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Some Novel Polymeric Nanocomposites

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ABSTRACT
The nanocomposites described here all involve polymers and were chosen because they are already of commercial importance, show some promise of becoming so, or simply seem interesting. The field is so broad that some topics are mentioned only very briefly, and there is considerable emphasis on the polysiloxane nanocomposites studied by the author's research group. Some are typically prepared using techniques very similar to those used in the new sol–gel approach to ceramics, with either the polymer or the ceramic being the continuous phase. Other dispersed phases include particles responsive to an applied magnetic field, intercalated or exfoliated platelets obtained from clays, mica, or graphite, silsesquioxane nanocages, nanotubes, dual fillers, porous particles, spherical and ellipsoidal polymeric particles, and nanocatalysts. Also described are some typical studies involving theory or simulations on such particle reinforcement. Experiments on ceramics modified by dispersed polymers are equally interesting, but there is less relevant theory. Many of the fields mentioned have become so vast that the approach taken here is simply to describe general approaches and characteristics of the composites, list some specific examples, and provide leading references (with some emphasis on studies that are relatively recent or in the nature of reviews).

1. Sol–Gel Ceramics

A relatively new type of nanocomposite involves the synthesis of "ultrastructure" materials, that is, materials in which structure can be controlled at the level of around 10 nm. An example of such a synthesis is the "sol–gel" hydrolysis of alkoxysilanes (organosilicates) to give silica, SiO_2.[1,2] The reaction is complicated, involving polymerization and branching, but a typical overall reaction may be written

$$Si(OR)_4 + 2H_2O \rightarrow SiO_2 + 4ROH \qquad (1)$$

where the $Si(OR)_4$ organometallic species is typically tetraethoxysilane (tetraethylorthosilicate, TEOS). In this application, the precursor compound is hydrolyzed and then condensed to polymeric chains, the chains become more and more branched, and finally a continuous highly swollen gel is formed. It is first dried at moderately low temperatures to remove volatile species, and then fired into a porous ceramic object, which can be densified. Not surprisingly, the production of ceramics by this novel route has generated a great deal of interest.

2. Fillers in Elastomers

2.1. Generation of Approximately Spherical Particles. The same hydrolyses can be carried out within a polymeric matrix to generate *particles* of the ceramic material, typically with an average diameter of a few hundred angstroms.[1–3] The polymer typically has end groups, such as hydroxyls, that can participate in the hydrolysis–condensation reactions.[4,5] Such end groups provide better bonding between the two rather disparate phases, but bonding agents may also be introduced for this purpose. Properties are generally much improved when the particles are attached to the polymer matrix by covalent bonds.

This approach has been used to form silica-like phases in a wide variety of polymers, as illustrated in Table 1.[6–10] The one that has been studied the most in this regard is poly(dimethylsiloxane) (PDMS) $[Si(CH_3)_2{-}O{-}]$.[7] This is because PDMS is a relatively weak elastomer in need of reinforcement and is capable of easily absorbing the precursor materials generally used in the sol–gel process. Considerable reinforcement of elastomers can be achieved

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Table 1. Typical Polymers in Nanocomposites with Silica

types of polymers	examples	refs
elastomeric	poly(dimethylsiloxane)	6, 7
	hydrocarbon elastomers	8
glassy	polystyrene	8, 9
partially crystalline	nylons	8
rigid-chain	polyimides, benzobisoxazole polymers	9
naturally occurring	linseed oil	10

in this way. This method for introducing reinforcing particles has a number of advantages over the conventional approach in which separately prepared filler particles are blended, with difficulty, into the un-cross-linked elastomer before its vulcanization.[11,12] Because of the nature of the in situ precipitation, the particles are well dispersed and are essentially unagglomerated (as demonstrated by electron microscopy). The mechanism for their growth seems to involve simple homogeneous nucleation, and since the particles are separated by polymer, they do not have the opportunity to coalesce.

A typical transmission electron micrograph of such a filled material shows[13] the particles to be relatively monodisperse with most of them having diameters in the range of 100–200 Å.

The remainder of this section provides some additional details on the use of this technique.[3,4] In particular, the methods can be quite general, in that a variety of other precursor materials can be utilized; for example, titanates can be hydrolyzed to titania, aluminates hydrolyzed to alumina, and metal carbonyls photolyzed or thermolyzed to metals or metal oxides Some ceramic phases other than silica are described elsewhere.[4,8,9,14]

It is also possible to polymerize conducting polymers such as polyaniline within polysiloxane matrices.[15] As is evident from Table 1, the method can also be used in a variety of polymers (organic as well as inorganic, nonelastomeric as well as elastomeric). Basic catalysts give precipitated phases that are generally well-defined particles, whereas the acidic catalysts give more poorly defined, diffuse particles.[16] In some cases, bicontinuous (interpenetrating) phases result.[17] It is also possible to generate the catalyst and other reactants themselves in situ, to give composites of unusually high transparency.[18]

Interesting "aging" effects are frequently observed in these systems. If the precipitated particles are left in contact with the hydrolysis catalyst and water, they appear to reorganize so that their surfaces become better defined and their sizes become more uniform.[19]

The reinforcing ability of such in situ generated particles has been amply demonstrated for a variety of deformations.[3,4,8,20] In the case of uniaxial extension, the modulus [f^*] frequently increases by more than an order of magnitude with the isotherms generally showing the upturns at high elongations that are the signature of good reinforcement.[21,22] Typical results are shown in one portion of Figure 1, where α is the extension.[23] As is generally the case in filled elastomers, there is seen to be considerable irreversibility in the isotherms, which is thought to be due to irrecoverable sliding of the chains over the surfaces of the filler particles upon being strained. Analogous results document the reinforcement observed in biaxial extension. These curves exhibit maxima and minima that will be a challenge to those seeking a better molecular understanding of filler reinforcement in general.

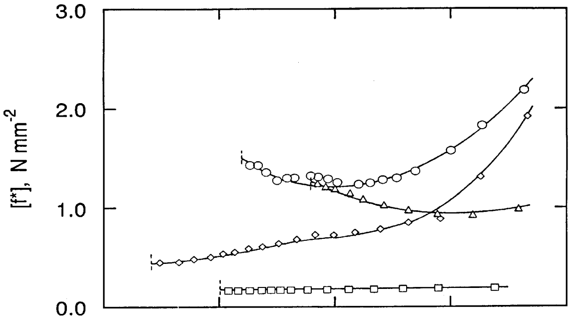

FIGURE 1. Stress–strain isotherms in elongation for PDMS elastomers that were unfilled (□) and reinforced in situ with particles of either silica (△),[23] titania (◇), or silica–titania mixed oxides (○).[24,25] Reprinted with permission from ref 25. Copyright 1994 Rubber Division, ACS.

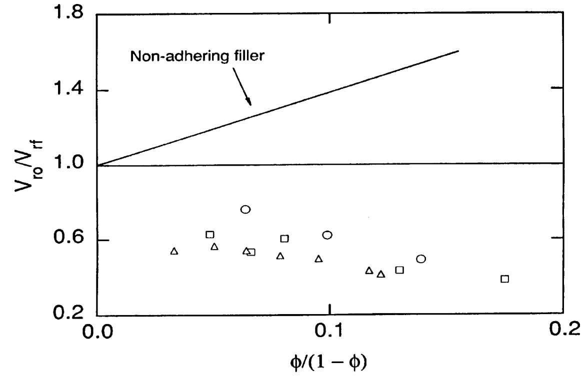

FIGURE 2. Plot of volume fraction ratio, V_{ro}/V_{rf}, characterizing the swelling of an unfilled PDMS network relative to that of a filled PDMS network against filler loading expressed as volume ratio of filler to PDMS, $\phi/(1 - \phi)$ (where ϕ is the volume fraction of filler).[25] The various symbols refer to silica, titania, and silica–titania mixed oxides, but all lie on essentially the same line, and all indicate good bonding. Reprinted with permission from ref 25. Copyright 1994 Rubber Division, ACS.

Some fillers other than silica, for example titania, do give stress–strain isotherms that are reversible, indicating interesting differences in surface chemistry, including increased ability of the chains to slide along the particle surfaces.[24] Such results are also illustrated in Figure 1.[24] Increases in modulus can be lower but with increase in extensibility. The bonding of PDMS to silica, titania, or silica–titania mixed oxide particles is however strong enough to suppress *swelling* of the polymer, as is illustrated in Figure 2.[25] These results involve equilibrium swelling measurements obtained on unfilled and filled PDMS elastomers to estimate the degree of adhesion between elastomer and filler particles.[25] The results differ greatly from those to be expected for non-adhering fillers, indicating good bonding between the two phases. Obviously, resistance to separation from the surface in such swelling tests does not contradict the chains having

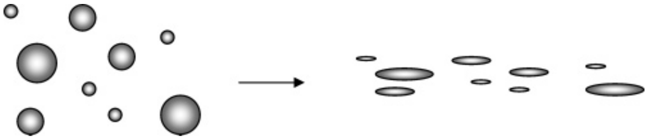

FIGURE 3. Deformation of spherical filler particles into prolate ellipsoids.

considerable mobility *along* the surfaces of some types of particles, as was just described.

A variety of techniques have been used to further characterize these in situ filled elastomers.[3,4] Density measurements, for example, yield information on the nature of the particles. Specifically, the densities of the silica-type particles are significantly less than that of silica itself, and this indicates that the particles presumably contain some unhydrolyzed alkoxy groups, some voids, or both.

A number of studies using X-ray and neutron scattering[26,27] have also been carried out on filled PDMS elastomers.[3,28]

2.2. Glassy Particles Deformable into Ellipsoidal Shapes. It is also possible to obtain reinforcement of a PDMS elastomer by polymerizing a monomer such as styrene to yield hard glassy domains within the elastomer.[29] Roughly spherical polystyrene (PS) particles are formed, and good reinforcement is obtained as is shown in a portion of Figure 3.

It is possible to convert the essentially spherical PS particles just described into ellipsoids.[4,30] First, the PS–PDMS composite is raised to a temperature well above the T_g of PS. It is then deformed and cooled while in the stretched state. The particles are thereby deformed into ellipsoids and retain this shape when cooled. Uniaxial deformations of the composite give prolate (needle-shaped) ellipsoids, and biaxial deformations give oblate (disc-shaped) ellipsoids.[30,31] This is shown schematically in Figure 3. Such ellipsoidal particles have been characterized using both scanning and transmission electron microscopy. This gives values for their axial ratios and provides a measure of the extent to which their axes were aligned in the direction of stretching. In these anisotropic materials, elongation moduli in the direction of the stretching were found to be significantly larger than those of the untreated PS-PDMS elastomer, whereas in the perpendicular direction they were significantly lower. This is shown in several portions of Figure 4.[30] Such differences were to be expected from the anisotropic nature of the systems. In the case of nonspherical particles in general, degrees of orientations are also of considerable importance. One interest here is the anisotropic reinforcements such particles provide, and there have been simulations to better understand the mechanical properties of such composites.[32,33]

2.3. Magnetic Particles. Incorporating reinforcing particles that respond to a magnetic field is important with regard to aligning even spherical particles to improve mechanical properties anisotropically. This and related information is given in Table 2.[4,15,34] Considerable anisotropy in structure and mechanical properties can be obtained, as was demonstrated for PDMS.[35] Specifically, the reinforcement is found to be significantly higher in the direction parallel to the magnetic lines of force.

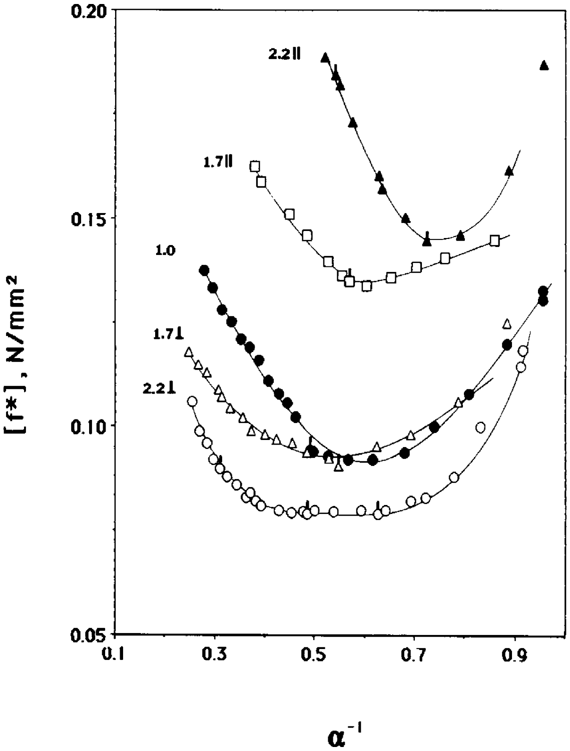

FIGURE 4. Stress–strain isotherms for PDMS–polystyrene composites.[30,81] The results are for the unfilled PDMS and the PDMS reinforced with particles that were either spherical or deformed into prolate ellipsoids. Values of the draw ratio during the deformation are indicated for each curve. In the case of the ellipsoidal particles, one curve corresponds to modulus measurements taken parallel to the direction of the stretching force used to deform (and orient) the particles, and the other was taken perpendicular to this direction. Reprinted with permission from ref 81. Copyright 1990 American Chemical Society.

Table 2. Electromagnetic Phases

type	examples	refs
magnetically responsive particles	ferrites	4
electrically semiconducting polymers	polyaniline	15
quantum dots	CdSe	34

2.4. Layered Fillers. Exfoliating layered particles such as the clays, mica, or graphite is being used to provide very effective reinforcement of polymers at loading levels much smaller than in the case of solid particles such as carbon black and silica.[36–38] Other properties can also be substantially improved, including increased resistance to solvents and reduced permeability and flammability. Some studies involving clays are described in Table 3[36–42] and on other layered fillers elsewhere.[43–46]

2.5. Polyhedral Oligomeric Silsesquioxanes (POSS). These fillers are cage-like silicon–oxygen structures and have been called the smallest possible silica particles.[47] The most common structure has eight silicon atoms, each carrying an organic group. The particles on which none of the groups are functionally reactive can be simply blended into elastomers such as PDMS using the usual mixing or compounding techniques. POSS molecules

Table 3. Montmorillonite Clays

type of polymer	examples	refs
elastomeric	poly(dimethylsiloxane)	39
	hydrocarbon elastomers	37
glassy	polystyrene	36
partially crystalline	nylons	40
rigid-chain	triphenylphosphate polymer	38
naturally occurring	chitosan	41
foamed	polysulfone	42

Table 4. Polyhedral Oligomeric Silsesquioxanes (POSS)

bonding functionality	polymers	refs
1	poly(dimethylsiloxane)	47
2	various copolymers	5
3 or higher	various (cross-linked) thermosets	48

Table 5. Nanotubes

types	polymers	refs
single-walled	poly(methyl methacrylate)	51
	polyacrylonitrile	52
multi-walled	polycarbonate	53
	polystyrene	52

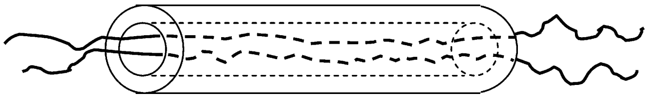

FIGURE 5. Polymer chains being threaded through a porous inorganic material such as a zeolite by polymerizing monomer that had been absorbed into one of the channels or cavities.

Table 6. Dual Fillers

filler 1		filler 2			
type	examples	type	examples	polymers	refs
particles	carbon black	layered filler	mica	nitrile rubber	54
	fly ash		mica	unsaturated polyester	55
	carbon black		clay	nylon 6	56

Table 7. Porous Fillers

porous fillers	polymers	refs
zeolites	polystyrene, poly(ethyl acrylate)	57,60
	poly(ethyl acrylate)	61
mesoporous silica	polystyrene, poly(ethyl acrylate)	57
silica nanotubes	polystyrene, poly(ethyl acrylate)	57

Table 8. Nanocatalysts

metal particle	type of polymer	polymer example	refs
Pd	water-soluble homopolymer	poly(vinyl pyrrolidone)	65
	anionic polymers	poly (methacrylic acid)	66
	cationic polymers	poly(diallyl dimethyl ammonium chloride)	67
	amphiphilic block copolymers	polystyrene-*b*-poly(ethylene oxide)	67
	latex (as support)	poly(vinyl pyrrolidone) on poly(vinylidene chloride) latex	67
Pt	water-soluble homopolymer	poly(vinyl pyrrolidone)	67
Ag, Au	water-soluble homopolymer	poly(ethylene oxide), poly(vinyl pyridine)	66

having one reactive functional group can be attached to a polymer as side chains. Those with two reactive groups can be incorporated into polymer backbones by copolymerization, and those with more than two can be used for forming cross-links, yielding network structures. Some relevant studies are described in Table 4.[5,47,48]

2.6. Nanotubes. Carbon nanotubes are also of considerable interest with regard to both reinforcement and possible increases in electrical conductivity.[49,50] There is considerable interest in characterizing the flexibility of these nanotube structures, in minimizing their tendencies to aggregate, and in maximizing their miscibilities with inorganic as well as organic polymers. Some studies of this type are referenced in Table 5.[51−53]

2.7. Dual Fillers. There can be a considerable advantage to using a combination of fillers of different types, for example, particles and layered sheets. One frequently obtains a synergistic effect in that the improvements in properties obtained are frequently more than expected from simple additivity. In addition, the first filler may have a solubilizing effect, making incorporation of the second easier. Relatively little has been done in this regard, but some relevant work is cited in Table 6.[54−56]

2.8. Porous Fillers. Some fillers such as zeolites are sufficiently porous to accommodate monomers, which can then be polymerized. This threads the chains through the cavities with unusually intimate interactions between the reinforcing phase and the host elastomeric matrix.[57−59] Such an arrangement is illustrated in Figure 5, and some relevant references are provided in Table 7.[57,60,61] Unusually good reinforcement is generally obtained. Also, because of the constraints imposed by the cavity walls, these confined polymers frequently show no glass transition temperatures or melting points.[33]

2.9. Fillers with Controlled Interfaces. By the appropriate choice of chemical structures, chains that span filler particles in a PDMS-based composite can be designed so that they are either durable, are breakable irreversibly, or are breakable reversibly.[62,63]

2.10. Silicification and Biosilicification. There has been some interest in generating silica-like particles using templates, as is done by Nature in biosilicification processes.[64] Various particle shapes have been obtained, but fibrous forms would be of particular interest if they self-assembled into anisotropic structures with anisotropic properties. Platelet forms of silica, on the other hand, would be an interesting synthetic analogue to the naturally occurring clays, particularly with regard to their possible abilities to provide reinforcement and decreased permeabilities at very low concentrations.

2.11. Nanocatalysts. A variety of catalytically active metal nanoparticles have been prepared by the reduction of metal salts. Generating them in a polymer solution and then drying them puts a protective polymer layer around the particles for increased shelf life and provides the possibility of increased reaction selectivity when the polymer-coated particles are redispersed in a reaction medium. Some examples are listed in Table 8.[65−67]

A specific example would be colloidal palladium nanocatalysts prepared by in situ reductions of palladium chloride immobilized and protected by either of two water-soluble polymers. The particle sizes and size distributions of the palladium colloids were determined by transmission electron microscopy, while their morphologies were investigated by small-angle X-ray scattering. Their selectivities as catalysts were determined by comparing the extents of hydrogenation of carefully chosen pairs of small-molecule olefins. There was found to be high hydrogenation selectivity, for example, with regard to cyclic versus noncyclic olefins. Selectivity should be improved by careful choice of the immobilizing polymer and by its use at relatively high concentrations. Some selectivity possibilities are illustrated in Figure 6.

The use of gel collapse to shrink a swollen polymer coating to reduce catalytic activity is illustrated in Figure 7. By careful choice of comonomers and compositions, the buildup of reactants could cause the collapse, and the resulting decrease in permeability would slow the reaction until more reactants were introduced. The ability to repeat this in cyclic sequences would make such a system a "chemical governor", in that limiting the rate of the reaction would parallel the mechanical device on some cars that limits their speed.

2.12. Theory and Simulations on Filler Reinforcement. Some relevant theory and simulations are described in Table 9.[68−76]

For example, Monte Carlo computer simulations have been carried out on a variety of filled elastomers[71] in an attempt to obtain a better molecular interpretation of how such dispersed phases reinforce elastomers. In the first step, distribution functions for the end-to-end vectors of the chains were obtained by applying Monte Carlo methods to rotational isomeric state representations of the chains.[77] Conformations of chains that overlapped with any filler particle during the simulation were rejected. The resulting perturbed distributions were then used in the three-chain elasticity model to obtain the desired stress−strain isotherms in elongation.

The filler particles were found to increase the end-to-end separations of the chains. These results on the chain-length distributions are in agreement with some subsequent neutron scattering experiments on silicate-filled PDMS.[78] The corresponding stress−strain isotherms in elongation showed substantial increases in stress and modulus with increase in filler content and elongation that are in at least qualitative agreement with experiment.

3. Polymer-Modified Ceramics

If the hydrolyses in silane precursor−polymer systems are carried out using relatively large amounts of the silane, then the silica generated can become the continuous phase with the elastomeric polysiloxane dispersed in it.[1,2] Some examples are described in Table 10.[4,8,79] The resultant composite is a polymer-modified glass or ceramic, frequently of very good transparency.

Properties of particular interest are modulus, impact resistance, ultimate strength, maximum extensibility, viscoelastic responses, and transparency. The hardness of such a composite, for example, can be varied by control of the molar ratio of alkyl R groups to Si atoms, as is illustrated for PDMS in Figure 8.[80] Low values of R/Si yield a brittle ceramic, and high values give an elastomer. The most interesting range, R/Si $\cong$ 1, can yield a relatively tough ceramic of increased impact resistance.

Some improvements in impact strength in such composites are illustrated in Figure 9.[79] Specifically, impact strengths of some PDMS−SiO_2 samples were determined by the Charpy pendulum test and by the falling-weight test.[79] As can be seen from the figure, the larger the amount of PDMS used, the higher the impact strength. When the material is subjected to an impact test, the rubbery PDMS component can absorb a great deal of energy by motions of the PDMS chains and can ameliorate the growth of cracks and fracture. Microscopy of fracture surfaces of brittle samples typically shows smooth fracture surfaces, as was observed in the case of the composite

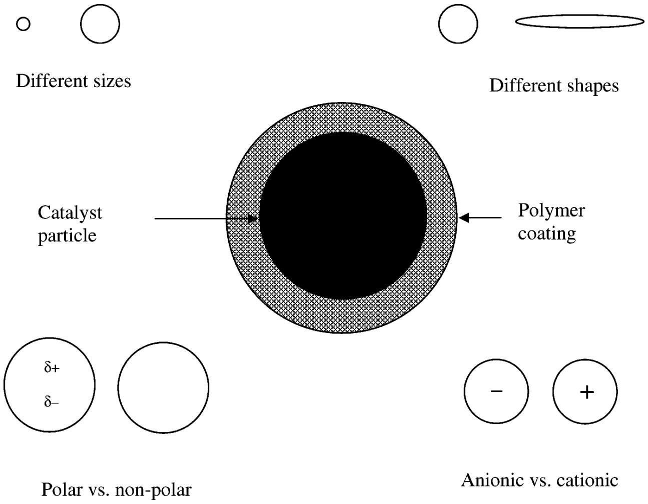

FIGURE 6. Possible ways a polymer coating on a nanocatalyst particle could improve reaction selectivity, for example, on the basis of size, shape, polarity, or charge.

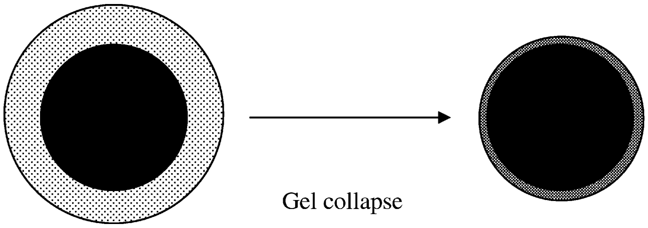

FIGURE 7. The possible use of the collapse of a polymer coating on a nanocatalyst particle to hinder approach of a substrate and thus to decrease the rate of a chemical reaction.

Table 9. Some Relevant Theory and Simulations

approach	goal	refs
analytical theory	reinforcement	68−70
Monte Carlo simulations	chain conformations around filler particles and reinforcement	71, 72
molecular dynamics simulations	chain conformations around filler particles and reinforcement	73−75
self-consistent field theory with Markov chain statistics	dispersion of polymers into clay galleries	76

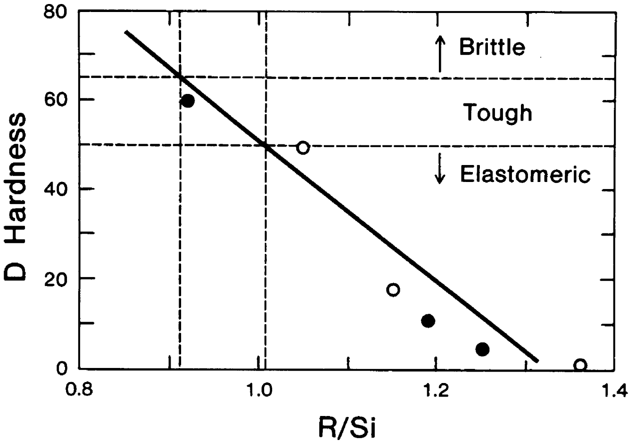

FIGURE 8. The hardness of a silica–PDMS composite as a function of the relative numbers of R alkyl groups and Si atoms in the silica. Reprinted from ref 80 with kind permission of Springer Science and Business Media (copyright 1987).

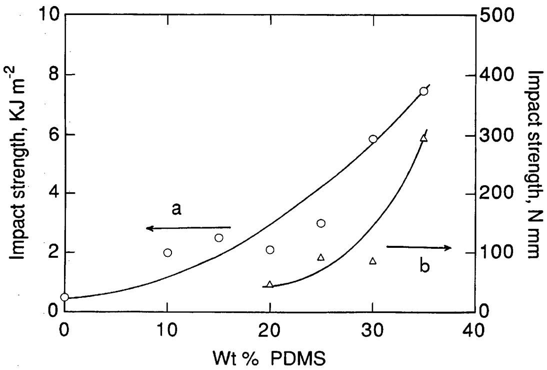

FIGURE 9. Dependence of two estimates of the impact strength on the amount of PDMS in PDMS-modified SiO_2 glasses.[79] One curve (a) corresponds to results obtained from the Charpy swinging-pendulum test and the other (b) to the falling-weight test. Reprinted with permission from ref 79. Copyright 1995 The Society of Polymer Science, Japan.

Table 10. Polymer-Modified Ceramics

ceramic continuous phase	polymeric dispersed particles	refs
SiO_2	poly(dimethylsiloxane)	79
TiO_2	both elastomers and thermoplastics	4, 8
ZrO_2	both elastomers and thermoplastics	4

silica samples having relatively low PDMS contents. In contrast, samples with high PDMS contents had fracture surfaces showing some degree of “whitening” or shearing.[79] This suggests a ductile, energy-absorbing response to the impacts, with increased resistance to crack propagation.

4. Conclusions

One of the most useful outcomes from this rather personal survey would be to inspire others to enter this interesting and challenging area of polymer science and engineering and to contribute to the investigation and applications of some of these intriguing nanocomposites.

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