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Rubber-like elasticity of organically modified silicates

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Rubber-like stress–strain behaviour was observed in the organically modified silicates (ORMOSILS) in which tetraethoxysilane (TEOS) and polydimethyl siloxane (PDMS) were used as the inorganic and polymeric components, respectively. The flexibility and rubber-like elasticity of ORMOSILS increase with increasing volume fraction of incorporated PDMS. When the nominal mass ratio of TEOS/PDMS was less than 1.5, the ORMOSILS began to show the rubber-like elasticity. Three conceptual models of the structure of ORMOSILS that results from the fundamental reaction between TEOS and PDMS were used to interpret the experimental results.

1. Introduction

Some of the novel organically modified silicates (ORMOSILS) systems made via the sol–gel process have attracted wide interest in recent years because of their superior, unique properties; for example, as highly antiabrasive coating, non-linear optically active gels, etc. [1–5]. The general character of the sol–gel reaction scheme is basically a condensation polymerization reaction that allows the incorporation of suitable polymeric/oligomeric components into the sol–gel network, if such polymers or oligomers have appropriate functional groups. Therefore, the sol–gel process provides the opportunity to synthesize organic–inorganic nanocomposites or microcomposites that are impossible to prepare by a traditional high-temperature process due to the decomposition of organics. In addition, the incorporation of organics into the sol–gel precursor sols greatly improves the preparation of monolithic glasses that easily crack during the drying procedure of the sol–gel process because of the loss of structural integrity [6, 7].

One of the most spectacular phenomena in this novel nanocomposite is the rubber-like behaviour. Such a rubber-like property will contribute to glasses with enhanced toughness and perhaps ductility. Some mechanical properties of this rubber-like material have been tested, but most of the studies have been concentrated towards the factors affecting the structure of these materials, such as the acid content and composition [3–5, 8]. However, the molecular or phenomenological basis of elasticity of these materials is still unclear. The present investigation was conducted to construct appropriate models to explain the mechanism of the rubber-like elasticity of the organically modified silicates. The system of tetraethoxysilane (TEOS) modified by polydimethylsiloxane (PDMS) was used in this study.

2. Experimental procedure

High-purity TEOS alkoxide and silanol-erminated PDMS with molecular weight of about 1700 (Petrach system) were used as the inorganic and polymeric components, respectively. Isopropanol and tetrahydrofuran (THF) were used as the solvents and HCl was the acid catalyst.

The procedure for sample preparation is described as follows. Measured amounts of TEOS, PDMS and THF were mixed thoroughly with isopropanol, to which was added a solution mixture of distilled water, hydrochloric acid, and isopropanol. The reactants are mixed in a flask, and immediately refluxed and stirred in a water bath at 80 °C for 30 min. After quickly cooling to room temperature, the solution was cast into a prepared mould and sealed. After a long gelation time of 2 weeks, the wet gels were dried at room temperature for 1 week, followed by further drying at 50 °C in a drying oven for 48 h in air. In our experiment, we changed the fraction of TEOS/PDMS ratio, and kept constant the stoichiometric molar ratio of H_2O/TEOS at 3 and HCl/TEOS at 0.3.

The stress–strain experiments were carried out with an Instron machine using an initial strain rate of 0.5 mm min^{-1}. Dogbone-shaped samples for the test were 5 cm. The fracture surfaces were examined by scanning electron microscopy (SEM). The mass ratio of TEOS/PDMS is described in this paper.

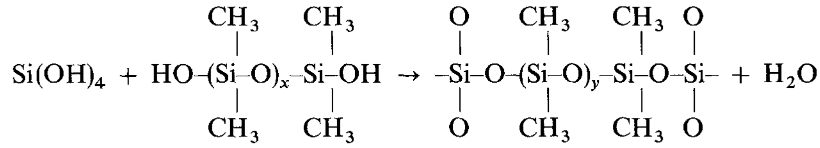
2.1. Reaction scheme

The schematic reaction mechanism has been proposed by Wilkes *et al.* [3]. They incorporated hydroxyl-terminated PDMS oligomer into a sol–gel system based on the TEOS and the reaction scheme is shown below.

Hydrolysis

$$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH \quad (R = C_2H_5)$$

Polycondensation



$$Si(OH)_4 + HO\text{-}(\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O)_x\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}OH \rightarrow \text{-}\overset{O}{\underset{O}{Si}}\text{-}O\text{-}(\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O)_y\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}O\text{-}\overset{O}{\underset{O}{Si}}\text{-} + H_2O$$

The relative rates and extents of these two reactions will particularly depend on the amount of water added and the acidity of the system. Hence, residual ethoxy groups may exist and self-condensation of the silanol-terminated PDMS can take place. This will affect the network structure.

2.2. Structure modelling

Simplified schematic models for the hybrid system have been discussed by Huang *et al.* [8]. It is not likely that all ethoxy groups may be converted to hydroxyl groups in the hydrolysis reaction. Thus, the conditions under which the hydrolysis reaction is carried out will affect the extent of polycondensation. The residual ethoxy groups may later undergo further hydrolysis and polycondensation of $Si(OH)_4$ which remain distributed in the system to act as phase-separated block and segmented copolymers.

A schematic illustration of the structure of the TEOS–PDMS hybrid system based on the reaction scheme is shown in Fig. 1. Most silica gel species are bonded with PDMS, and some unpolycondensed PDMS are dispersed in this system. It is suggested that the silica species and the PDMS exist on a microscopic scale. Highly condensed silica clusters and phase separations are not illustrated in this structure to simplify the structural model. If all silica gel species are separated and bonded to PDMS, the structure can be expressed simply by Model 1 shown in Fig. 2a. If all the silica gel species are connected with each other and PDMS also bonds between these silica gels, the structure can be expressed by Model 2 shown

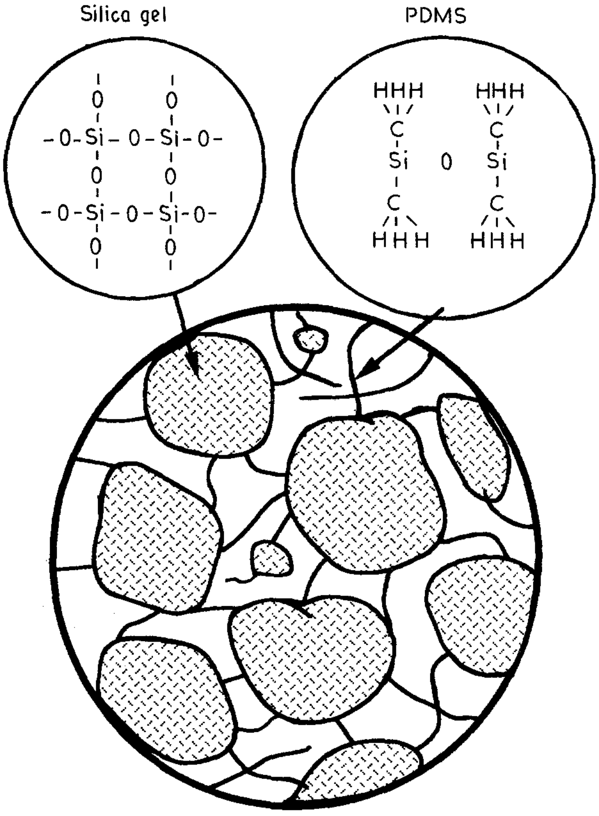


Figure 1 Schematic illustration of the structure of the TEOS–PDMS hybrid system.

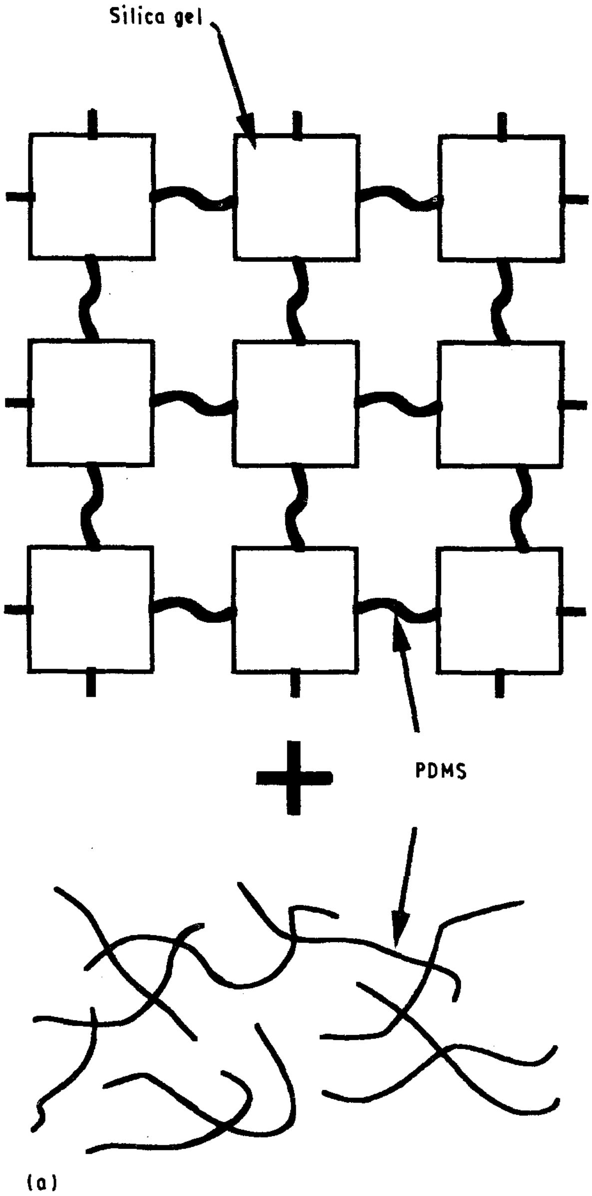


Figure 2 (a) Model 1 with all silica gel species separated by PDMS. (b) Model 2 with all silica gel species connected. (c) Model 3, a structure between Model 1 and Model 2.

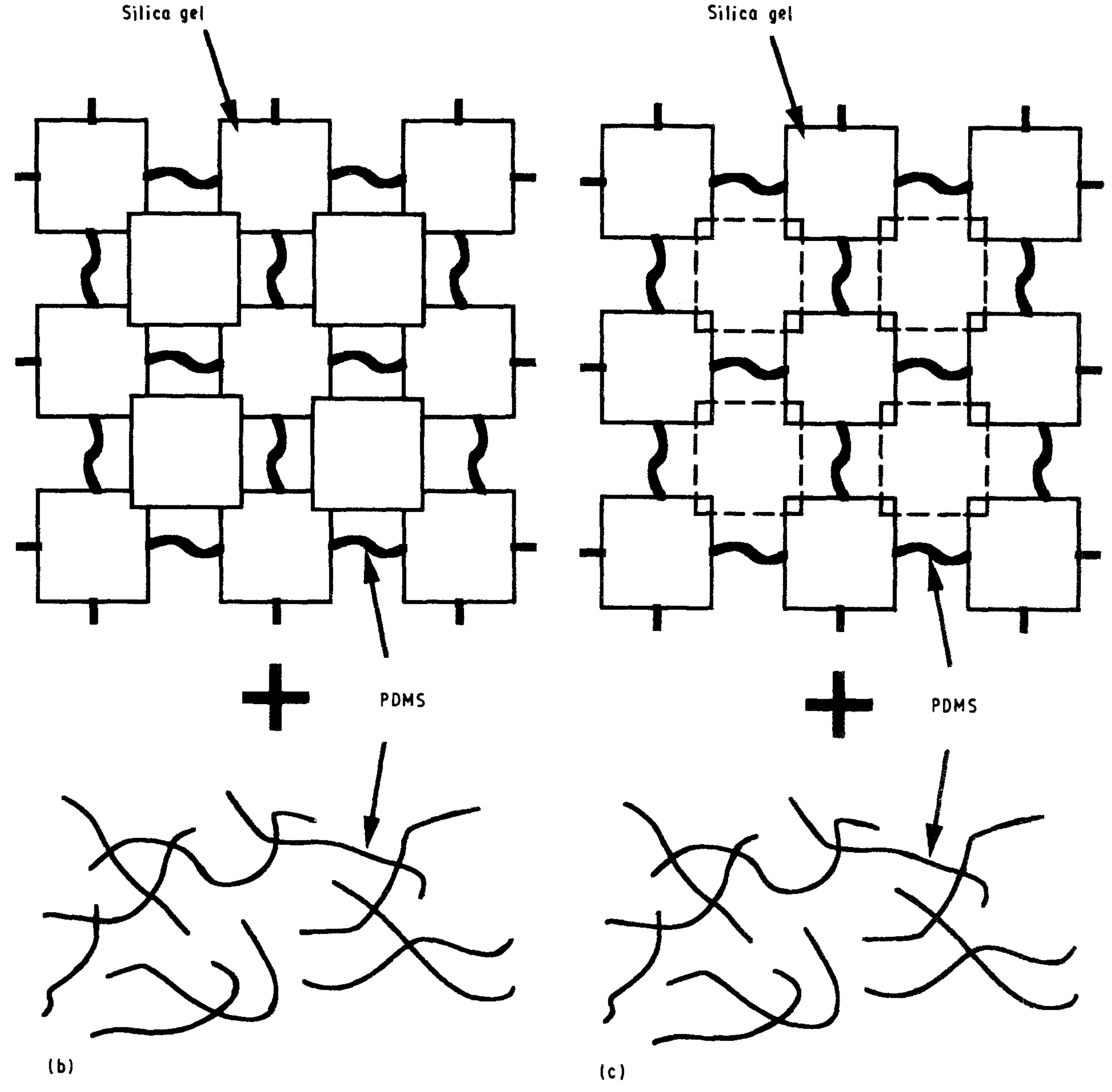


Figure 2 Continued

in Fig. 2b. A structure between Model 1 and Model 2, in which only partial connection of the silica gel species exist, is expected to be as in Model 3 and is shown in Fig. 2c.

These models are based on the following assumptions.

1. The system is homogeneous. Even the unpolycondensed PDMS are distributed in this system homogeneously.
2. All the silica gel species have the same properties and are bonded with PDMS under the same conditions in all directions.
3. There is no cross-linking between these PDMS which connect the silica species.
4. The amount of unpolycondensed PDMS is very small, producing little contribution to the mechanical properties of the system.

These assumptions are used to simplify the structural model, although defects, such as phase separation, have been observed in some cases [8].

2.3. Theoretical elasticity

When we apply a unidirectional tensile load to the structure of Model 1, each element will be displaced in the loading direction, and there will be no stress on the PDMS connected in the other directions if no slippage occurs between the silica gel species. Model 2 can be treated as a composite in that the strain in the loading direction of each constituent is the same because all silica gels are connected together, where the Young's modulus, $E(2)$, of the system becomes

$$E(2) = (f_2/3)E_2 + (1 - f_2)/E_1 \qquad (1)$$

where E_1 is the elasticity modulus of silica gel, E_2 is the molecular elastic modulus of PDMS, and f_2 is the volume fraction of PDMS. In Model 1, the stress in the loading direction of each phase is the same. The Young's modulus of the system, $E(1)$, is

$$E(1) = (f_2/3)/E_2 + (1 - f_2)/E_1 \qquad (2)$$

where $E(1)$ and $E(2)$ are the lower and upper bounds of the elastic moduli, respectively. The elastic modulus of Model 3 is then between $E(1)$ and $E(2)$.

The stress–strain relationship for the rubber-like materials was first represented by the Mooney–Rivlin relation as the dependence of the elastic modulus on reciprocal elongations [9–11].

$$F^* = F/2A(S - S^{-2}) = C_1 + C_2S^{-1} \qquad (3)$$

where F is the load, A is the area of the initial cross-section, and S is the strain ($S = 1 +$ engineering strain). C_1 and C_2 are constants independent of elongation. C_1 is an approximation to the high-deformation modulus, and C_2 is a measure of the increase in non-affineness with increase in elongation.

3. Results and discussion

For the application of these theoretical equations of elasticity, the molecular elastic modulus of PDMS has to be known. No experimental data on this property of PDMS have been found. However, we can use the equation of state of a single polymer chain [12]

$$f = 2kTb^2r \qquad (4)$$

where $b^2 = (3/2)/(2nl^2)$, f is the applied force and r is the displacement, k is the Boltzmann constant, T the absolute temperature, l the length of the bond and n the number of the bonds of the polymer chain. The equation is just Hooke's law for a spring with modulus $2kTb^2$. In our experiment PDMS with a molecular weight of 1700 was used; therefore, the calculated n is about 23 and the Si–O bond length in PDMS is about 0.164 nm. Then the calculated molecular elastic modulus of PDMS is about 10 MPa, and the average elastic modulus of the silica dried gel is about 5 GPa obtained in our experiment. These elastic moduli of the PDMS molecule and the pure silica gel are substituted into Equations 1 and 2.

Fig. 3 shows $E(1)$, $E(2)$ and the experimental data of Young's modulus obtained via different volume fractions of PDMS. The amount of unpolycondensed PDMS cannot be measured at the present time. The nominal fraction of PDMS was used in this paper. It was found that the structure of the material is close to Model 1, if the nominal volume fraction of PDMS is larger than 0.73 (TEOS/PDMS $\leqslant$ 60/40). On the other hand, the structure is similar to Model 2, if the volume fraction of PDMS is less than 0.4 (TEOS/PDMS $\geqslant$ 76/24). Between these volume fractions of PDMS ($0.73 \geqslant f_2 \geqslant 0.4$), the structure can be attributed to Model 3. Because the difference in the elastic modulus between the silica gel and the PDMS is very large, PDMS would dominate the elastic behaviour in Model 1 but would be subsidiary in Model 2. This indicates that the structure of Model 1 is more flexible and rubber-like than the other models.

The elastic modulus can also be affected by other factors, such as porosity. As shown in Table I, the porosity will increase as the fraction of incorporated PDMS increases, and thus decreases the strength of ORMOSILS largely. However, the porosity factors can be the characters of these models. For example, the complete separation of the silica gel species in Model 1 gives a higher porosity than Model 2 and Model 3 in which the silica gel species, or some of them, are connected to each other.

Fig. 4 shows the stress–strain curves with different fractions of TEOS/PDMS plotted against reciprocal elongation, as suggested by Equation 3. The elongations of these materials are not very large which may be due to the low molecular weight of the PDMS used in this study, and the stiffness effect of the block silica gel in the material. Therefore, the constant C_1 is not

TABLE I The porosity and tensile strength of ORMOSILS with different compositions

Composition TEOS/PDMS	Porosity (%)	Strength (MPa)
100/0	1–5	58–76
90/10	10–16	35–43
80/20	20–30	18–15
70/30	25–35	10–15
60/40	60–70	2–3
50/50	65–75	2–3

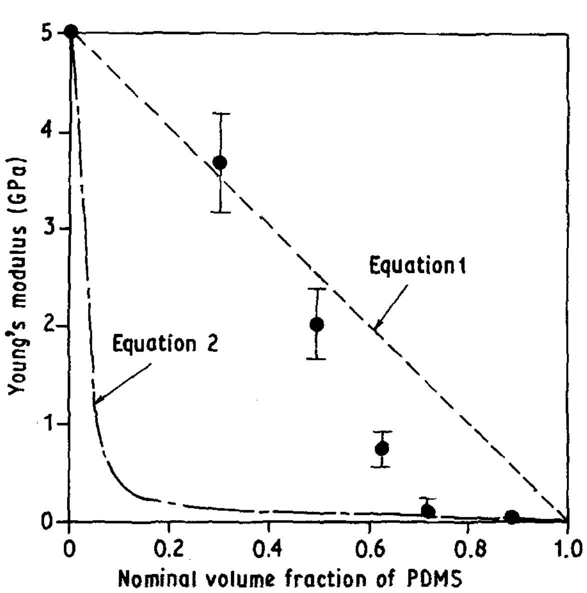


Figure 3 Elastic modulus versus different volume fractions of incorporated PDMS.

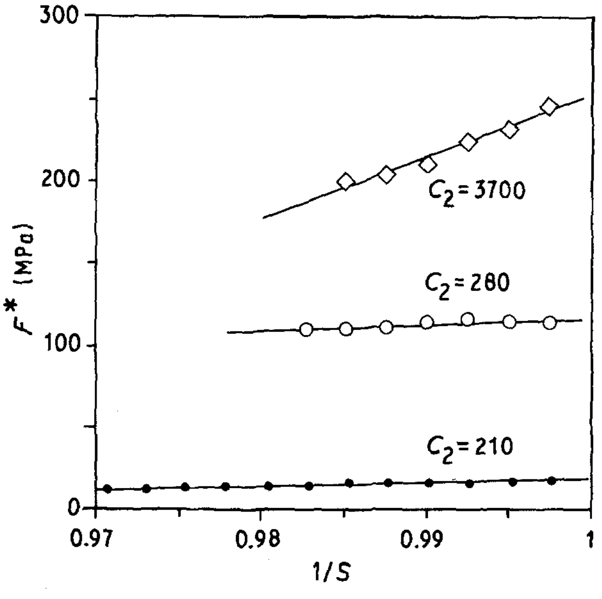


Figure 4 The stress–strain curves with different fractions of TEOS/PDMS following the relation of Equation 3. TEOS/PDMS: (◇) 80/20, (○) 70/30, (●) 60/40.

suitable for use by extrapolation. The elongation of the samples with PDMS/TEOS > 40/60 were much larger than the elongation of samples with PDMS/TEOS < 40/60. The higher degree of incorporated of PDMS would produce a higher possibility of isolated silica gel species as expressed in Model 1; therefore, a higher degree of incorporated of PDMS or a increase in PDMS/TEOS ratio would produce a higher inclination toward the rubber-like character. The constant C_2, or the slope shown in Fig. 4 decreases with decreasing fraction of TEOS/PDMS, therefore increasing the flexibility.

Another typical representation is the nominal stress as a function of elongation, which is shown in Fig. 5. It was found that the sample incorporated with PDMS can increase the fracture toughness which could be measured by the area under the curve. The extremely good compressibility of the sample with TEOS/PDMS = 60/40 compared to other samples can be explained by the porous structure of Model 1. Because the silica gel species are separated by PDMS, many pores exist among the silica gel and PDMS. When the material is under a compressive load, the silica gel species will have space to move in and out, being rearranged via the flexible PDMS without breakage. The structures of Model 2 and Model 3, on the other hand, have insufficient space for the movement of the silica gel species connected to each other, and thus are more rigid than the structure of Model 1.

The scanning electron micrographs of the fracture surfaces of these materials are shown in Fig. 6. The porous structure in Fig. 6a can explain the low fracture strength and high compressibility of this material incorporated with a high PDMS content. Fig. 6b shows some hackle fracture character on the fracture surface but with a lot of cracks among those hackles. The cracks or fracture branches can deflect the crack tip to increase the toughness of the material. The fracture branches may be caused by the breaking of the weakest bonds of PDMS. Fig. 6c shows the typical fracture surface of brittle silica gel, which has mirror, mist and hackle, and Wallner lines and striations [13]. Such a fracture pattern is mainly observed in isotropic, homogeneous, and dense materials, being very sensitive to flaws that cause the crack initiations. Therefore, the effect of porosity on the fracture behaviour of low PDMS content silica gel becomes important.

The models of the structure can be used to interpret the behaviour of elasticity of the ORMOSILS. On the other hand, the structure of ORMOSILS can be

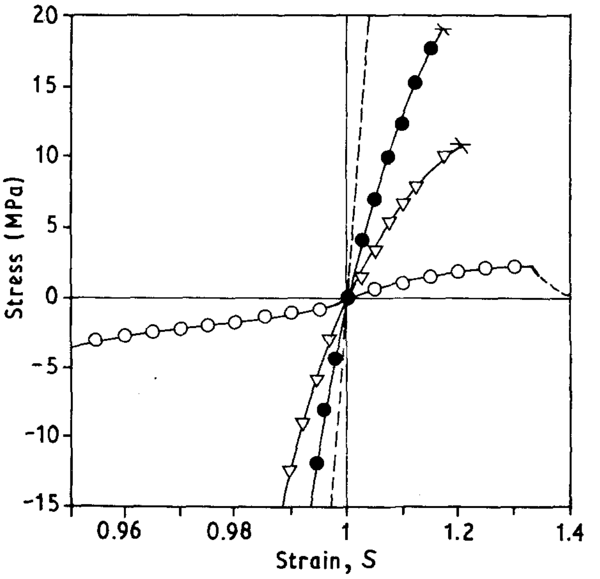


Figure 5 Typical stress–strain curves for different TEOS/PDMS ratios. TEOS/PDMS: (---) 100/0, (●) 80/20, (▽) 70/30, (○) 60/40.

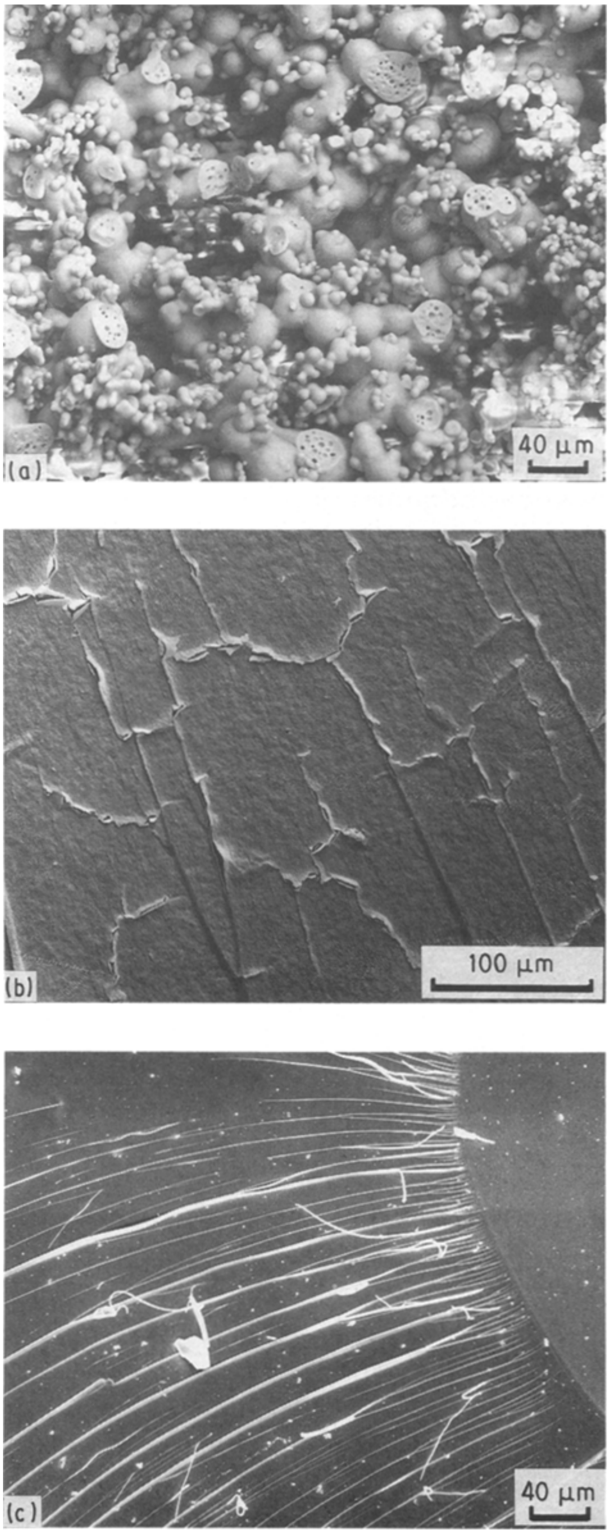


Figure 6 (a) Fracture surface of the sample with the composition TEOS/PDMS = 60/40. (b) Fracture surface for TEOS/PDMS = 70/30. (c) Fracture surface for TEOS/PDMS = 80/20.

changed by many factors, for example, the addition of polymeric component, the amount of the oligomer added which was studied in this paper, the oligomer molecular weight, the difference between the solubility of the oligomer and the glassy component in the solvents used, and the reaction temperature employed. Further studies are currently in progress on the structural transition of ORMOSILS under different reaction conditions while correlating to the rubber-like behaviour.

4. Conclusion

Three rational models of the structure of the organically modified silicates were successfully used to convey the theoretical and experimental studies on the elasticity of this material. The flexibility and the rubber-like elasticity of ORMOSILS is increased with increasing volume fraction of incorporated PDMS. The fracture toughness is also improved by increasing PDMS which can modify the structure of ORMOSILS interpreted by the three models. The structure of Model 1 shows the best compressibility. The different characters of the fracture surfaces can be used to identify the different structures of ORMOSILS.

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