Thermal Properties and Flame Retardancy of Polyglycidyloxypropyl Silsesquioxane/Layered Titanate Nanocomposites

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ABSTRACT: Polyglycidyloxypropyl silsesquioxane, which has an excellent heat resistance, was combined with sheet-like and spherical titanate as nano-fillers. The burning property of the composites was related to the shape of the dispersed titanate. A burning test was carried out according to the UL-94 test method. As a result, though the test specimen burned from one end to the other in the spherical titanate filled composite system, a fire extinguishing property was observed in the sheet-like titanate filled composite system. The extinguishing time of the latter system classified V-0 in the specification test. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2649–2655, 2008

Key words: thermosets; nanocomposites; thermal properties; fillers; high performance polymers

INTRODUCTION

Recently, an environmental issue has become especially important in the industrial fields and some chemical materials have already been regally restricted for use in products. Generally, halogen containing compounds and phosphorous-containing additives have been used to provide a flame retardancy to electrical encapsulation materials and laminates. However, it is predicted that halogenated additives may generate dioxin derivatives as toxic materials.[1] Though phosphorous-type resins as reasonable safety materials have been studied in many reports,[2–4] it has become urgently necessary to develop alternative materials in the terms of better environmental safety.

Lu and Hamerton[5] presented an overview of recent developments in halogen-free flame retardant polymers, for example, silicon and nitrogen-containing flame retardants. As one of the other methods, it is well known that the formation of a foaming mass which shields the polymer surface from the heat source and air is effective. Iji et al.[6,7] reported that the benzoguanamine modified phenol-biphenylene type epoxy resin system shows a high flame retardancy. They concluded that it is due to the release of non-flammable nitrogen gas derived from the benzoguanamine unit and thermal stability derived from the biphenylene unit.

On the other hand, we have already reported the hybridization of epoxy resin as an organic component and alkoxy silane as an inorganic component by the hydrolysis-condensation reaction.[8–10] In these systems, they show high glass transition temperature and thermal decomposition temperatures. However, we could not prepare the materials which have a self-extinguishing property. As mentioned above, one of the efficient methods to achieve self-extinguishing is to break off the diffusion of low molecular weight flammable gas as which are generated during burning. In this study, the hybrid material was then combined with a particular-shaped inorganic filler to prevent the generated flammable gas from diffusing to the flame source, and the flame retardancy was investigated.
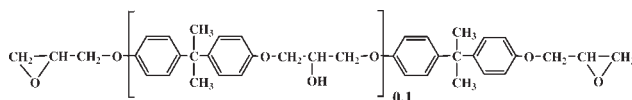
EXPERIMENTAL

Materials

The epoxy resin used in this study was the diglycidyl ether of the bisphenol A type epoxy resin (DGEBA; JER 828EL, JER, Tokyo, Japan; M_w = 380, Epoxy equivalent = 190 g/equiv),
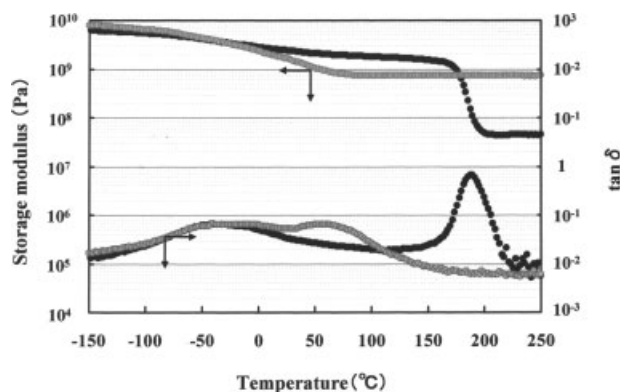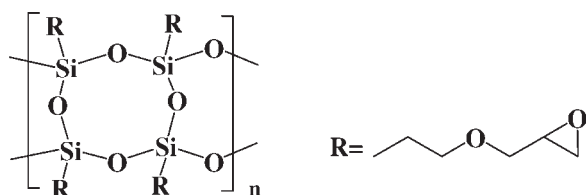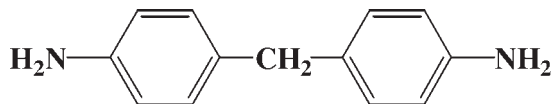
Figure 1 Dynamic mechanical properties of the (●) DGEBA and (◉) PGSQ systems.

and the polyglycidyloxypropyl silsesquioxane (PGSQ; KHE-1000, Nippon Kayaku, Tokyo, Japan; M_w = 3700, Epoxy equivalent = 171 g/equiv).

The curing agent was 4,4'-diaminodiphenylmethane (DDM; M_w = 198, Kanto Chemical, Tokyo, Japan).

As fillers, an organo-layered titanate (HTO-ODA (0.2 equiv)-LL; Otsuka Chemical, Osaka, Japan)[11] and spherical titanate (Wako Chemical, Osaka, Japan) were used.

Preparation of the epoxy/titanate system

A mixture of titanate and PGSQ was stirred at 80°C, 135 rpm, for 3 h and then degassed for 10 min. After adding a stoichiometric amount of curing agent, the mixture was cured at 80°C for 2 h, 150°C for 2 h, and 190°C for 4 h. It was confirmed by FT-IR measurements that the final conversion of the epoxy groups in the cured resin was greater than 90%.

Measurements

The chemical conversion of the epoxy groups was confirmed by FTIR spectroscopy (SPECTRUM 2000; Perkin-Elmer).

Wide angle X-ray diffraction (WAXD; R-AXIS, Rigaku, Tokyo, Japan) was used to evaluate the basal spacing of the layered titanate. The basal spacing was

calculated by the Bragg's formula ($n\lambda = 2d \sin \theta$). Diffraction patterns were obtained with Cu-Kα (λ = 0.154 nm) radiation generated at 40 kV and 60 mA.

A dynamic mechanical analysis of the cured system was completed using a non-resonance forced vibration viscoelastometer (Rheogel-E-4000; UBM, Kyoto, Japan) in the tension mode. The frequency and amplitude of the vibration were adjusted to 10 Hz and ±5 μm, respectively. The heating rate was 2°C/min and the measured temperature range was from −150°C to 250°C. The sample dimensions were ~4.5 × 30.0 × 0.4 mm³.

A thermogravimetric analysis was carried out using TG (TG-DT6200; SII nanotechnology, Tokyo, Japan). The sample weight was 20 mg and the purge gas was air. The heating rate was 20°C/min and the measured temperature range was from 100°C to 800°C.

The morphology of the titanate and their composites was observed using a scanning electron microscope (SEM; JSM-6700F; JEOL, Tokyo, Japan). Prior to the examination, the surfaces were coated with a thin platinum layer (200 Å) to improve the conductivity and prevent charging.

The morphology of the phase structure was observed using a transmission electron microscope (TEM, JEM-1210; JEOL). An ultra-thin section of the specimen for the TEM observations was prepared using an ultramicrotome (Reichert Ultracut E; Leica) with a diamond knife. The specimens were not treated with any staining techniques. The thickness of specimens was 50 nm and the acceleration voltage was 150 kV.

The flame retardancy of the cured systems was determined using the UL-94 method from Underwriters Laboratories. The sample dimensions were ~127 × 12.7 × 4 mm³. The height from the top of the Bunsen burner to the bottom of the test specimen was always at 9.5 mm. Five sample bars were used for this test. All test specimens twice underwent a 10 s ignition, and the total time until each specimen show a self-extinguishing feature was recorded.
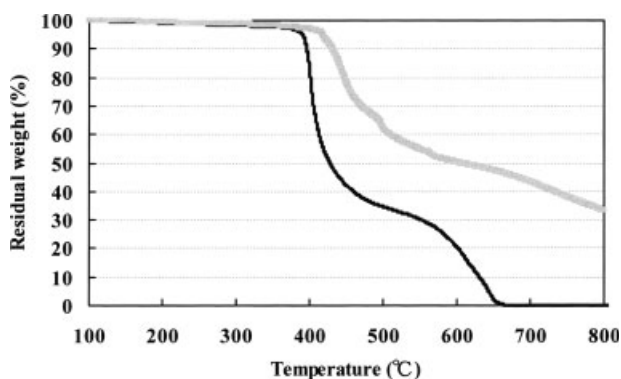

Figure 2 TGA curves of the (●) DGEBA and (◉) PGSQ systems.
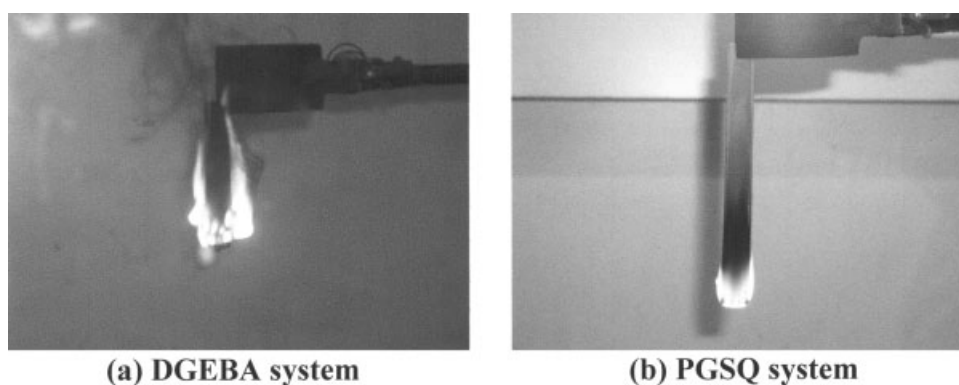
(a) DGEBA system   (b) PGSQ system

Figure 3 Test specimens of the (a) DGEBA and (b) PGSQ systems after ignition.

Optical photographs showed the state of the test specimens 20 s after the second ignition.

RESULTS AND DISCUSSION

Thermal properties of DGEBA and PGSQ systems

The temperature dependence of the dynamic mechanical properties of the DGEBA and PGSQ systems are shown in Figure 1. In the DGEBA system, the storage modulus showed a significantly high decrease that originated in the glass-rubbery transition around 180°C. The storage modulus in the rubbery plateau region over 200°C was 4.4×10^7 Pa. On the other hand, in the polyglycidyloxypropyl silsesquioxane (PGSQ) system, it retained the high modulus of 7.3×10^8 Pa in the higher temperature region over 100°C, though the relaxation peak, which could be predicted as the molecular motion of the aliphatic chains between the inorganic moiety and epoxy group, was observed between 30 and 100°C. On the basis of these results, it was clearly determined that the PGSQ system had a high thermal stability. We have already reported that the epoxy/silica hybrids show a significantly considerably low tan δ peak and unclear glass transition temperature.[8–10] This is due to the silica network, which has a high heat resistance. In this system, a similar tendency was observed.

The thermal decomposition property of DGEBA and PGSQ are shown in Figure 2. The initial decomposition temperature, at which a 5% mass loss occurs, for the PGSQ system (418°C) was about 30°C higher than that for the DGEBA system (390°C). Moreover, the yield at 800°C in the PGSQ system (33.3 wt %) was considerably higher than the theoretically calculated $SiO_{3/2}$ content (23.6 wt %). This result means that the PGSQ prevents the epoxy matrix from undergoing thermal decomposition. On the other hand, we confirmed that the cured PGSQ system partially shows a nano-size phase separation structure of the inorganic components. The nano-size

inorganic phase certainly contains some organic components, because the glycidyloxypropyl groups as the side chains of PGSQ forcibly bond to the backbone moiety consisting of an inorganic component. As previously mentioned, the PGSQ system undergoes a nano-size inorganic phase separation. However, it is considered that all inorganic components are not always in the separated phase, but most of them are in the miscible state.[12] It is expected that the inorganic component prevents thermal decomposition of the organic component in the soluble part. On the other hand, Ni and Zheng[13] reported that the nano-size silsesquioxane in the epoxy matrix acts as physical crosslinking sites and efficiently reinforces the epoxy network as an organic component. On the basis of these considerations, it can be suggested that the excess yield at 800°C originated in the organic component protected by the miscible inorganic networks. As a result, it was indicated that the PGSQ system has an excellent thermal stability and flame retardancy.

The state of the test specimen after ignition was observed and shown in Figure 3. The pictures show their flammability 20 s after ignition. As a result, the
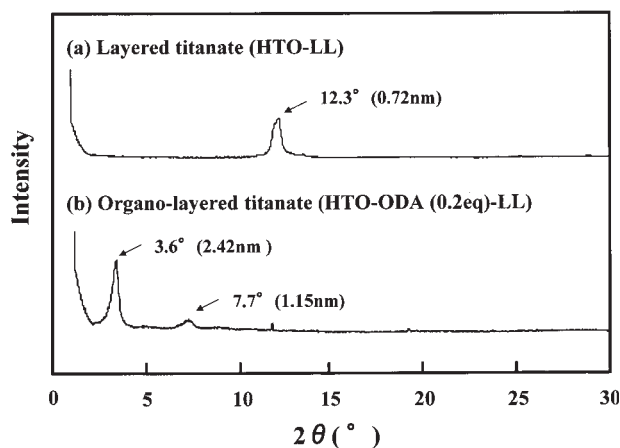

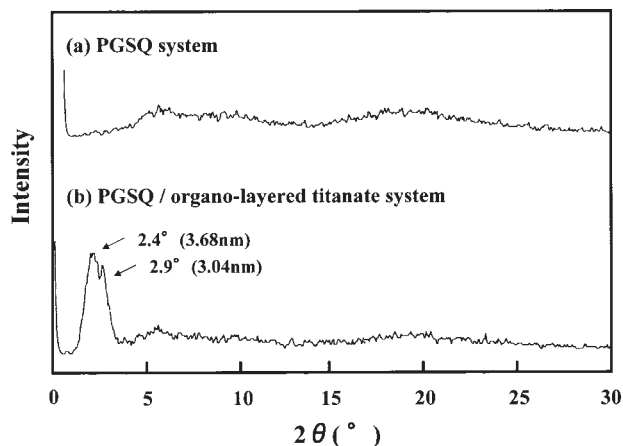**Figure 4** SEM photographs of the titanate having different shapes.

Figure 5 XRD patterns of the layered titanate and organo-layered titanate.

DGEBA system vigorously blazed up for a relatively short time. On the other hand, the PGSQ system burned out more slowly and a difference in the flammability was indicated. This result suggests that the PGSQ matrix slightly prevents the composite material from burning, regardless of the fact that the $SiO_{2/3}$ content as an inorganic component was only about 20%. This determines the thermal stability of PGSQ, which has fine miscibility of organic and inorganic components by covalent bond.

Dispersion of the different shaped titanate filler

Two different types of the titanate fillers observed by SEM are shown in Figure 4. The (a) HTO-ODA (0.2equiv)-LL forms a laminated structure of thin titanate sheets (thickness: ca. 1 nm) and the sheet size was about 10–20 μm. On the other hand, (b) the spherical-shaped titanate has a 100–200 nm average diameter.

In this study, we then used HTO-ODA (0.2equiv)-LL, which is a layered titanate treated with alkyl mono-ammonium chloride (derived from octadecyl

amine and HCl aq). The WAXD patterns of the untreated layered titanate (HTO-LL) and organo-layered titanate (HTO-ODA (0.2 equiv)-LL) are shown in Figure 5. The diffraction peak of the (a) layered titanate was at 12.3°. On the basis of the result, we found that the basal spacing of the layered titanate was 0.72 nm. On the other hand, some peaks were observed in (b) the organo-layered titanate and their peaks shifted to the lower angle side of 2θ than (a) the layered titanate. Generally, it is known that cations between the interlayer in the layered inorganic materials, such as clay, are easily exchanged by typical "alkyl ammonium ions."[14–17] This result means that the interlayer spacing of the titanate expanded due to the introduction of the alkyl ammonium ion. From their diffraction peaks, the basal spacing is mainly about 2.4 nm and another is about 1.2 nm.

The WAXD patterns of the unmodified PGSQ and PGSQ/organo-layered titanate composite systems are shown in Figure 6. The PGSQ system showed only amorphous halos based on the network structure. This means that the inorganic component of the PGSQ forms an amorphous structure. On the other hand, the PGSQ/organo-layered titanate system showed some peaks at 2.4°–2.9°as 2θ. As previously mentioned, the PGSQ system forms an amorphous polymer network. Therefore, it is considered that these peaks are derived from the interlayer spacing of the combined organo-layered titanate. Compared to the diffraction pattern of the organo-layered titanate in Figure 5, the basal spacing was considerably expanded from about 2.4 nm to 3.7 nm. This suggests that the PGSQ matrix was introduced into the layered structure of the titanate and the nano-composites material can be prepared in this system.

The morphologies of (a) the PGSQ/organo-layered titanate and (b) the PGSQ/spherical titanate composites were investigated using SEM (Fig. 7). In the (a) PGSQ/organo-layered titanate system, an aggregated
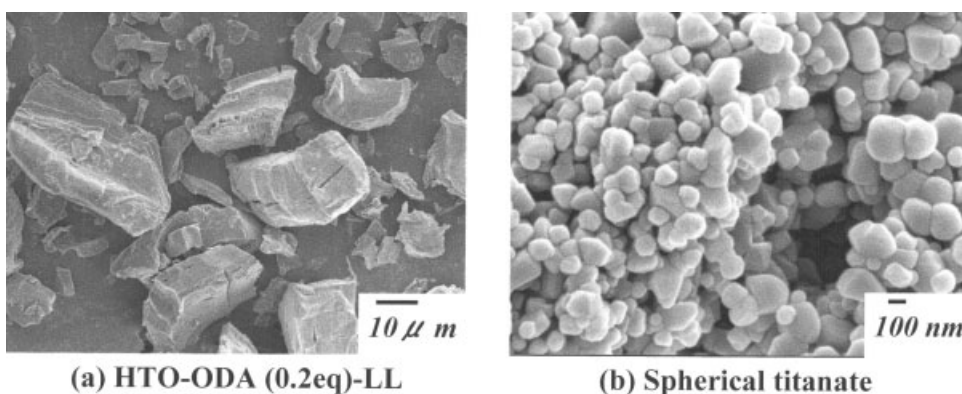

(a) HTO-ODA (0.2eq)-LL

(b) Spherical titanate

Figure 6   XRD patterns of the PGSQ and PGSQ/organo-layered titanate systems.

(a) PGSQ / organo-layered titanate
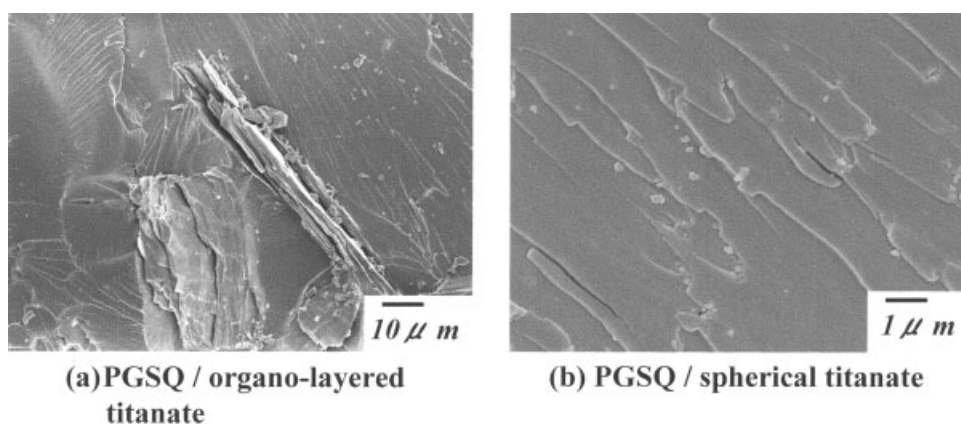
(b) PGSQ / spherical titanate

Figure 7 SEM photographs of the PGSQ system (titanate content: 5 wt %).

layered titanate structure was observed with about a 5 μm thickness. On the other hand, the spherical titanate in the epoxy matrix showed a good uniform dispersion.

To discern the dispersion of the layered titanate on a micro level, the nano-scale morphology of the PGSQ/organo-layered titanate composites is shown in Figure 8. The nano-composite system showed many dark and bright spots. The dark spots indicate the inorganic components in this system, which are the siloxane network structure and layered titanate, because of their difference in the transmitted electronic density between the organic component and inorganic component. This result means that the PGSQ system forms a microscopic phase separation structure.[12] Moreover, the combined layered titanate is composed of several stacked titanate layers in the matrix. Although they do not disperse as a sheet of titanate, it seems that their interlayer spacing in the nano-composite was certainly enlarged. However, the layered structure was not always observed in the whole field of view. This means that the stacked layered titanate disperses as an aggregated structure, as already mentioned.
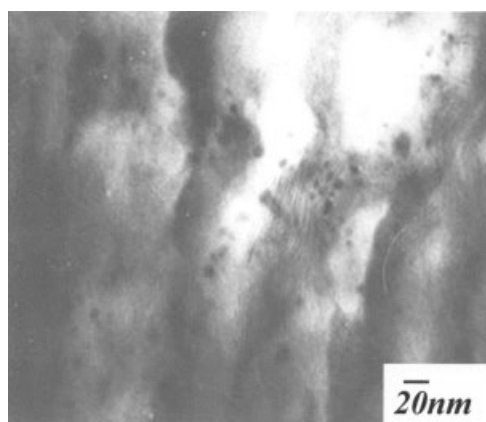
Flame retardancy of DGEBA and PGSQ/titanate systems

The relationship between the titanate content and extinguishing time of the DGEBA and PGSQ/organo-layered titanate, and PGSQ/spherical titanate system is shown in Figure 9. The DGEBA/organo-layered titanate system burned out without self-extinguishing regardless of the titanate content level. Similarly, the PGSQ/spherical titanate system also burned out, although the PGSQ matrix exhibited a thermal stability based on the TGA data (Fig. 2). On the other hand, the PGSQ/organo-layered titanate system showed a self-extinguishing feature after 8 s even for the relatively low titanate contents (5 wt %) and was classified UL V-0. These results suggest that the sheet-like structure, which has a large scale surface area, of the organo-layered titanate affects the self-extinguishing feature of the PGSQ system, because the difference in the PGSQ/spherical and organo-layered titanate is only the shapes of the fillers.

Generally, it can be predicted that the sheet-like structure can easily prevent the gas diffusion. Actually, in this system, some dripping was observed by explosion of the test specimen as evidence of this

Figure 8 TEM photographs of the PGSQ/organo-layered titanate system (titanate content: 5 wt %).
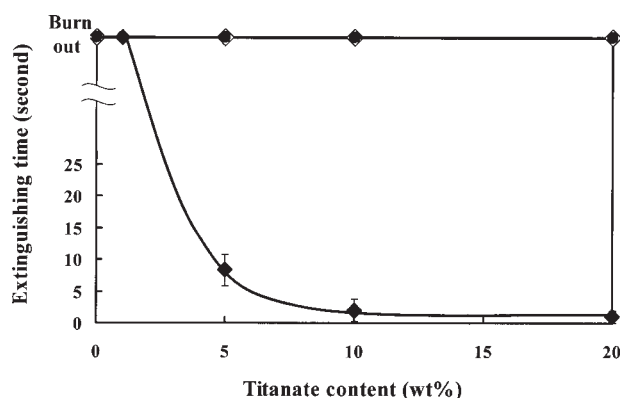

Figure 9 Flammability test of each cured system. (◇) DGEBA/organo-layered titanate, (◆) PGSQ/organo-layered titanate, (●) PGSQ/spherical titanate systems.

(a) DGEBA / organo-layered titanate

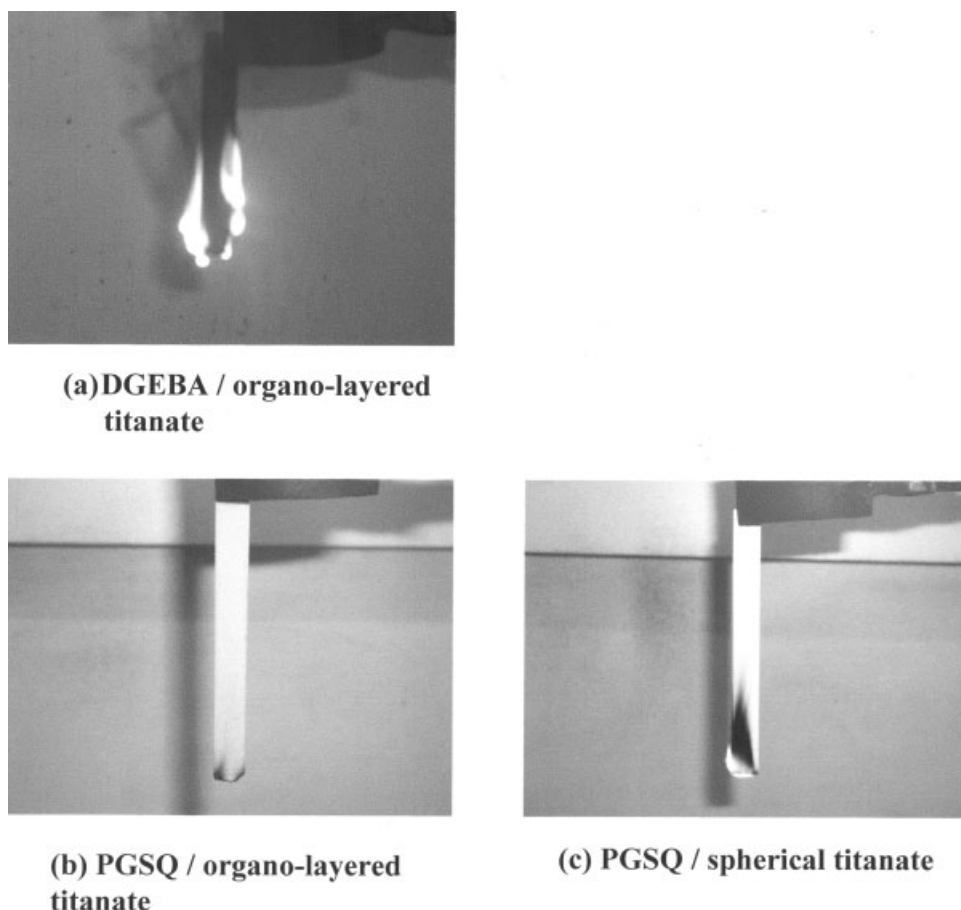(b) PGSQ / organo-layered titanate

(c) PGSQ / spherical titanate

Figure 10 Test specimens of the DGEBA and PGSQ/titanate systems after ignition. (Titanate content: 10 wt %).

projection. Therefore, we suspect that the flammable gases which occurred by burning cannot diffuse to the burning source. However, if the matrix resin, such as DGEBA, has only a low thermal stability, it seems that the flame retardancy effect based on the filler shape hardly appears.

The state of the test specimen after the second ignition was observed and shown in Figure 10. The pictures show their flammability after ignition for 10 s. The DGEBA/organo-layered titanate system showed a vigorously increased blazing, similar to Figure 3(a). In (b) PGSQ/organo-layered titanate system, the test specimen showed a rapid self-extinguishing just after ignition and some non-flamed drippings of the species were observed. In the (c) PSGQ/spherical titanate system, though the smaller flame was observed than in the Figure 10(a) system, the test specimen finally blazed up. From the difference in the burning behavior between the PGSQ/organo-layered titanate and spherical titanate systems, it is considered that flame resistance of the PGSQ/organo-layered titanate system is due to the encapsulation of the generated flammable gas in the matrix by the high gas barrier property of the lay-

ered titanate. On the basis of these results, it is considered that the composition of the high heat resistance matrix and gas barrier filler was required to achieve the self-extinguishing property.

CONCLUSION

The polyglycidyloxypropyl silsesquioxane (PGSQ) showed a higher thermal stability than DGEBA. The layered titanate using an organically treatment procedure was intercalated into PGSQ matrix and the interlayer spacing of the laminated titanate and nano-composites was prepared. The nano-composites exhibited a self-extinguishing property and classified as UL V-0 even for a 5 wt % layered titanate content. We considered that this result originated from the high heat resistant matrix and filler having a large surface area due to their sheet-like titanate structure, because it is expected that the diffusion of a flammable gas generated by burning is prevented by the layered titanate having high a gas barrier property.

The PGSQ and layered titanate were provided by Nippon Kayaku and Otsuka Chemical, respectively.

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