyamides

In one study of this type, the polymer employed was mixed-isomer aromatic polyamide having good solubility and thermal stability, with silica as the inorganic phase [21]. The condensation reaction employed was

$$H_2N-Ar-NH_2 + Cl-\overset{O}{\underset{\|}{C}}-Ar'-\overset{O}{\underset{\|}{C}}-Cl \rightarrow -[HN-Ar-NH-\overset{O}{\underset{\|}{C}}-Ar'-\overset{O}{\underset{\|}{C}}]_n- + HCl$$
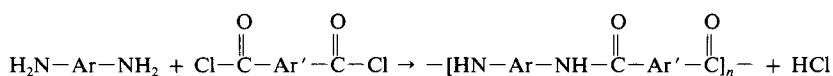
where Ar = 25% *p*-phenylene, 75% *m*- phenylene; and Ar′ = all *p*-phenylene.

In order to obtain the solubility required in the sol–gel process, a few *meta* (*m*) rings were introduced into the primarily *para* (*p*) polymer chains. A mixture of 1,3- and 1,4-phenylene diamines and terephthaloyl chloride were thus used to make mixed-isomer aromatic polyamides. The regularity of the chain was thereby distorted, and the possibility of crystallization of the polymer reduced. Bonding between the phases was facilitated using aminophenyltrimethoxylsilane, in which the amino group can react with the phthaloyl chloride end-capped polymer, and the methoxysilane groups undergo hydrolysis. The composition of these composites was varied by changing the linear polymer chain length and relative amounts of tetramethoxysilane as a source of the silica.

TGA results showed that thermal decomposition occurred in a single step starting at approximately 450°C. The decomposition temperature of poly(1,4-phenylene terephthalamide) has been reported to be around 500°C. The introduction of 25 mol% *m*-phenyls into the chains has thus significantly lowered this temperature. There were small initial weight losses at lower temperatures that were probably due to organic groups remaining from the incomplete hydrolysis and condensation reactions between methoxylsilane with water. The decomposition temperature was found to be independent of the molecular weight of the linear polymer chains, however. The results seemed to indicate stable bonding between the organic and inorganic components. The weight of residue at 800°C was almost proportional to the silica content in both cases, and the thermal decomposition temperature of the hybrid material prepared was around 440–460°C.

Some experiments [22] have been carried out on poly(phenylene-terephthalamide) chains having carbonyl chloride end groups prepared by reacting a mixture of *m*- and *p*-phenylene diamines with terephthaloyl chloride, and then end-capping them with the bonding agent aminophenyltrimethoxysilane. The aramid polymer thus prepared was also used to synthesize hybrid materials in which it was chemically bonded to a silica network produced in-situ by hydrolyzing tetramethoxysilane. Films prepared from this hybrid material were yellow but transparent, and

quite tough. More specifically, the stress–strain curves for the chemically bonded systems showed considerable increases in tensile strength as compared with that of the pure polyamide. This is illustrated in Fig. 2 [22]. The increase in ultimate strength, however, then decreased with silica contents greater than 20%, and the length at rupture also decreased with an increase in silica content. Scanning electron microscopy (SEM) results carried out on cross sections of the interphase-bonded films showed that particle size increased as the amount of silica in the continuous organic phase increased. It was not possible to detect silica particles in materials having 15% or less silica, presumably because of their smaller sizes. In any case, the particles observed were spherical and had diameters of approximately 0.5 μm. Values of the hardness of the interphase-bonded hybrid films exhibited a gradual increase in hardness as the silica content increased, reaching perhaps a saturation value of durometer hardness D-2 of approximately 90.

There was found to be a considerable decrease in water absorption with an increase in the amount of silica [22]. The physical bonding between the inorganic and organic phases apparently reduces the absorption of water, which presumably occurs primarily on the amide group in the polymer [23, 24]. This could be very important with regard to both mechanical and dielectric properties.

Polyimides

Hybrid materials have also been prepared from polyimides and tetramethoxysilane by using several other silicon alkoxides which had been suitably modified so as to act as bonding agents between the ceramic and polymer phases [25]. They were aminophenyltrimethoxysilane (APTMOS) (I), (aminoethylaminomethyl)-phenethyltrimethoxysilane (II), and 1-trimethoxysilyl-2-(m,p-chloromethyl)phenyl-ethane (III), as shown in Scheme 1. They are often described as high-temperature silane coupling agents for improving the bonding between polyimides and glass fibers. These bonding agents can undergo hydrolysis and polycondensation along with the tetramethoxysilane to form silica or polymeric silicates, while the groups at their other ends (such as the amino and chloro groups) provide good bonding with the polyimide. The reactions were carried out in the polyimide precursor, polyamic
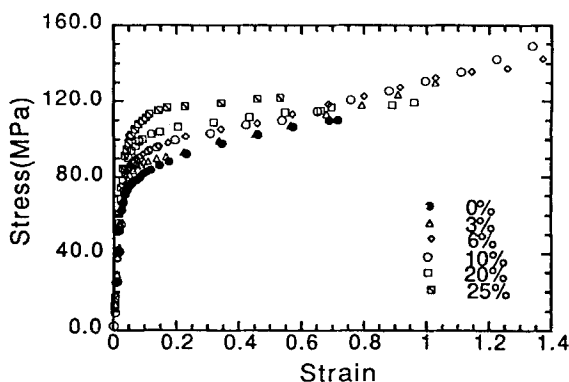

FIG. 2.   Stress–strain curves of aramid-silica films having interphase bonding [22].

CH$_2$CH$_2$Si (OCH$_3$)$_3$

ClCH$_2$

H$_2$N ——⟨ ⟩— Si (O CH$_3$)$_3$ ⟨ ⟩ ⟨ ⟩— CH$_2$CH$_2$Si (OCH$_3$)$_3$

CH$_2$NHCH$_2$CH$_2$NH$_2$

I **II** **III**

SCHEME 1.

acid, which was then cyclized at high temperatures. These specific aromatic compounds were chosen for their high thermal stability, which is comparable to that of the polyimide.

The stress–strain curves for the samples containing different amounts of bonding agent **I** showed that at even 0.5 wt% bonding agent, there was some improvement. Studies of all three bonding agents at 10, 20, and 30 wt% demonstrated that the higher the silica content, the larger the reinforcement. Bonding agent **I** gave the best results of the three studied.

The structures of these composites were studied by energy- dispersive x-ray diffraction analysis [26]. The silicon distribution maps identified the dispersed silicon existing on the surface of the fracture cross-sections. The composites were also examined by scanning electron microscopy, which gave important information on their morphologies. The fracture surface of the pure polyimide and hybrid films containing 20% silica showed particles that could be pure silica or a mixture of silica and silsesquioxanes (RSiO$_{1.5}$). The average particle size observed in samples obtained without adding APTMOS is in the range of 1 to 2 μm. Addition of a few percent of the APTMOS reduced the particle size to approximately 1 μm, with a more homogeneous size distribution and with rougher particle surfaces. Furthermore, the corresponding films were found to be transparent! The aminophenyl group on the substituted silicon trialkoxide probably reacts with the polymer chains, possibly improving the compatibility of the silica with the polymer. It apparently also has the tendency to prevent the formation of high molecular weight silicates, thus reducing the size of the clusters.

Another type of high-temperature polymer, the polybenzoxazoles, is also being treated by some of these in-situ precipitation techniques [27].

One of the challenges in this area of high-performance polymers is to obtain significant improvements in these classes of materials since they are relatively resistant to bonding to reinforcing phases and already have superb thermal and mechanical properties.

ACKNOWLEDGMENTS

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