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Symposium Review

Some Novel Polysiloxane Elastomers and Inorganic-Organic Composites[1]

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This review describes the use of polysiloxanes in developing two novel types of materials. In the first approach, polysiloxane elastomers were prepared so as to have unusual network chain length distributions, thereby improving their ultimate properties. The technique involved end linking mixtures of very short and relatively long functionally terminated chains of poly(dimethylsiloxane) to give bimodal networks. Such (unfilled) elastomers show very large increases in reduced stress or modulus at high elongations because of the very limited extensibility of the short chains present in the networks. This non-Gaussian behavior also appears in compression or biaxial extension, as obtained by inflation of sheets of the material. Non-Gaussian theories taking into account this limited chain extensibility were found to be in good agreement with experiment. The composites were prepared using techniques very similar to those employed in the sol-gel pproach to ceramics. Alkoxysilanes or related metaloorganic materials were hydrolyzed in the presence of polymer chains, for example, polysiloxanes and polyoxides, that have reactive end groups such as hydroxyls. The end groups bond the polymer chains into the silica or related ceramic material formed in the hydrolysis, thus forming inorganic-organic composites. When the polymer chains are in excess, they constitute the continuous phase, with ceramic-type material appearing as reinforcing domains. 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 were characterized by stress-strain measurements, density determinations, differential scanning calorimetry, electron microscopy, X-ray and neutron scattering, and NMR spectroscopy.

KEY WORDS: Bimodal elastomers; reinforcing fillers; end linking; modulus; ultimate properties; silica; electron microscopy; scattering; nuclear magnetic resonance.

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INTRODUCTION

The most serious problem in obtaining structure-property relationships in the area of rubberlike elasticity is the difficulty in getting independent information on the structure of the elastomer being characterized [1–8]. The very network structure required for the recoverability aspect of this type of elasticity makes these materials essentially intractable. Specifically, they are inherently insoluble in all solvents, and one must therefore forfeit the techniques widely used to characterize polymers by measuring the properties of their solutions.

If, however, the networks are formed by end linking functionally terminated chains, instead of haphazardly joining chain segments at random, then the very nature of the process can provide the desired structural information. If the end-linking reaction can be taken essentially to completion, then the functionality of the cross-links is the same as that of the end-linking agent, and the molecular weight M_c between cross-links is the same as that of the starting chains prior to their being end linked [1–8]. This information thus provides a direct estimate of the cross-link density in an elastomer.

There have been a number of interesting studies and applications of such "model," "ideal," or "tailor-made" elastomers [1–8]. One example is the use of a known cross-link density to predict a value for the modulus, which can then be compared to the experimental value to estimate any contributions from interchain entanglements. Since a series of end-linking agents containing various numbers of functional groups is readily available, networks of varying junction functionality can be easily prepared. The way the moduli of such networks varies with functionality can then be used to provide an additional test of theory. These very specific end-linking techniques have also been used to prepare interpenetrating networks, by using two different (noninterfering) end-linking reactions for the two networks. If the end linking is carried out in the presence of cyclic molecules, then the fraction of the cyclics trapped due to being threaded by the network chains can be used to obtain information on the shapes or spatial configurations of the cyclic molecules. Finally, if the stoichiometry is intentionally unbalanced by having more chain ends than reactive groups from the end-linking molecules, networks of known numbers of dangling chain ends can be prepared and used to characterize the effects of these network irregularities on mechanical properties.

The present review, however, illustrates the utilization of this technique for (i) the preparation of networks that have a bimodal distribution of network chain lengths and, as a result, unusually good ultimate properties and (ii) the determination of the effect of such bimodal distributions on strain-induced crystallization through the study of bimodal networks that are crystallizable.

The second major area of interest in this review derives from the fact that there are a number of disadvantages to reinforcing an elastomer by the usual technique of blending a finely divided filler (such as carbon black or silica) into a polymer before cross-linking it. A number of alternative, novel techniques have therefore been under development. Examples of such new techniques are discussed below. They are readily extended to the preparation of composites in which, by phase inversion, the continuous phase is the ceramic-type material, with the polymer chains as the dispersed phase.

BIMODAL NETWORKS

Elongation Studies

Noncrystallizable Bimodal Networks

End linking a mixture of very short and relatively long chains yields a bimodal distribution of network chain lengths. These elastomers can have very peculiar distributions, as illustrated in Fig. 1. The most interesting properties are observed when the mole percentage of the short chains is very high, for example, 96%. Because the molecular weight of the short chains is so much lower than that of the long chains, however, they represent only a small weight percentage of the material. Such networks have generally been prepared from poly(dimethylsiloxane) (PDMS), a polymer which is noncrystallizable under most conditions because of its very low melting point (~ −40°C). These bimodal networks were in fact first studied at a sufficiently high temperature (25°C) that contributions from strain-induced crystallization were avoided. The properties thus determined were of considerable interest since they indicated that the bimodal nature of the distribution improved the ultimate properties of the elastomer [6–10]. Specifically, the values of the ultimate strength were very high considering the correspondingly high values of the maximum extensibility. They were thus unusually tough elastomers. It was also found to be possible, however, to improve the impact resistance of highly cross-linked thermosets by end linking long chains into these predominantly short-chain materials [8].

Measurements of the mechanical and optical properties of these networks as a function of temperature and degree of swelling demonstrated that crystallization or other intermolecular organization was not the origin of the unusual properties [9]. They were thus seen to be intramolecular. In addition, infrared and Raman spectroscopy indicated that bond angle

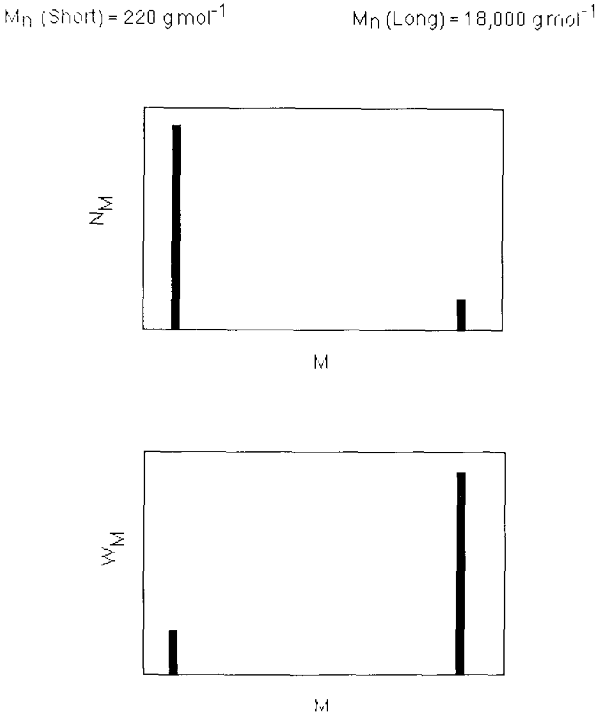

Fig. 1. Schematic distributions for a bimodal elastomeric network having short and long chains of the specified values of the number-average molecular weight. The upper sketch shows the number distribution, and the lower, the weight distribution.

distortion was generally of relatively minor importance [11]. The observed increases in modulus and ultimate strength therefore have to be due to the limited extensibility of the very short chains in the networks.

Characterization of this limited chain extensibility requires, of course, a non-Gaussian distribution function [12] for the end-to-end separation *r* of the short network chains. Ideal for this case is the distribution obtained by Fixman and Alben [13] and recommended particularly for very short chains. It was found to give a much better approximation to the highly reliable Monte Carlo results than does the Gaussian limit, particularly in the most important region of very high extension [14].

The parameters in the Fixman–Alben distribution can be adjusted to give very good approximations to the most reliable distributions for PDMS chains, namely, those obtained from Monte Carlo simulations. This is illustrated in Fig. 2 [14]. These Fixman-Alben distributions can then be used in the standard equations for rubberlike elasticity (6, 12) to calculate

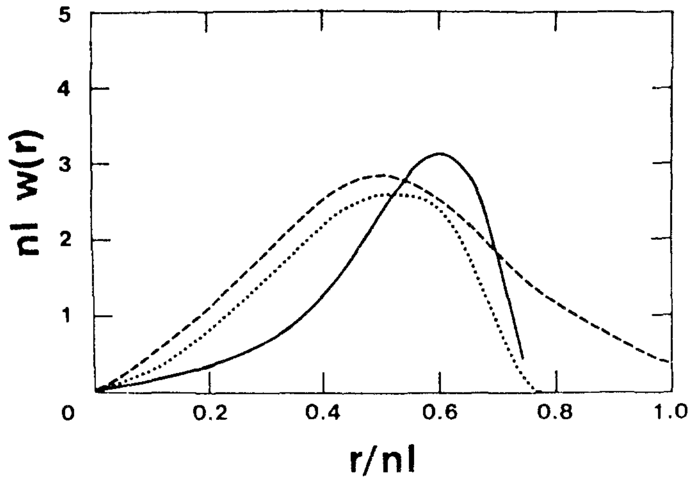

Fig. 2. Radial distributions $w(r) = 4\pi r^2 W(r)$ obtained for poly(dimethylsiloxane) (PDMS) chains having 20 skeletal bonds [14]. The solid line is from a Monte Carlo simulation, the dashed line the Gaussian approximation, and the dotted line the Fixman–Alben result.

stress-strain isotherms in elongation for bimodal PDMS networks. Typical results are shown in Fig. 3 [14]. The observed upturns in the modulus or reduced stress [f^*] at high values of the elongation α are well reproduced by the calculated results. The overall results are thus quite satisfactory and would encourage other applications of these distributions, for example, to segmental orientation in networks containing very short chains.

Crystallizable Bimodal Networks

Experiments on crystallization in PDMS bimodal networks were very difficult and led to ambigous results, presumably because of the very low melting point of the polymer. For this reason the bimodal networks chosen for these types of experiments were prepared from poly(ethylene oxide), which has a relatively high melting point (~65°C) and thus readily undergoes strain-induced crystallization. Such crystallization in an elongated elastomer is very important since it can greatly increase its toughness. The aspect of relevance here is the use of these networks to elucidate the dependence of strain-induced crystallization on network chain length distribution. Decrease in temperature was found to increase the extent to which the values of the ultimate strength of the bimodal networks exceed those of the unimodal ones [19]. This suggests that bimodality facilitates strain-induced crystallization.

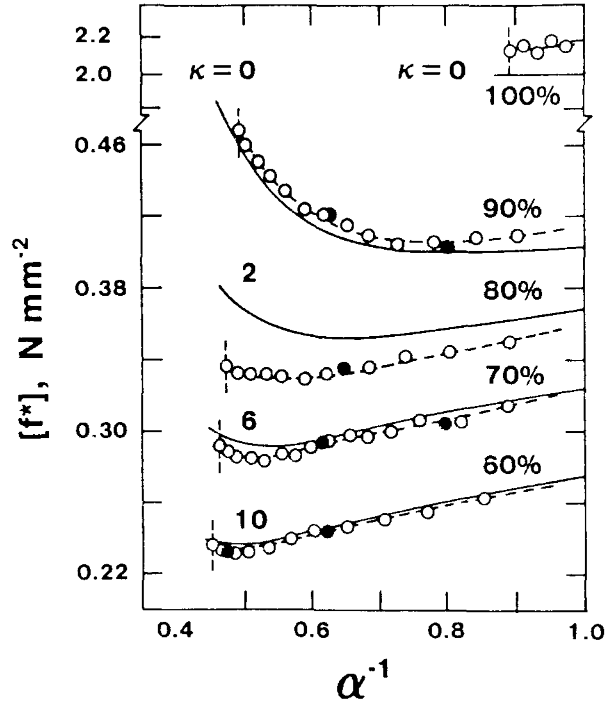

Fig. 3. Mooney–Rivlin plots (6, 12) for some bimodal PDMS networks (M_c = 660/18,500 g mol^{-1}) [14]. The circles and dashed lines represent experimental data, with the filled ones locating data taken out of sequence to test for reversibility. The solid curves give the results of the theoretical calculations. Each set of experimental data and corresponding theoretical curve is labeled with the mole percentage of short chains present in the network. The values of κ specified for the theoretical curves are those required in the Flory–Erman theory [15–18].

Other Types of Deformation

Bimodal PDMS networks have also been found to have unusually good mechanical properties in other types of deformation. For example, they have been studied in biaxial extension (equivalent to compression) by inflating sheets of the material. Typical results are shown in Fig. 4 [20]. As can readily be seen, reinforcing upturns in the modulus occur for both high extensions ($\alpha > 1$) and high compressions ($\alpha < 1$). Other studies have shown these materials to have unusually good tear strengths [21, 22].

NOVEL REINFORCING FILLERS

There are a number of disadvantages to reinforcing an elastomer by the usual technique [23, 24] of blending a finely divided filler (such

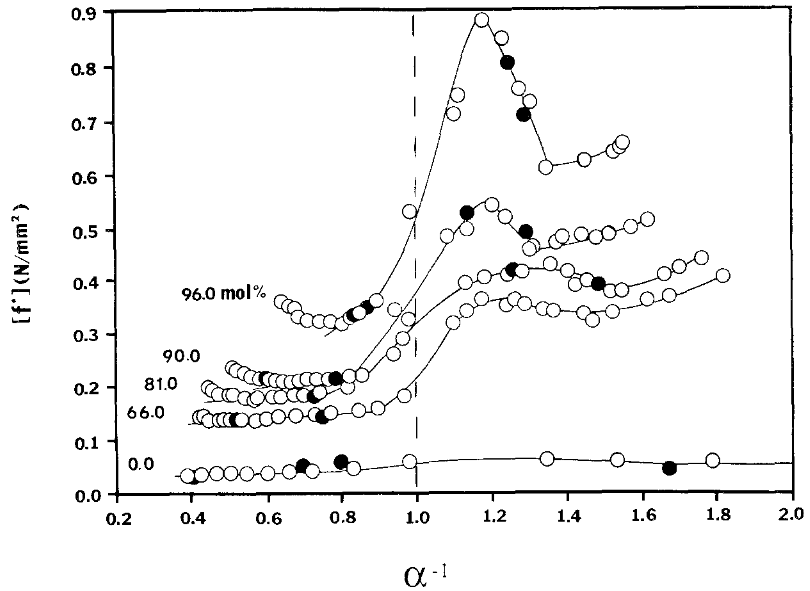

Fig. 4. Representative stress-strain isotherms for (unswollen) unimodal and bimodal PDMS networks in uniaxial and biaxial extension at 23°C [20]. Each curve is labeled with the mole percentage of the much shorter chains ($M_n = 550$ vs 18,000 g mol^{-1}). The open circles represent data points measured with increasing deformation, and the filled circles data obtained out of sequence to test for reversibility.

as carbon black or silica) into a polymer before cross-linking it [25]. A number of alternative, novel techniques are therefore also under development. Examples of such techniques are presented here, with a strong emphasis on results beyond those described in three recent reviews, which are at least partly on the same subject [6, 7, 26]. They include hydrolysis of organometallic compounds within a polymeric matrix to give ceramic particles such as silica and titania. The semi-inorganic polymer PDMS has been most studied in this regard. The case where the ceramic predominates and becomes the continuous phase is also discussed. Finally, an alternative approach where monomers such as styrene or methyl methacrylate are polymerized *in situ* to give reinforcing glassy polymers is also described.

In the case where the continuous phase is elastomeric, the subject of greatest interest is the reinforcement provided by the ceramic-like fillers. It is easy to switch the focus, however, so that the elastomer is viewed as only a matrix in which the ceramic materials are being generated. In this "matrix isolation" approach [27], X-ray and neutron scattering techniques, for example, can be used to obtain information that transcends these particular systems. It should be useful in a variety of areas, including the new sol-gel technique for preparing ceramics of carefully controlled ultrastructure [28–33]. If the concentration of the metalloorganic material being hydrolyzed is very large, phase inversion can occur. The ceramic is then the continuous phase and the polymer chains dispersed in it can be used to modify its properties considerably.

The following sections describe these "*In-Situ* Precipitations," "Polymer-Modified Ceramics," and "*In Situ* Polymerizations."

In Situ Precipitations

Typical Hydrolysis Reactions

The most important reaction in this area is the acid- or base-catalyzed hydrolysis of tetraethoxysilane (TEOS), absorbed into a polymer. Under the assumption that the condensation is complete, the reaction is described by the chemical equation [6, 26]

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \qquad (1)$$

Analogous reactions [28–33] can be carried out, however, on titanates [34–36], aluminates [37], and zirconates [38]. In the sol-gel technique, the process first gives a (swollen) gel, which is then dried, fired, and densified into a final, monolithic piece of silica [28–33]. There have now been a number of additional studies using essentially the same reactions, but in a very different context [6, 26]. Specifically, the hydrolysis reactions are carried out within a polymeric matrix, with the ceramic frequently generated in the form of very small, well-dispersed particles. When the matrix is an elastomer, these particles provide the same highly desirable reinforcing effects obtained by the usual blending of a filler (such as carbon black) into polymers (such as natural rubber) prior to their being cross-linked ("cured") into tough elastomers of commercial importance [23, 24].

In the studies cited, these reactions were carried out in three ways [6, 26]. In the first, the polymer is cross-linked and then swelled with the organometallic, which is then hydrolyzed *in situ.* In the second, hydroxyl-terminated chains are blended with enough TEOS to both end link them and provide silica by the hydrolysis reaction. Thus, curing and filling take place simultaneously, in a one-step process. In the final technique, TEOS is blended into polymer having end groups (e.g., vinyls) that are unreactive under hydrolysis conditions. The silica is then formed in the usual manner [Eq. (1)], and the product dried. The resulting slurry of polymer and silica is stable and can be cross-linked later using any of the standard cross-linking techniques, such as vinyl-silane coupling [6, 39, 40].

Some typical reinforcement results, in pure shear, are shown in Fig. 5

[41]. The increases in modulus at high elongations are seen to be quite substantial.

The kinetics of these sol-gel reactions are also being studied [42] using air-pressure deformation measurements [43] on the gels, in a manner similar to that used to characterize thermoreversible polyethylene gels [44]. Some typical results are shown in Fig. 6 [42]. The modulus is

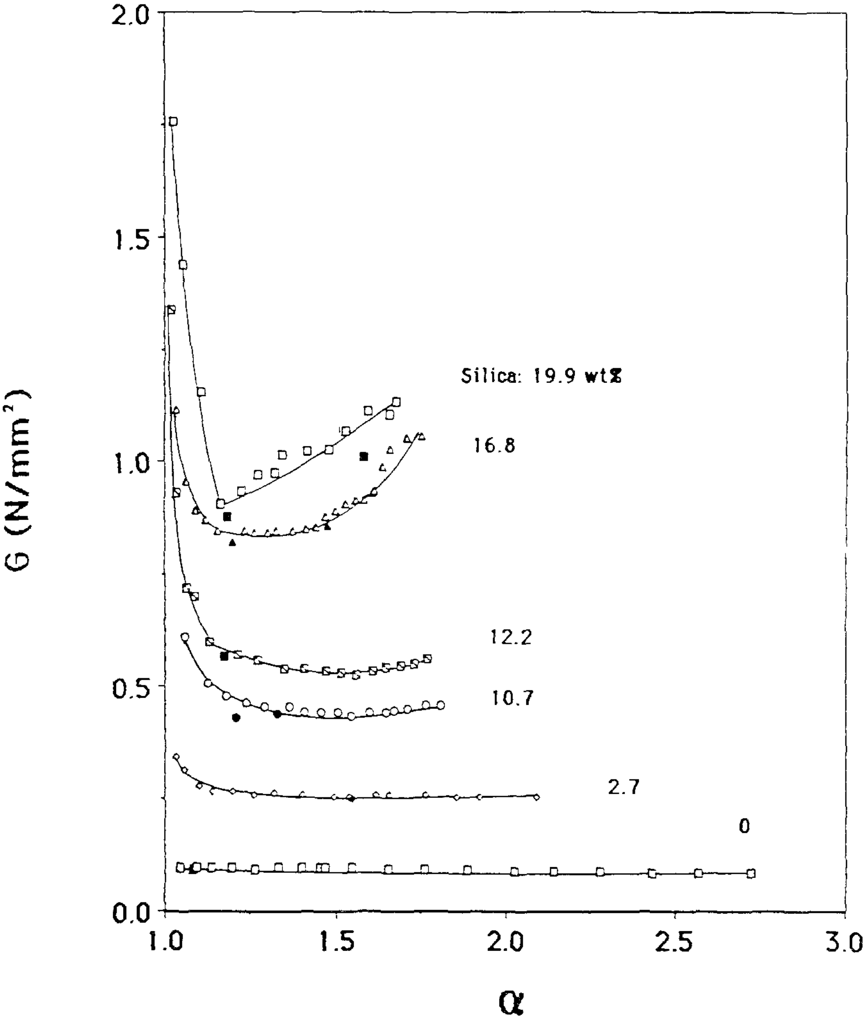

Fig. 5. Stress-strain isotherms in pure shear for PDMS elastomers containing the specified amounts of *in situ* precipitated silica [41]. The silica was generated from TEOS which had been absorbed into the network after it was cross-linked.

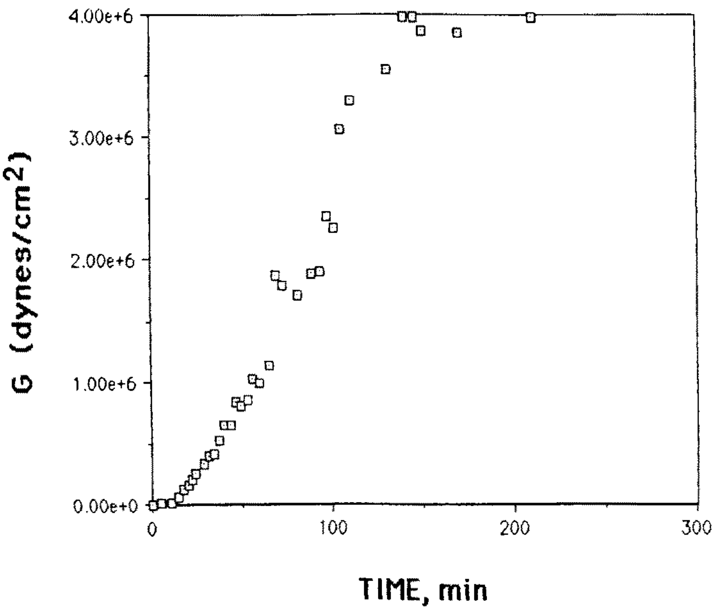

Fig. 6. The deformation modulus shown as a function of time for the base-catalyzed hydrolysis of tetraethoxysilane in a water-ethanol system [42].

seen to remain at zero for a considerable period of time, while the hydrolysis, condensation, and branching reactions are occurring. As soon as the branching is sufficiently extensive to cause cross-linking, after approximately 10 min in this case, gelation occurs and the modulus begins to develop. Although these preliminary data scatter, the curve does seem to be S-shaped, with the modulus asymptotically reacing its equilibrium value. It is conceivable, however, that even after the modulus has reached this maximum value, considerable molecular reorganization is occurring.

Comparisons Among Various Silica-Based Fillers

There is a variety of ways to generate silica-type fillers useful for reinforcing PDMS networks, only three of which are described above. The extent to which such fillers provide reinforcement was characterized in a recent study [45]. The materials and techniques employed were (i) incorporating a commercial silica which has been treated with hexamethyldisilazane, (ii) incorporating silica which had been precipitated from a silicate in an aqueous dispersion with PDMS, (iii) precipitating silica directly into PDMS during its curing, (iv) precipitating silica directly into a swollen PDMS network after it was cured, (v) incorporating silica prepared from tetraethoxysilane (TEOS) and containing some PDMS, and

(vi) incorporating silica prepared from partially hydrolyzed TEOS and also containing some PDMS. The resulting filled elastomers showed the largest values of the ultimate strength in the case of iv and vi and the largest value of the rupture energy for iv.

Other Polymers

Most of the studies to date have involved PDMS, primarily because of its great miscibility with TEOS. Similar studies [46] on the related polymer, poly(methylphenylsiloxane), however, are of considerable importance. This is because of the stereochemically irregular structure of the polymer, which prevents it from undergoing strain-induced crystallization [6, 47]. Good *in situ* generated reinforcement was also achieved in this polymer, suggesting that such crystallization is not important for this type of reinforcement [46].

The same techniques have also been shown to give good reinforcement in polyisobutylene elastomers [48] and in poly(ethyl acrylate) [49]. In the latter case, it appears that the precipitation can be carried out during an emulsion polymerization [49].

Other Ceramic-Type Fillers

Silica particles in PDMS elastomers can be a problem at high temperature, since the silanol groups on their surfaces can cause degradation of the polymer [35, 50]. For this, and other, reasons, a variety of other fillers has been precipitated into this polymer. Included are titania (TiO_2) [34–36], alumina (Al_2O_3) [37], and zirconia (ZrO_2) [38].

These nonsilica fillers also provide good reinforcement. One interesting difference, however, is the observation that the stress-strain isotherms in these cases frequently have much better reversibility [36]. This is presumably due to different interactions between the surface groups present on these particles and the polar Si–O–Si linkages in the PDMS chains making up the elastomeric matrix.

Aging Effects

Permitting precipitated silica particles to remain in contact with their aqueous catalyst solution can permit them to "age" or "digest" [51, 52]. Electron microscopy results suggest that some reorganization is occurring, with the particles becoming better defined, more uniform in size, and possibly even less aggregated. There seem to be interesting parallels with "Ostwald ripening" in the area of colloid science [53].

Density Measurements

Comparisons between the values of weight percentage filler obtained from density measurements and the values obtained directly from weight increases can give very useful information on the filler particles. For example, the fact that the former estimate is smaller than the latter in the case of silica-filled PDMS elastomers [54] indicates that there are probably either voids or unreacted organic groups in the filler particles.

Calorimetry

Differential scanning calorimetry measurements at low temperatures were carried out on PDMS elastomers containing *in situ* precipitated silica [55]. The presence of the silica was found to reduce both the extent of crystallization and the rate of crystallization when the elastomers were in the unstretched state. This is in interesting contrast to similar studies of PDMS in the stretched state, where the filler may facilitate the crystallization process, for example, by decreasing the effective lengths of the network chains [56].

Electron Microscopy

Both transmission [6, 26, 51] and scanning [57] electron microscopy have been used to characterize these novel composite materials. The information obtained in this way includes (i) the nature of the precipitated phase (particulate or nonparticulate), (ii) the average particle size, if particulate, (iii) the distribution of particle sizes, (iv) the degree to which the particles are well defined, and (v) the degree of agglomeration of the particles.

One interesting result of this type is the conclusion that basic catalysts generally yield particles that are well defined, whereas acidic catalysts yield particles that are rather "fuzzy" [26, 51]. This conclusion is in agreement with results obtained earlier in sol-gel ceramics investigations [58].

Scattering Studies

A number of X-ray and neutron scattering studies have been carried out on these filled elastomers [6, 26, 59, 60]. Although the results are generally consistent with those gotten by electron microscopy, there are some intriguing differences. Of particular interest is the observation that some fillers which appear to be particulate in electron microscopy appear to consist of a continuously interpenetrating phase by scattering measurements [59, 60]. Additional comparisons could certainly be very illuminating in this regard.

Nuclear Magnetic Resonance (NMR) Spectroscopy

It is also possible to use ^1H and ^{29}Si magic angle spinning NMR spectroscopy and ^1H NMR two-dimensional Fourier-transform spin-echo methods to image the PDMS-SiO_2 composites [32, 61]. These nondestructive techniques are particularly useful for characterizing nonuniform silica distributions in these materials.

POLYMER-MODIFIED CERAMICS

The technique of hydrolyzing an organometallic substance such as an alkyl silicate can be generalized to make the silica generated the continuous phase, with domains of PDMS dispersed in it. A great deal of the important work in this area has been carried out by H. K. Schmidt, G. L. Wilkes, and others [28–33, 62–64]. This application requires, of course, relatively high concentrations of the silicate. By varying its amount, composite materials can be obtained, ranging from relatively soft elastomers, to tough hybrid materials, to brittle ceramics [62–64]. Some typical results are shown in Fig. 7 [65], where this change is brought about by decreasing the amount of PDMS (increasing the amount of silica) in a PDMS–SiO_2 composite. In some cases [60], bicontinuous systems can result, possibly through spinodal decompositions. In all of these cases, important properties to be correlated with composition include impact resistance, ultimate strength, maximum extensibility, and viscoelastic effects.

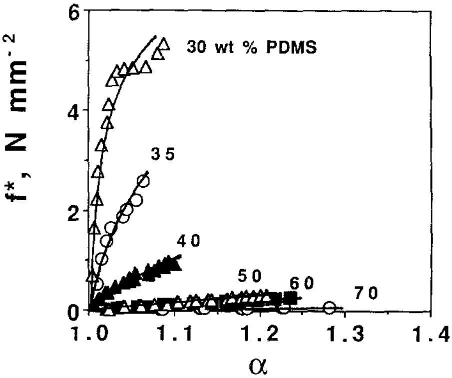

Fig. 7. The nominal stress shown as a function of elongation for PDMS-SiO_2 composites having various amounts of PDMS, of molecular weight 1700 g mol^{-1} [65].

IN SITU POLYMERIZATIONS

Isotropic Systems

It is also possible to obtain reinforcement by polymerizing a monomer such as styrene to yield hard glassy domains within the elastomer [66]. In PDMS, low concentrations of styrene give a low molecular weight polymer that acts more like a plasticizer than a reinforcing filler. This is shown by the stress-strain results obtained, for example by the initial decrease in the energy of rupture. This conclusion is supported by the absence of evidence for polystyrene (PS) particles at lower styrene concentrations [66]. Polyisobutylene has also been reinforced in this manner [67]. In both cases, the particles are roughly spherical and the system isotropic. The particles can be deformed into prolate or oblate ellipsoids, however, by deforming the elastomer uniaxially or biaxially above the T_g of PS and then cooling it in the deformed state [57].

The glassy particles thus generated are relatively easy to extract from the elastomeric matrix, which means that there is little effective bonding between the two phases. It is possible, however, to get excellent bonding onto the filler particles. One way is to include some $R'Si(OC_2H_5)_3$ in the hydrolysis, where R′ is an unsaturated group. The R′ groups on the surfaces of the particles then participate in the polymerization, thereby bonding the elastomer chains to the reinforcing particles [68]. Alternatively, the $R'Si(OC_2H_5)_3$ can be used as one of the end-linking agents, placing unsaturated groups at the cross-links [69]. Their participation in the polymerization would now tie the PS domains to the elastomer's network structure.

The PS domains have the disadvantage of having a relatively low glass transition temperature T_g (~100°C) [70] and being totally amorphous. Above T_g they would therefore soften and presumably lose their reinforcing capability. For this reason, similar studies have been carried out using poly(diphenylsiloxane) as the reinforcing phase [71]. It has a relatively high T_g of 49°C, is crystalline, and has an extraordinarily high melting point of about 500°C [72, 73].

Anisotropic Systems

It is possible to convert the essentially spherical PS domains described above to rod-like ellipsoidal particles [57]. First, the PS-elastomer composite was raised to a temperature well above the T_g of PS. It was then stretched uniaxially and cooled while in the stretched state. The particles were deformed into prolate ellipsoids and retained this shape when cooled. When the deforming force was removed, the elastomer was observed to retract, but only part of the way back to its original dimensions. The particles themselves were characterized using scanning and transmission electron microscopy and found to have axial ratios of approximately 2 and to have their axes preferentially oriented in the direction of the high-temperature stretching. The reinforcement they provided was characterized using stress-strain measurements in elongation at room temperature. In these anisotropic materials, the modulus in the direction parallel to the original stretching direction was found to be significantly higher than that of the untreated (isotropic) PS-PDMS elastomer, whereas in the perpendicular direction it was significantly lower.

It is also possible to generate oblate ellipsoids by stretching such a PS-PDMS elastomer biaxially, for example, by inflation of a sheet of the material. Such experiments have been carried out [74].

ZEOLITE FILLERS

One of the main problems with the fillers typically used to reinforce elastomeric materials is the fact that they are amorphous. A better

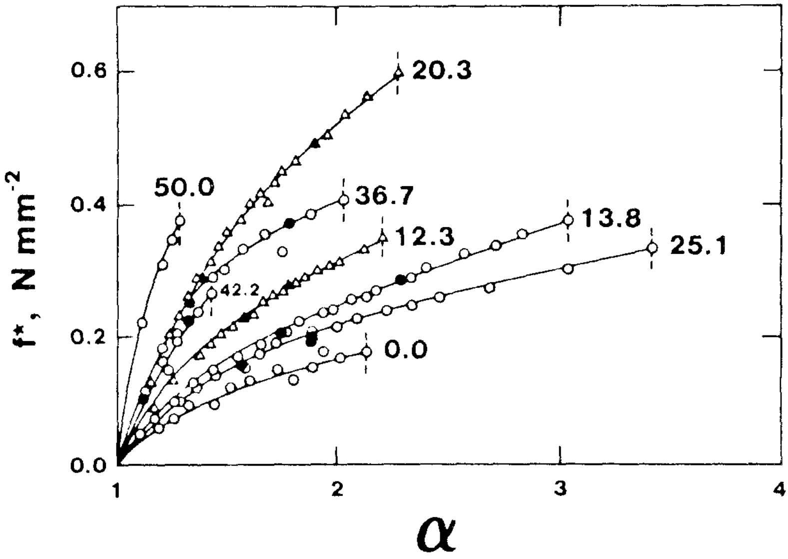

Fig. 8. Stress-strain isotherms at 25°C for zeolite-filled PDMS elastomers [75]. The circles represent results obtaining using a zeolite with a relatively small cavity (diameter of 3 Å), and the triangles using a zeolite with a significantly larger cavity (diameter of 13 Å). The open symbols represent data points measured with increasing deformation, and the filled symbols data obtained out of sequence to test for reversibility. Each curve is labeled with the weight percentage zeolite present in the elastomer, and the vertical dashed lines locate the rupture points.

molecular understanding of how reinforcing materials in general improve the mechanical properties of an elastomer could result from the use of particles that are crystalline and of known structure. The zeolites meet these criteria and have the additional intrigiung advantage of having cavities of varying sizes. Some reinforcing effects of such zeolite fillers in PDMS elastomers are shown in Fig. 8 [75]. The zeolite having cavities with a diameter of 13 Å are much more effective at reinforcement than the one having cavities with a diameter of 3 Å. It is tempting to conclude that the former provides better reinforcement because its cavities are large enough to permit penetration by the PDMS chains. This is pure conjecture, however, and additional experiments (such as neutron scattering) will have to be carried out to test this idea.

ACKNOWLEDGMENTS

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