Development in Organic-Inorganic Hybrid Elastomers Prepared by the Sol-Gel and Related Processes

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The efforts to obtain organic-inorganic hybrid materials are described from a viewpoint of using elastomeric matrix to accommodate inorganic rigid component and the sol-gel reactions to obtain hybrid materials. In the development of inorganic fillers for the reinforcement of rubbers, silane coupling agents became used for a better adherence of the interface between organic matrix and inorganic filler surface. Moisture curing by 3-aminopropyl triethoxysilane of halogen-containing rubbers in the presence of silica particles enabled us to conduct curing and reinforcement simultaneously. *In situ* formation of silica particles in elastomeric matrix was achieved by conducting the sol-gel process of tetraethoxysilane (TEOS) in the rubbery matrix. Increase of modulus and tensile strength at break was recognized, which suggests inclusion of silica particles in vulcanizates. The sol-gel process on TEOS and triethoxysilyl-terminated polyethers resulted in the formation of organic-inorganic hybrid gels, the structure and dynamic mechanical properties of which are described.

KEY WORDS : Elastomer/ Sol-gel process/ Moisture cure/ Silica/ *In situ* reinforcement/ Organic-inorganic hybrid

1. INTRODUCTION

Rubber is a class of polymeric materials, which is expected to show rubbery elasticity when in use. Natural rubber is noted for its versatility as an elastomeric material.[1,2] Synthetic rubbers which appeared later became of general use after compounding of carbon black as an effective reinforcer.[3,4] Other than carbon black, only silica has been known as such in spite of formidable investigations to develop reinforcing fillers for synthetic rubbers.[3-5]

Conventionally, a silica-rubber composite or a silica-reinforced rubber is prepared by the mixing and compression molding curing techniques. A hydrated silica of particle size ranging from 20 to 80 nm is typically used for reinforcing rubbers. Because of the small size and large specific surface area, the incorporation of silica into rubbers *via* the normal mixing techniques causes viscosity build up. It can also deactivate commonly used curing agents and accelerators to result in the reduction of optimum cure. These problems are partially overcome or minimized by specific additives and mixing procedures.[6]

The other important difficulty lies on the incompatibleness of inorganic silica filler with organic rubber. The developments for overcoming this difficulty by making use of the sol-gel process[7,8] are described in this report. This approach takes advantage of the sol-gel process

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which can be carried out at much lower temperature than the conventional methods of inorganic glass synthesis.

2. EFFECT OF SILANE COUPLING AGENT ON RUBBER-FILLER SYSTEM

For the effective reinforcement of rubbers, it has been known that a few conditions are requested for fillers. They have to show specific physical and chemical properties: to be very fine particles the diameter of which is of sub-microns is necessary and they also should have a very large surface area and chemisorption ability. Coupling agents are assumed to enhance the surface chemical reactivity toward rubber molecules to result in a better dispersion of inorganic fillers in the rubber matrix.[9] One example of reactions of a silane coupling agent is shown in Figure 1.

The reactions involved are hydrolysis of alkoxysilyl group and the following condensation of silanol groups, which are essentially the same reactions used in the sol-gel process. The chemical bonding between inorganic filler and rubber molecule is assumed to increase the compatibility between the two. In fact, we found that the silica grafted with polybutadiene (PB-*g*-Si) was a better reinforcer for butadiene rubber than silica as it was.[10] Silane coupling agent having vinyl group is expected to eliminate the procedures to synthesize PB-*g*-Si.
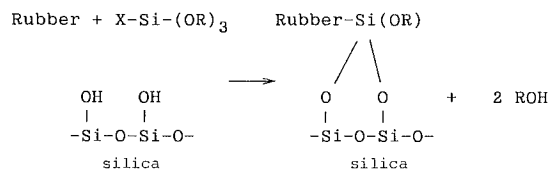
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Rubber + X-Si-(OR)₃    Rubber-Si(OR)
                                  / \
   OH   OH          ⟶          O   O    +   2 ROH
    |    |                      |   |
  -Si-O-Si-O-                 -Si-O-Si-O-
      silica                      silica
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Figure 1.   Reaction scheme of silane coupling agent for rubber/silica composite.   X = NH_2, CH_2 = CH, SH, epoxy etc.

3. MOISTURE CURING OF RUBBER/SILICA MIXTURE

Moisture or silane cure of halogen-containing rubber by 3-aminopropyl triethoxysilane (APS) is schematically shown in Figure 2.[11-15] Again, hydrolysis and the following condensation of alkoxysilyl groups are the key reactions. The interesting points of this technology include a good possibility of continuous process for curing rubbers. From a viewpoint of reinforcement, the moisture cure in the presence of silica particles is most interesting. The resulting composite was assumed to be represented as shown in Figure 3, and proved to have excellent tensile properties.[11,13,15]

APS cured 1-chlorobutadiene-butadiene rubber (CB-BR)/silica was under pulsed nuclear magnetic resonance measurement by spin echo technique.[11] This method enabled us to evaluate the volume fraction of immobilized layer which gave rise to thickness of the layer by Equation (1)[16,17]

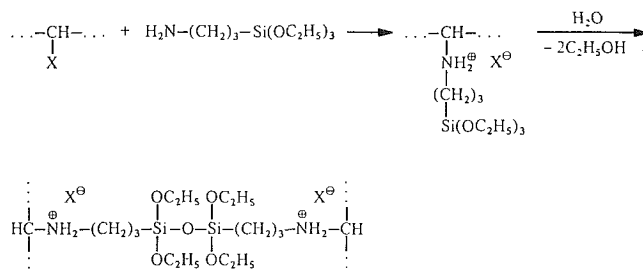$$\Delta r_c = \frac{m^{1/3}}{3} \cdot r \cdot \frac{V_c}{V_f} \tag{1}$$

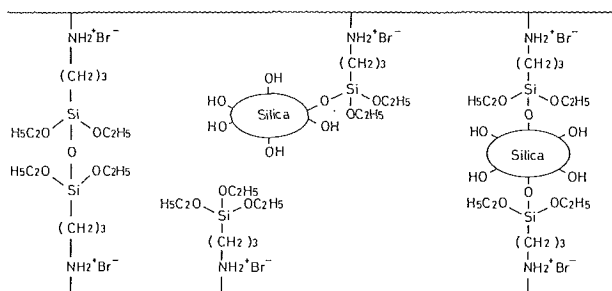Figure 2. Moisture or silane cure of halogen-containing rubber by 3-aminopropyl triethoxysilane (APS).

Figure 3. Schematic representation of the structure of moisture cured halogenated rubber/APS with silica.
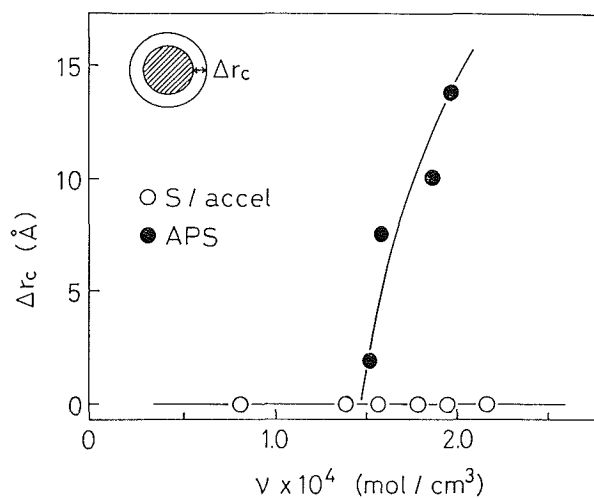

Figure 4. Thickness (r_c) of immobilized layer of CB-BR/silica composites at different curing stage. S/accel is sulfur cure by sulfur and organic accelerators.

where m $= 1$ (assuming no aggregation of silica particles), r is mean radius of silica, V_c is the volume fraction of immobilized layer, and V_f is that of silica. Figure 4 shows the observed thickness of the layer at different curing stage. While no formation of the bound rubber (*i.e.* immobilized layer) was observed for sulfur cured CB-CR/silica system, APS cure formed the layer, the thickness of which increased with the progress of APS cure. The moisture cure of halogen-containing rubbers by APS afforded a good reinforcement by introducing chemical bondings between rubber and filler as well as crosslinking of rubber.

4. RUBBER/SILICA COMPOSITES BY THE SOL-GEL PROCESS

As mentioned earlier, to compound very fine silica particles and to disperse them well in the rubber matrix are most important to enjoy excellent reinforcements. A simple and useful method of silica incorporation into rubbers is by the *in situ* sol-gel process which is considered a novel technique.[18] This process involves the swelling of a precured rubber in a silica precursor *e.g.* tetraethoxysilane (TEOS) and subjecting the TEOS-swollen network to hydrolysis and condensation reactions thus generating silica particles in the rubber network. The conversion of TEOS to silica can be acid- or base-catalyzed reactions which are shown in Figure 5.[8] In this section, the preparation of silica rubber composites with poly(dimethyl siloxane) (PDMS), styrene-butadiene rubber (SBR) or epoxidized natural rubber (ENR) by *in situ* sol-gel method is described. Similar studies on the other polymers *e.g.* poly(methyl methacrylate)[19] and poly(vinyl acetate)[20] also appeared recently, but they are not included here.

HYDROLYSIS

$$\equiv Si-OC_2H_5 \;+\; H_2O \;\rightleftharpoons\; \equiv Si-OH \;+\; C_2H_5OH \qquad (1)$$

CONDENSATION

$$\equiv Si-OC_2H_5 + HO-Si\equiv \;\rightleftharpoons\; \equiv Si-O-Si\equiv \;+\; C_2H_5OH \qquad (2)$$

$$\equiv Si-OH \;+\; HO-Si\equiv \;\rightleftharpoons\; \equiv Si-O-Si\equiv \;+\; H_2O \qquad (3)$$

OVERALL REACTION

$$Si(OC_2H_5)_4 \;+\; 2H_2O \;\rightleftharpoons\; SiO_2 \;+\; 4C_2H_5OH \qquad (4)$$
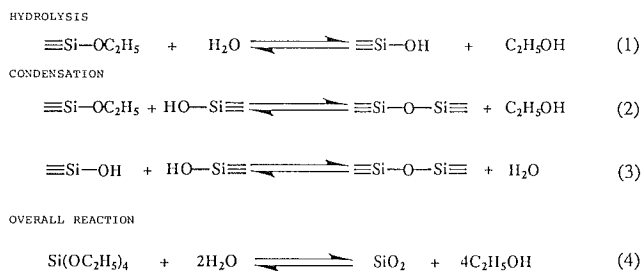
Figure 5. Hydrolysis and condensation reactions of TEOS.

4.1 *In situ* formation of silica in silicone rubber matrix

Mark *et al.* carried out the sol-gel synthesis of silica in silicone rubber matrix using tetraethoxysilane (TEOS) and ethyl amine as a catalyst.[21-23] The tensile properties of rubber vulcanizates are usually described by the Mooney-Rivlin equation:

$$\sigma = 2 (C_1 + C_2/\alpha)(\alpha - 1/\alpha^2) \qquad (2)$$

where σ is stress, C_1 and C_2 are constants, and α is
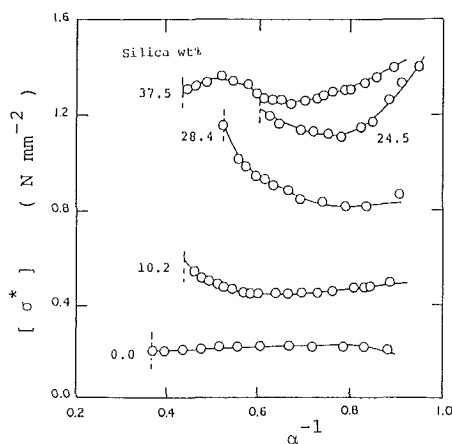
$$\alpha = l/l_0 \qquad (3)$$

Figure 6. Reduced stress of silicone elastomers compounded with *in situ* prepared silica by ethyl amine. (Ref. 22)

where l and l_0 are elongations after and before stretching, respectively. For general discussions, so-called reduced stress is often of use:

$$[\sigma^*] = \sigma/(\alpha - 1/\alpha^2) \tag{4}$$

A linear plot according to Equation (2) shows the validity of the Mooney-Rivlin Equation. The plots for silicone elastomers compounded with *in situ* prepared silica by ethyl amine are shown in Figure 6.[22] The linearity is not always established, but increase of the stress by the inclusion of *in situ* silica is demonstrated. When the silica component was predominant, the products were glasses toughened by silicone elastomer.

4.2 *In situ* silica reinforcement of styrene-butadiene rubber

An application of *in situ* sol-gel method for diene rubbers is very attractive because of their conventional uses. However, there is a difficulty of incompatibleness between diene rubbers and TEOS in comparison with silicone rubber. We overcame this point by swelling the rubber in a polar organic solvent in which both TEOS and the rubber are soluble. *In situ* silica reinforcement of styrene-butadiene rubber (SBR) by the sol-gel process[24,25] was introduced in this part.

SBR was sulfur-cured according to the compounding recipe as shown in Table 1. Its vulcanized sheet was subjected to swelling in tetrahydrofuran at 30°C for 30 min, followed by soaking in TEOS with or without catalyst in the presence of small amount of water. The catalyst used was *n*-butylamine or hydrochloric acid. The swollen vulcanizates were kept at 50°C to conduct the sol-gel reaction of TEOS in the rubber matrix. The resulting vulcanizates were silica stocks by *in situ* filling technique, and were subjected to the tensile measurement. The effect of *in situ* silica on modulus of SBR vulcanizates is shown in Table 2 and Figure 7. By amine catalyst the effect of silica compounding was clearly observed. Increase of modulus and tensile strength was recognized, which suggests the inclusion of silica particles in the vulcanizates.

Table 1. Compounding recipe of SBR

Materials	Parts by weight
SBR	100
ZnO	5
Stearic acid	1.5
Sulfur	0.5
MSA[a]	0.5

[a] N-Oxydiethylene-2-benzothiazol sulfenamide

Table 2. Effect of *in situ* silica on tensile properties of SBR vulcanizates

Sample code	The sol-gel reaction		Tensile properties		
	Silica	Catalyst	M_{300} (MPa)	T_B (MPa)	E_B (%)
RV	Without	Without	0.57	3.84	1360
RV-N	With	Without	0.70	4.05	1090
RV-A	With	HCl	0.56	3.50	1340
RV-B	With	*n*-Butylamine	1.14	6.19	1090
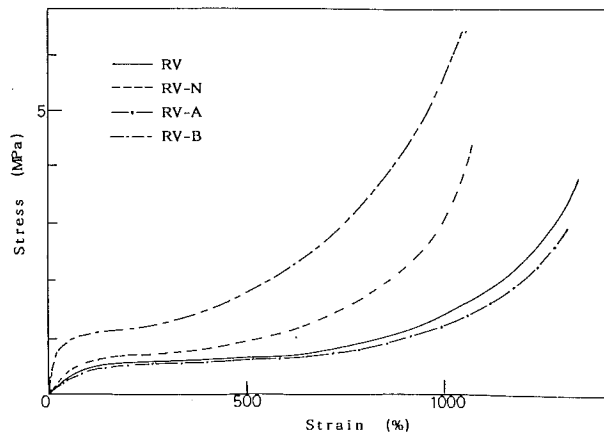
Figure 7. Tensile stress-strain curves of SBR vulcanizates with or without *in situ* silica.

Against *n*-butylamine, hydrochloric acid did not show the reinforcement effect, *i.e.*, the mechanical properties were almost same with that of the vulcanizate without silica. This is considered to be due to the reactivity of ethoxysilyl groups by the catalyst. Generally, it is reported that four ethoxysilyl groups of TEOS are liable to react to form a network structure in the presence of base, but in acidic condition one or two of ethoxysilyl groups of TEOS react to be followed by the formation of the linear-typed silicates. Interestingly, the system without catalyst also shows some improvement of mechanical properties. Further studies on this

point will be done in future. Anyway, we assume that the attractive effect of silica filling by the sol-gel process depends on the more homogeneous and fine dispersion of silica particles in rubber matrix. Different from the studies described in Section 5, the chemical bondings between organic and inorganic materials will not present in these composites. When inorganic silica was a major component, the incineration of the composite produced porous silica particles.[26-28]

4.3 *In situ* silica reinforcement of epoxidized natural rubber

ENR was found curable by amines in the presence of a phenolic compound,[29-31] thus ENR was reacted with APS to afford APS precured ENR. The ENR-APS precured system is suitable for a sol-gel process with TEOS since the alkoxysilyl groups of the APS which is already linked to the rubber can undergo the same hydrolysis and condensation reactions. The preparation of ENR-APS network which involves ring opening of the epoxy groups is made feasible by using bisphenol A as catalyst.[30] Thus, by subjecting the ENR-APS network to a sol-gel process, a composite in which the silica is chemically bound to the rubber network is expected.

Figure 8 represents the sol-gel process of a ENR-APS network in TEOS showing the formation of the chemical bond. Table 3 shows the tensile properties of the ENR-APS vulcanizates before and after the sol-gel reaction. The cure time refers to heatpress time taken to prepare the precured sheets, which were subjected to swelling in TEOS and the subsequent sol-gel reaction in *n*-butylamine aqueous solution. It should be noted that the initial vulcanizates could be considered semi cured or under cured but cured well enough such that they were homogeneous and easy to handle in the following experiments. The significant change
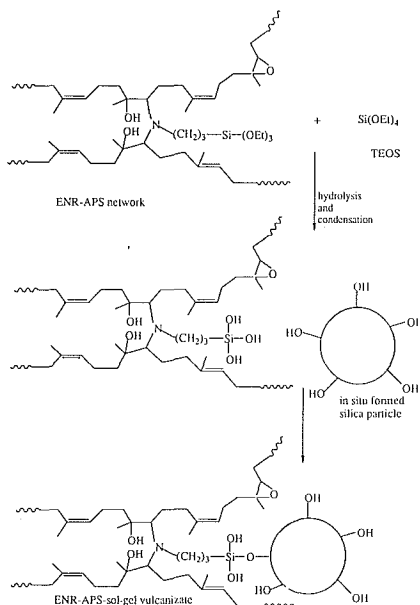

Figure 8. The sol-gel process of a ENR-APS network in TEOS.

Table 3. Tensile properties of initial vulcanizates and their corresponding properties after *in situ* sol-gel treatment

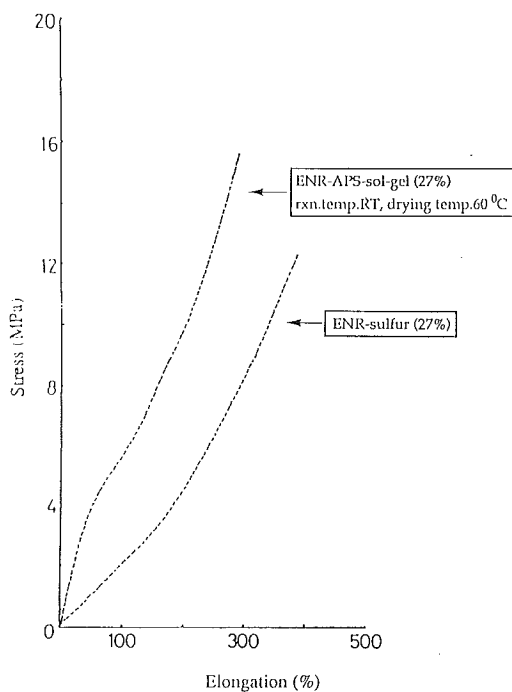| Properties	Cure time (min)			
	30	40	50	60
Initial				
M_{100}(MPa)	0.32	0.35	0.45	0.47
T_B(MPa)	0.61	0.76	1.03	1.24
E_B(%)	260	280	280	310
After sol-gel				
M_{100}(MPa)	5.14	4.79	4.63	4.15
T_B(MPa)	15.61	14.65	13.89	13.84
E_B(%)	290	320	305	295

Figure 9. Tensile stress-strain curves of ENR-APS-sol-gel network and ENR-sulfur network.

in tensile properties observed in the final vulcanizates is obviously due to the silica incorporated into the samples.

The ENR-APS sol-gel system is also compared with a typical ENR-sulfur system that contains the same amount of silica. The sulfur system is prepared by the conventional method using commercial grade silica and a typical recipe.[2] The comparative stress-strain curves

Table 4. Dynamic mechanical properties of sol-gel and sulfur-cured ENR
vulcanizates having the same amount of silica

Vulcanizate	Tan δ peak[a](^{0}C)	Storage modulus (10^8dyne/cm^2)		
		0 ℃	30℃	50℃
ENR-APS-sol-gel	−29	5.14	3.18	2.58
ENR-sulfur	−24	4.30	2.56	2.17

[a] Corresponding to the glass transition temperature of rubber matrix

and dynamic mechanical properties between the two systems are shown in Figure 9 and Table 4, respectively. It is noteworthy that the initial tensile properties of ENR-APS precured sheet *i.e.* before the incorporation of silica are significantly lower than those of the ENR-sulfur vulcanizate without silica. It is obvious that the elastic moduli (M_{100}, M_{200}, *etc.*) and tensile strength of the sol-gel vulcanizate are higher than those of the silica-reinforced ENR-sulfur vulcanizate. From the dynamic mechanical property data, it is clear that the relatively high moduli and tensile strength of the sol-gel vulcanizates are not glass transition temperature (T_g) related but rather due to a more efficient silica reinforcement. This is demonstrated by E' data at three different temperatures in the rubbery region which indicate that the sol-gel vulcanizate has a relatively high crosslink density. The data lend support to the presence of crosslinks or chemical bonds between the silica particles and the rubber networks.

5. HYBRID GELS FROM TELECHELIC OLIGOMER HAVING HYDROXYL GROUPS AND TEOS

5.1 Hybrid Gels from Polysiloxane and TEOS

By making use of the low temperature process, Wilkes *et al.* conducted the sol-gel reactions of TEOS with acid catalyst in the presence of poly(dimethylsiloxane) carrying hydroxyl groups *i.e.* Si-OH.[32] Very transparent hybrid materials resulted, and the products were mechanically silicone rubbers reinforced with silica. They named the product as "Ceramer", which means a hybrid of ceramics and polymer.

5.2 Hybrid Gels from Polyethers and TEOS

The technique by Wilkes apparently seemed to work on many organic polymers containing hydroxyl groups, for example, polyethylene glycol (PEG), polypropylene glycol (PPG), and polytetramethylene glycol (PTMG) which were all commercially available.[33] However, it was found that these polymers were almost completely solvent extracted from the composites.[34,35] Table 5 summarizes the results.
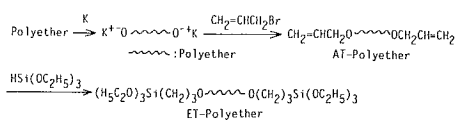
In order to prepare a hybrid material of polyether and silica, it is necessary to synthesize alkoxysilyl-terminated polyether for the sol-gel process with alkoxysilanes.[35-39] The synthetic route of this polymer is shown in Figure 10.[33-37] Figure 11 shows dynamic mechanical property of the hybrid from triethoxysilyl-terminated poly(oxytetramethylene) (ET-PTMO) and TEOS. Dynamic mechanical properties are described by three parameters:
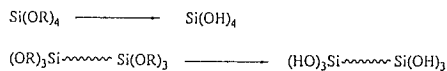
$$E^* = E' + iE'' \quad \text{(tensile mode)} \tag{5}$$

Table 5. Soxhlet extraction of the hybrids

Polymer/TEOS (molar ratio)	Decrease of wt (%)	Residual polymer (%)
1 / 0	0.68	—
1 / 0.5 HT-PDMS	16.7	77.5
1 / 0.55 PTMG	92.1	0
1 / 0.5 ET-PTMO	3.86	94.9
1 / O.52 PPG	93.3	0
1 / 0.65 ET-PPO	13.3	84.3
1 / 0.57 PEG	95.0	0
1 / 0.5 ET-PEO	22.0	73.8

Synthesis of ET-Polyether

$$Polyether \xrightarrow{K} K^{+-}O \sim\sim\sim O^{-+}K \xrightarrow{CH_2=CHCH_2Br} CH_2=CHCH_2O \sim\sim\sim OCH_2CH=CH_2$$
$$\sim\sim\sim : Polyether \qquad AT\text{-}Polyether$$
$$\xrightarrow{HSi(OC_2H_5)_3} (H_5C_2O)_3Si(CH_2)_3O \sim\sim\sim O(CH_2)_3Si(OC_2H_5)_3$$
$$ET\text{-}Polyether$$

Hydrolysis

$$Si(OR)_4 \longrightarrow Si(OH)_4$$

$$(OR)_3Si \sim\sim\sim Si(OR)_3 \longrightarrow (HO)_3Si \sim\sim\sim Si(OH)_3$$

Condensation

$$\left.\begin{array}{l} Si(OH)_4 \\ (HO)_3Si \sim\sim\sim Si(OH)_3 \end{array}\right\} \longrightarrow -Si\text{-}O\text{-}Si\text{-}O \sim\sim\sim O\text{-}Si\text{-}O\text{-}Si\text{-}$$

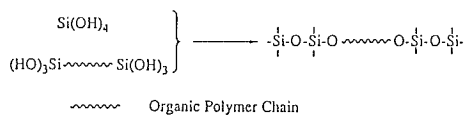$$\sim\sim\sim \quad \text{Organic Polymer Chain}$$

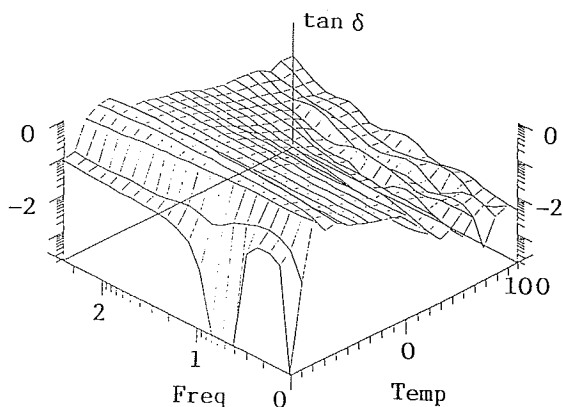Figure 10. The synthetic route of the hybrid gel.

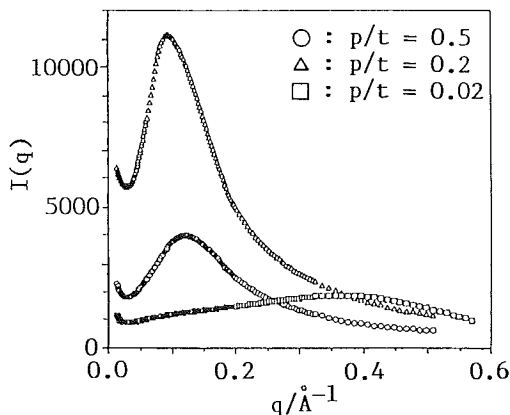Figure 11. Dynamic mechanical properties of the hybrid gel.

Figure 12.   Temperature and frequency dependences of loss tangent of the hybrid gel.

$$G^* = G' + iG'' \quad \text{(shear mode)} \tag{6}$$

$$\tan \delta = E''/E' = G''/G' \tag{7}$$

where E' and G' are storage moduli, E" and G" are loss moduli, and tan δ is loss tangent. Figure 11 shows temperature and frequency dependences of the loss tangent.   The mechanical loss of the material was found to be large under very wide conditions, which suggested that this material might be of use for damping of mechanical vibrations.

As indicated in Table 5, this material resisted to solvent extractions.   However, this result does not mean that polyether and silica did not segregate at all.   The small-angle X-ray scattering (SAXS) curves of the hybrid materials are shown in Figure 12.[10]   The presence of maxima suggests microphase separation in the hybrids.   The Debye spacings from the maxima in Figure 12 were 60Å, 62Å, and 88Å.   It is suggested that even in these hybrids, phase separation between organic polymer and silica was unavoidable.   However, these separations were of less than 100Å, which means very good mixing of organic polymer and silica has been established in the ET-PTMO/TEOS mixture after the sol-gel reaction.

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