

# Reinforcement of Poly(dimethylsiloxane) Networks by Montmorillonite Platelets

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**ABSTRACT:** A PDMS network, synthesized from a vinyl-terminated precursor, was reinforced by plate-like montmorillonite (volclay) particles with different surface cations. The optimal ratio of crosslinker-to-PDMS precursor was ascertained from the mechanical properties of networks prepared with different crosslinker concentrations. The elastic modulus of the polymer was enhanced by the montmorillonite particles. The increase in modulus was higher in the Li- than in the Na-volclay composites. The ultimate strength of the composites was also strongly enhanced by the small platelets, especially in presence of surface Li<sup>+</sup>. The stronger influence of Li-volclay on the mechanical properties of the composites can be attributed to the partial formation of an intercalated structure, which leads to thinner particles with a high aspect ratio. Both composite strength and modulus were proportional to the filler-volume-fraction, but the increase in strength was limited by rising particle agglomeration at high loading. In contrast to organic-modified montmorillonite, the inorganic surface of volclay catalyzed the thermal degradation of PDMS. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2175–2183, 2002

**Key words:** dispersions; mechanical properties

## INTRODUCTION

Polysiloxanes are an important class of polymeric materials, which play an important role in different applications because of their high thermal stability, low surface tension, and outstanding dielectric properties.<sup>1–3</sup> Their networks have the advantage of remaining elastic over a wide range of temperatures. Poly(dimethylsiloxane) (PDMS) is the most prevalent member of this class, but its mechanical strength in the unfilled state is poor.<sup>3,4</sup> For this and other reasons, most applica-

tions require that PDMS be reinforced by particulate fillers, and the reinforcement is considered as one of the most important processes in elastomer technology.<sup>5–7</sup> The most widely used fillers for reinforcing polysiloxanes are silica and carbon black, which are isometric, i.e., nearly spherical. However, acicular fillers, such as fibers, have also been applied. Composites of fibrous fillers usually show superior mechanical properties in the orientation direction of the fibers (orientation inevitably takes place during processing) but are weak in the others. Anisometric fillers, whose dimensions in two directions are significantly larger than in the third, i.e., platelets, were given much less attention, although from their geometry one might expect two-dimensional reinforcement.

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With isometric particles, better reinforcement is generally achieved, when the particles are small (high specific surface area). This has been attributed to the more efficient contact between the matrix and the filler. Therefore, fillers with small particle size are favored in particulate-reinforced polymers and nanocomposites are attracting large attention nowadays. Nanocomposites are multiphase materials in which at least one dimension of a phase is in the nanometer scale. Recently, Yuan and Mark<sup>8</sup> reported significant improvement of the mechanical properties of PDMS by blending it with isometric nano-sized fumed silica particles. Precipitation of the silica particles *in situ* also led to better dispersion of the filler, and hence, enhanced reinforcement.<sup>8,9</sup>

To combine both effects, anisometric nanoparticles (e.g., clays) have been used for polymer reinforcement.<sup>10–12</sup> Clay fillers such as smectites (e.g., montmorillonite) are plate-like particles, which consist of negatively charged 1-nm thick 2 : 1 aluminosilicate layers held together in stacks by interlayer cations. Each of these 2 : 1 (TOT) layers consists of one central alumina octahedral sheet surrounded by two silica tetrahedral sheets. In montmorillonite, the layer charge originates mainly from partial substitution of the octahedral  $\text{Al}^{3+}$  by  $\text{Mg}^{2+}$ . Typically, the charge deficiency in the montmorillonite TOT layers ranges from 0.2 to 0.4 electrons per half unit cell, and is balanced by the interlayer cations (usually alkali or earth alkali metals). Smectites are known to swell in water, so that they can be easily delaminated to give nano-sized platelets with high specific surface area. The surface of these platelets can be rendered organophilic by exchanging their inorganic cations with organic ammonium ions. Depending on the degree of delamination and re-aggregation of the exfoliated layers as well as on the polymer chain inclusion in the layered lattice, three types of composites are distinguished. When the polymer is unable to intercalate the aluminosilicate layers, conventional composites are obtained. In cases, where the polymer molecules are incorporated between the aluminosilicate layers but the TOT layers still keep registry with each other and a periodicity can be observed, an intercalated structure is realized. If the 1-nm thick layers are completely exfoliated (delaminated) and dispersed in the polymer matrix at distances far enough to avoid periodicity, exfoliated composites are formed. However, the necessary attributes for building an intercalated or

exfoliated structures as well as the composite structure–properties relationships are not fully understood yet. Whether the obtained composite can be called nano or not depends on the dimensions of the phases involved.

Nanocomposites of exfoliated organo-montmorillonites (OMT) and PDMS have been described by Burnside and Giannelis.<sup>13,14</sup> Their results indicate that the elastic modulus of these composites can be three times that of the polymer matrix. Wang et al.<sup>15</sup> intercalated PDMS in the galleries of OMT and showed that in this way substantial increase in the tensile strength (ca. five times that of the matrix at 8 vol % loading), comparable to that obtained with aerosilica nanofillers, can be obtained. All of the aforementioned studies used hydroxyl-terminated precursors to build up the elastomeric network. Takeuchi and Cohen<sup>16</sup> studied the reinforcing effect of OMT on PDMS networks prepared from hydroxyl- or vinyl-terminated precursors. They observed a higher modulus only in defect networks prepared from hydroxyl-terminated precursors. No improvement in the modulus of networks synthesized from vinyl-terminated precursors could be obtained. They concluded that no reinforcement is achieved unless the polymer chains have hydroxyl end groups, which can be anchored to the silicate filler.

However, vinyl-terminated PDMS, which can be crosslinked by hydrosilylation to give elastomeric networks, is quite popular in the industry because of the ease and reliability of this reaction. Therefore, PDMS networks from vinyl-terminated precursors filled with anisometric montmorillonite particles are of industrial interest. Because the dielectric strength usually goes hand in hand with the mechanical strength, such reinforced composites can be useful as engineering materials as well as electric insulators. Because of the swelling properties and the ease of delamination of organic modified montmorillonite in organic media, previous investigations focused on OMT composites.<sup>10–16</sup> Li–montmorillonite has only been used to synthesize poly(ethylene oxide) composites<sup>17</sup> in aqueous medium, although  $\text{Li}^+$  is known to be easily solvated by polar organic solvents, which can lead to swelling and delamination of the aluminosilicate layers in organic media.

In this study, the reinforcing effect of Li–montmorillonite platelets on a PDMS network obtained from a vinyl-terminated precursor is described and the mechanical properties of the

composites are compared to those of the corresponding Na–montmorillonite composites.

## EXPERIMENTAL

### Materials

Vinyl-terminated PDMS (DMS-V31,  $\eta_{25} = 1000$  cSt, 0.18–0.26% vinyl) and a platinum carbonyl complex (SIP 6829.0, 3–3.5% Pt) were purchased from Gelest Inc. (Tullytown, PA). The number-average molecular weight  $M_n$  of DMS-V31, denoted by the supplier to be  $28 \times 10^3$ , was found by chain-end determination with  $^1\text{H-NMR}$  (repetition rate = 35.5 s,  $90^\circ$  pulse, resolution = 0.1 Hz/point) to be  $19 (\pm 0.1) \times 10^3$ . Poly(methylhydrosiloxane) (PMHS,  $\eta_{25} = 15\text{--}40$  cSt, nominal  $M_n = 1.7\text{--}3.2 \times 10^3$ ), whose  $M_n$  was found by  $^1\text{H-NMR}$  (same conditions as above) to be  $2.2 (\pm 0.1) \times 10^3$ , was purchased from Aldrich (Buchs, Switzerland). The NMR measurements of the precursors were taken to be an accurate measure of the molecular weight, because they correlate well with gel permeation chromatographic data.<sup>18</sup>

Wyoming bentonite (volclay) was obtained from C. G. Meier-Gaissert (Zurich, Switzerland). Volclay is a natural bentonite, which has a cation exchange capacity of 0.722 mEq/g and contains ca. 90% montmorillonite in Na-form, ca. 7% quartz and ca. 3% feldspars. Its particle size has been reported.<sup>19</sup> Li–Volclay was prepared by exchanging the surface cations with  $\text{Li}^+$  in an aqueous dispersion.

### Sample Preparation

#### Unfilled PDMS

The required amounts of DMS-V31 and catalyst (30 ppm Pt of the total sample weight) were thoroughly mixed before the corresponding amount of crosslinker (PMHS) was added. The well-stirred mixture was then poured into a Teflon mold and degassed under reduced pressure before curing at  $100^\circ\text{C}$  for 3 h. The so obtained ca. 1-mm thick plaques were then carefully released from the mold, while avoiding to scratch the surface. Careful releasing proved to be critical in the case of the unfilled PDMS, because surface flaws led to lower mechanical properties. Dumbbell-shaped samples were stamped out of these sheets with a stainless steel gadget.

### Composites

The required amount of filler was allowed to swell in methyl ethyl ketone before the vinyl-termi-

nated PDMS precursor was added. The suspension was carefully mixed and sonicated, before the solvent was evaporated under reduced pressure. The necessary amount of catalyst (40 ppm Pt of the polymer weight) was then added followed by 12.5 mol % PMHS and the mixture stirred, degassed, and poured into a Teflon mold. The paste was carefully homogenized in the mold by stirring with a spatula and degassed once more before curing at  $100^\circ\text{C}$  for 3 h. Pastes, which were too viscous to give planar sheets on molding in this way, were pressed and cured in a brass frame between two Teflon sheets under reduced pressure. Dumbbell-shaped samples were stamped out of the resulting ca. 1-mm thick plaques with a stainless steel gadget.

### Mechanical Measurements

Stress–strain measurements of dumbbell-shaped specimens ( $2 \times 0.6 \times 0.1\text{-cm}$  test region) in uniaxial extension were carried out on a Mecmesin M1000 E tensile testing machine (West Sussex, UK). All measurements were taken at room temperature, and the average of four measurements for each sample is reported. The undeformed cross-sectional area  $A^*$  was determined by measuring the thickness and width of each sample with a micrometer. The reduced stress (elastic modulus) was calculated from

$$[f^*] = f^*/(\alpha - \alpha^{-2})$$

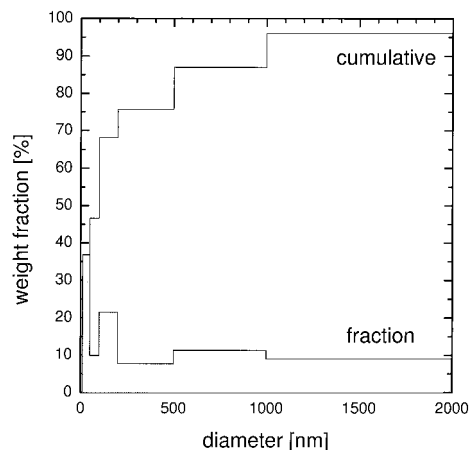
where  $\alpha = L/L_0$  is the elongation, and  $f^*$  is the nominal stress given by  $f^* = f/A^*$ .

### X-ray Diffraction (XRD)

Wide-angle diffraction patterns (WAXRD) from Na- and Li–volclay as well as from the 10 vol % PDMS composites were collected at room temperature on a D8 Advance diffractometer (Bruker AXS) using monochromatized  $\text{Cu-K}\alpha$  ( $\lambda = 0.15419$  nm) radiation (40 mA, 40 kV). The instrument was equipped with a graphite monochromator and a NaI scintillation counter. Si was used as an external standard for powders or a muscovite flake was placed on top of the composite samples and its 001 reflection at  $2\theta = 8.84^\circ$  used to calibrate the sample reflections.

### Scanning Electron Microscopy (SEM)

Cross-sections were cut perpendicular to the horizontal plane (the plane parallel to the plaque's



**Figure 1** Particle size distribution of volclay.

flat surface) of the samples using a razor blade. The face of the section was sputter coated with 5 nm of Pt and observed in a Hitachi S-900 “in-lens” field emission scanning electron microscope (FESEM) at 20 kV.

#### Thermogravimetric Analysis (TGA)

The TGA was carried out in an air stream as well as under flowing nitrogen at a heating rate of 20°C/min on a Perkin-Elmer 7 thermal analysis system (Perkin-Elmer, Norwalk, CT). The gas flow in both cases was ca. 50 mL/min.

#### Surface Area (BET)

The specific surface area (SSA) of volclay was determined by the Brunauer-Emmett-Teller gas adsorption method with nitrogen using a Gemini III 2375 surface area analyzer (Micromeritics Instrument Corp., Norcross, GA). Prior to the measurement, the powder was dried at 80°C under vacuum overnight, then scavenged with nitrogen on a FlowPrep 060 Degasser (Micromeritics) at 100°C for 2–3 h.

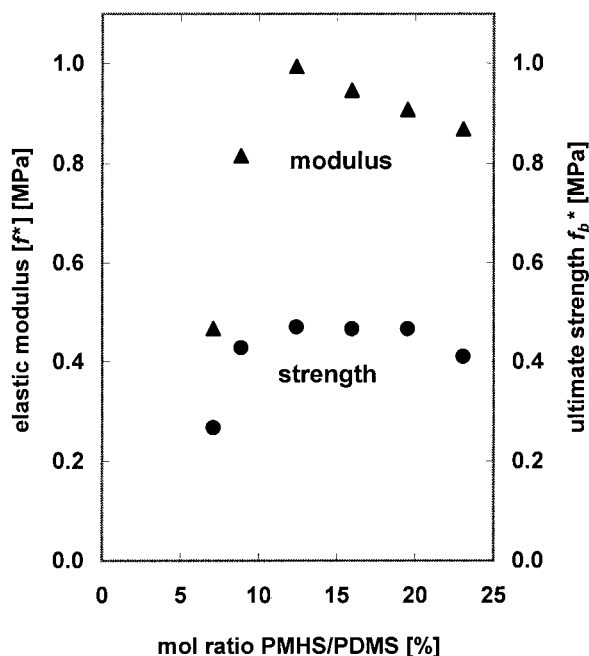
## RESULTS AND DISCUSSION

The particle size of the exfoliated volclay was determined by centrifugal sedimentation of an aqueous dispersion<sup>19</sup> and the data are plotted in Figure 1 (median diameter = ca. 100 nm). From X-ray measurements, it is known that the thickness of the exfoliated layers are ca. 1 nm.<sup>20</sup> These values are relevant in a polymer matrix only if the layers are fully exfoliated and dispersed but not

for aggregates or agglomerates. The increase in diameter due to agglomeration is expected to be relatively small compared to that in thickness, so that the aspect ratio (major to minor axis) of the stacks and agglomerates is very probably much smaller than that of the exfoliated layers. The specific surface area of volclay as measured by the nitrogen adsorption method (BET) was found to be 15.5 m<sup>2</sup>/g, which is very small compared to that of the 1-nm thick layers (760 m<sup>2</sup>/g). This shows that the volclay particles are quite thick (ca. 50 nm) in the dry state.

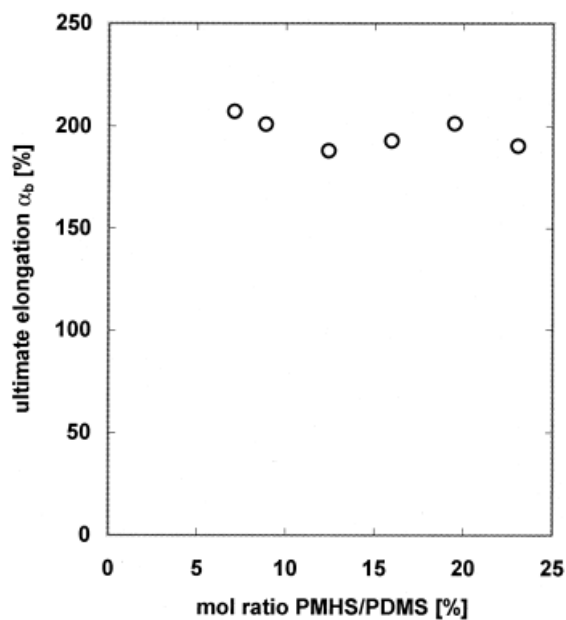
Model PDMS networks are usually prepared by end-linking a difunctional (e.g., vinyl-terminated) PDMS with a tri- or tetrafunctional crosslinker, for example, tetrakis(dimethylsiloxy)silane. Without side reactions, the ratio of silane hydrogens to vinyl groups ( $r$ ) is approximately one.<sup>21,22</sup> In fact, the optimal ratio of crosslinker to vinyl groups ( $r_{opt}$ ) is that which gives a network with the lowest amount of dangling chains, that is the lowest degree of equilibrium swelling, and leads to the highest elastic modulus.<sup>22–24</sup> In real networks,  $r_{opt}$  is often larger than one due to side reactions, kinetic (viscosity) or steric effects, and this ratio has to be experimentally determined.<sup>23,24</sup> In this study, a multifunctional crosslinker (PMHS) was used because of its popularity in the industry, and the optimal ratio of reactants was determined by measuring the mechanical properties of networks prepared with different compositions. This approach was preferred to the often-used equilibrium swelling measurement, because it is directly linked to the goal of this study (reinforcement of PDMS networks). Figure 2 shows the dependence of the reduced force [ $f^*$ ] and the tensile strength  $f_b^*$  of the PDMS network on the composition, given as the molar ratio of the reactants. It can be easily seen that there is an optimal concentration of crosslinker (in the vicinity of 12.5 mol %), above which the mechanical properties of the network deteriorate. A crosslinker concentration of 12.5 mol % was consequently used to prepare the composites. Contrary to modulus and strength, the ultimate elongation (elongation to break) does not significantly depend on the amount of crosslinker (Fig. 3).

The influence of increasing volume fraction of Na- and Li-volclay on the reduced force is shown in Figure 4. It can be seen that in both cases the modulus increased with increasing filler fraction. However, the Li-volclay enhanced the modulus more than the Na-volclay, so that [ $f^*$ ] of the 14 vol % composite was more than four times higher

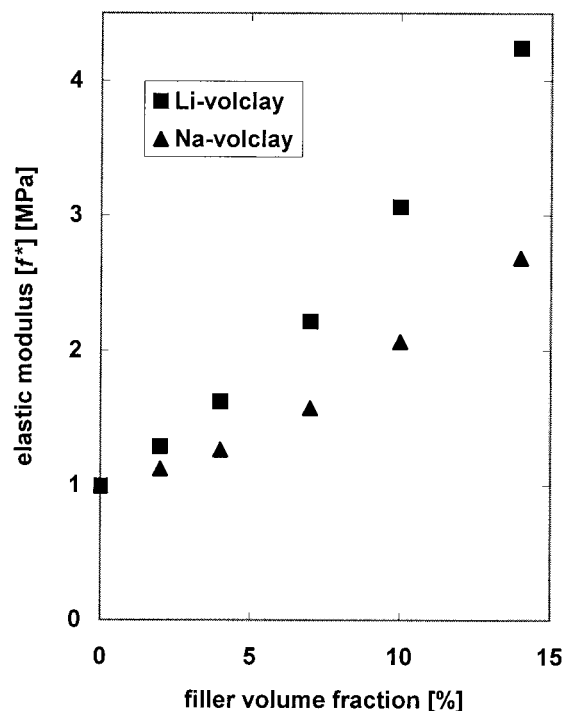


**Figure 2** Dependence of the modulus and ultimate strength of the unfilled PDMS network on the mol ratio of crosslinker to vinyl-terminated precursor.

than that of the polymer matrix compared to 2.5 times in the case of the Na-volclay. Figure 4 also shows that up to 14 vol %, the reduced force did



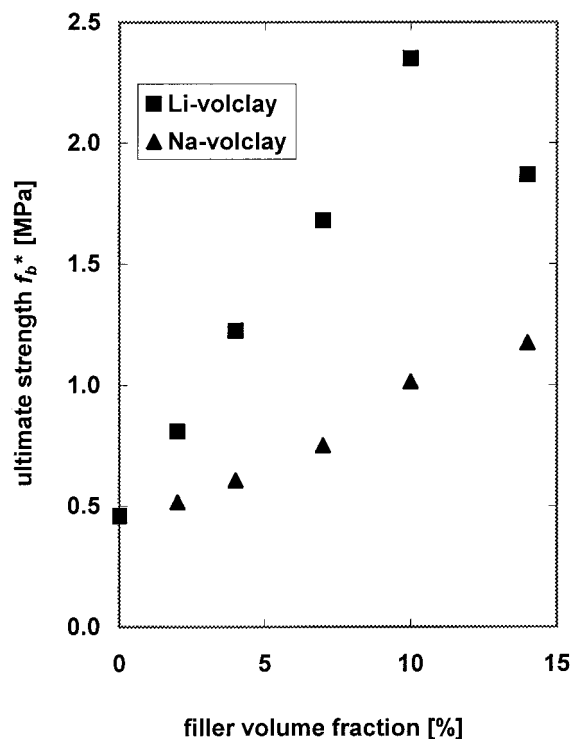
**Figure 3** Dependence of the ultimate elongation of the PDMS network on the mol ratio of crosslinker to vinyl-terminated precursor.



**Figure 4** Dependence of the ultimate strength of the volclay composites on the filler volume fraction.

not reach a saturation value. This is in contrast to the results obtained with OMT composites, where a maximum relative modulus was reached at 4% loading.<sup>14</sup> The dependence of the composites' ultimate strength on the filler type and volume fraction is shown in Figure 5. It can be seen that  $f_b^*$  appreciably increased with increasing filler fraction, so that the strength of the 14 vol % Na-volclay composite reached a value 2.5 times that of the PDMS matrix and no plateau value was reached. In the case of the Li-volclay, a maximum value for  $f_b^*$  (five times that of the matrix) was reached at a volume fraction of 10%. The large increase in modulus and strength of the volclay-PDMS composites obtained from vinyl-terminated precursors reported here is in contrast to the results of Takeuchi and Cohen for OMT composites.<sup>16</sup> The effect of the filler type and volume fraction on the ultimate elongation (elongation at break,  $\alpha_b$ ) of the composites is plotted in Figure 6. In the case of the Na-volclay,  $\alpha_b$  decreased continuously with increasing volume fraction of the filler, while in the Li-volclay composites it increased slightly to level off at 4 vol % then strongly fell above 10 vol %.

The above-mentioned findings can be brought in correlation with the structure of the compos-



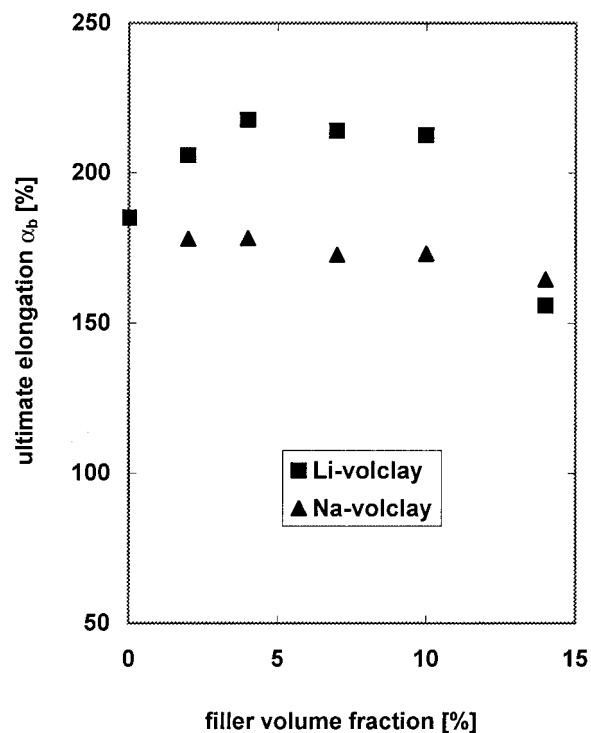
**Figure 5** Influence of the filler volume fraction on the ultimate strength of the volclay composites.

ites. The SEM micrographs (Fig. 7) of the Na- and Li-volclay composites at 10 and 14 vol % loading show the morphology of the composites. It can be seen that the particulates are uniformly distributed in all cases and that generally the Na-volclay composites contain more agglomerates than the Li-volclay composites. It is also ostensive that the 14 vol % Li-volclay composite [Fig. 7(c)] contains more agglomerates than the 10 % loading [Fig. 7(d)], while in case of the Na-volclay composites no appreciable difference between the 10 and 14% composites can be observed.

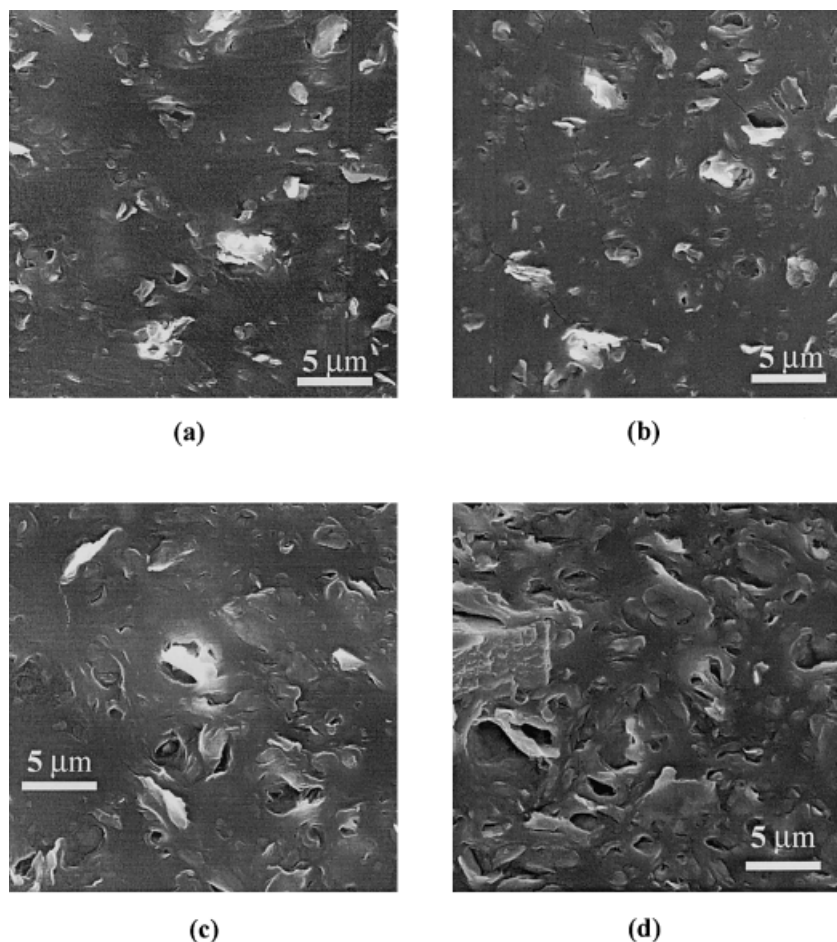
The WAXRD patterns of the Na- and Li-volclay as well as those of their PDMS composites are plotted in Figure 8, showing the 001 and 004 basal reflections of the filler. As can be seen, the basal reflection angles of Na-volclay did not change in the PDMS composite, thus indicating that the polymer chains did not intercalate the aluminosilicate layers. In case of the Li-volclay composites, the 001 basal reflection of montmorillonite was shifted by  $0.5^\circ$  to lower values, indicating that the basal-plane spacing was widened by ca. 0.09 nm. The 004 reflection was also shifted lower and became much broader. This suggests that, in this case, the polymer chains intercalated

the layered aluminosilicate lattice. These results correlate well with the observations made during the preparation of the composites. The Na-volclay swelled only slightly in methyl ethyl ketone, while the Li-volclay strongly swelled, then collapsed on evaporating the solvent despite the polymer presence. In other words, the exfoliated Li-volclay layers reaggregated, squeezing most of the polymer out of the galleries. It seems that solvating the clay surface by the polymer molecules is more important for preparing exfoliated composites than the diffusion of the polymer chains between the aluminosilicate layers.

These results show that the Na-volclay composites are of the conventional type, while the Li-volclay ones display a mixed structure (intercalated + conventional). However, all particles (stacks and agglomerates) are uniformly distributed in the polymer matrix. This uniformity manifests itself in the steady rise of the modulus with increasing volume fraction of the filler without reaching a plateau value. The presence of agglomerates did not limit the modulus enhancement, because the stress (and resulting strain) used to measure the modulus is too small to disintegrate the agglomerates and because the particulates are uniformly distributed in the matrix. The in-



**Figure 6** Influence of the filler volume fraction on the ultimate elongation of the volclay composites.



**Figure 7** SEM micrographs of sections cut perpendicular to the horizontal plane of composite samples (a) 10 vol % Na-volclay, (b) 14 vol % Na-volclay, (c) 10 vol % Li-volclay, (d) 14 vol % Li-volclay.

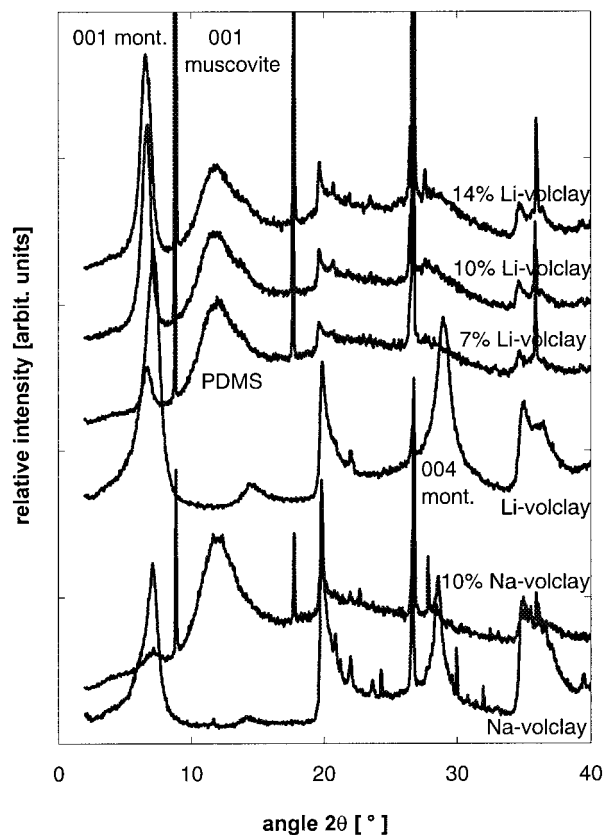
crease in modulus of the volclay composites is modest compared to that measured in comparable mica composites due to the small aspect ratio of the volclay particles.<sup>25</sup> The ultimate strength was appreciably enhanced by the small particle size of montmorillonite, but the appreciation was limited by the increase in number of agglomerates; a result that is in line with those obtained with PDMS–mica composites.<sup>25</sup>

The weight loss of the 10 vol % composites with increasing temperature in a nitrogen atmosphere is plotted in Figure 9. In contrast to the organo-modified aluminosilicates,<sup>9,15</sup> both Na- and Li-volclay enhanced the thermal degradation of PDMS. The weight loss in the Li-volclay composite was higher than in the Na-volclay one, which indicates that the degradation enhancement can be ascribed to a catalytic effect of the inorganic surface. The oxidative degradation of the same

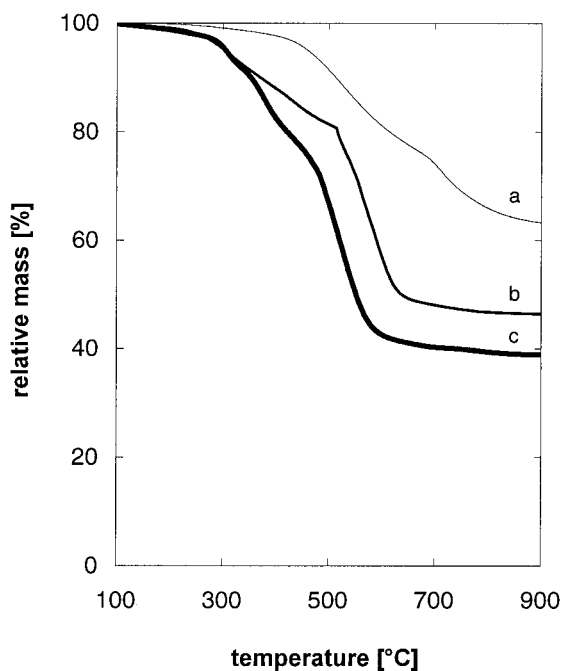
composites is shown in Figure 10. It can be seen that the unfilled PDMS degrades more readily in air than in nitrogen. The Li-volclay composite was also oxidized at a lower temperature than the unfilled polymer, thus supporting the catalysis hypothesis. The catalytic effect probably depends on the chemical composition of the filler and the nature of the surface cations. What is surprising is that the Na-volclay composite is a little bit more stable in air than PDMS itself.

## CONCLUSION

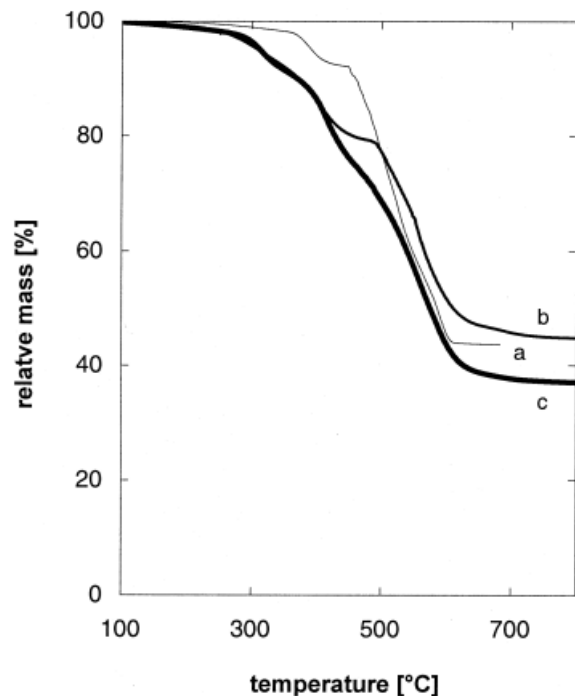
The incorporation of Na-volclay particles in PDMS leads to conventional composites, while Li-volclay gives a mixed structure (intercalated + conventional). The increase in elastic modulus and ultimate strength of the composites is propor-



**Figure 8** Comparison of the XRD patterns of Na- and Li-volclay with those of their PDMS composites.



**Figure 9** TGA traces recorded under nitrogen (a) unfilled PDMS, (b) 10 vol % Na-volclay, (c) 10 vol % Li-volclay.



**Figure 10** TGA traces recorded under air (a) unfilled PDMS, (b) 10 vol % Na-volclay, (c) 10 vol % Li-volclay.

tional to the filler-volume-fraction; however, the increase in strength can be limited by particle agglomeration at high loading. Li-volclay enhances the mechanical properties of the composites more than Na-volclay. This can be attributed to the formation of an intercalated structure, which leads to particulates of smaller thickness and hence higher aspect ratio.

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