

Flame Retardancy and Thermomechanical Properties of the Poly-(glycidylxypropyl) Phenyl Silsesquioxane/Layered Titanate Nanocomposites

Miyuki Harada, Shuichi Minamigawa, Kumiko Tachibana, Mitsukazu Ochi

Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita-shi, Osaka 564-8680, Japan

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ABSTRACT: Poly-(glycidylxypropyl) phenyl silsesquioxane (PGPSQ) was combined with an organo-layered titanate filler. The phase structure of the obtained composite was evaluated by XRD and TEM observations. Moreover, a burning test was carried out according to the UL-94 test method. The extinguishing time of the nanocomposites was classified V-0 even for the 1 wt % layered titanate content. Based on the results, it was clarified that the flame retardancy of the PGPSQ/organo-layered tita-

nate system was superior to the poly-(glycidylxypropyl) silsesquioxane (PGSQ)/organo-layered titanate system, which was reported in a previous paper. In addition, the layered titanate as a filler also improved the ductility of the PGPSQ. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 338–344, 2007

Key words: flame retardancy; nanocomposite; thermal property; toughness

INTRODUCTION

Epoxy resins are widely used for their excellent thermal and bonding properties. Recently, large quantities of them are being used in the electrical and other fields. For application in these fields, a good flame retardancy has been strongly required. Generally, halogenated or phosphorous type resins and additives have been used.^{1–3} However, these chemical products give rise to environmentally toxic materials⁴ and some halogenated materials are legally restricted for use. Therefore, it has become necessary to develop alternative materials in terms of better environmental safety.

As one of the ways to achieve this objective, it is known that the formation of a foaming mass which shields the polymer surface from the heat source and air is effective. Iji et al.^{5,6} 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 the thermal stability derived from the biphenylene unit.

In a previous paper,⁷ we have already reported that the polyglycidylxypropyl silsesquioxane (PGSQ)

showed a high thermal stability and flame retardancy without harmful additives, because it contains an inorganic component in the backbone moiety. Moreover, the PGSQ, which was combined with an organo-layered titanate, exhibited a self-extinguishing property with a 5 wt % content of the organo-layered titanate. On the other hand, it is generally well known that phenyl groups produce a high thermal resistance and can provide a high char yield at high temperature. Actually, Ni et al.⁸ has already reported that an epoxy resin containing phenylsilsesquioxane, which has a nanoinorganic structure, showed a high T_g and char yields at 750°C compared to the theoretical yields.

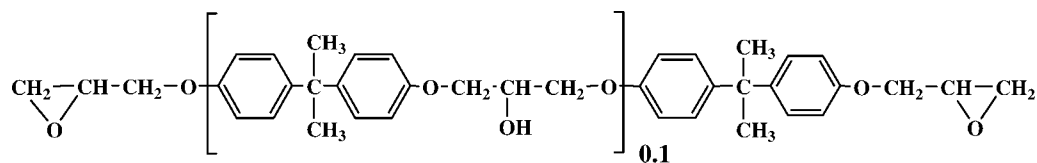
In this study, we used the partially phenyl induced poly-(glycidylxypropyl) phenyl silsesquioxane (PGPSQ) to improve their flame retardancy for the lower organo-layered titanate content. Namely, we tried to improve the flame retardancy by the multiplication effect of the high thermal stability of phenylsilsesquioxane and the gas barrier property due to the layered titanate.

EXPERIMENTAL

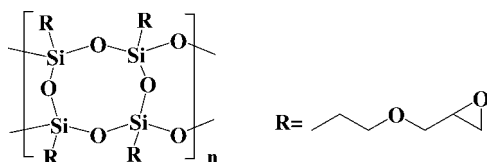
Materials

The epoxy resin used in this study was the diglycidyl ether of the bisphenol A type epoxy resin (DGEBA, JER 828EL, JER, $M_w = 380$, epoxy equivalent = 190 g/eq);

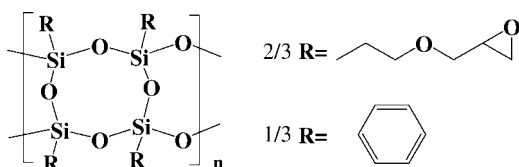
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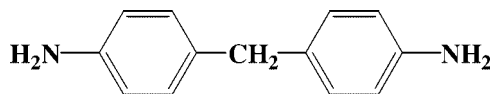
the polyglycidyloxypropyl silsesquioxane (PGSQ, KHE-1000, Nippon Kayaku, $M_w \cong 3700$, epoxy equivalent = 171 g/eq);



and poly-(glycidyloxypropyl) phenyl silsesquioxane (PGPSQ, KHE-3 containing 15 wt% MEK, Nippon Kayaku, $M_w \cong 3000$, epoxy equivalent = 235 g/eq).



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



As a filler, an organo-layered titanate (HTO-ODA (0.2 eq)-LL, Otsuka Chemical)⁹ was used.

Preparation of the epoxy/titanate system

A mixture of the titanate and PGSQ, or PGPSQ was stirred at 80°C, 135 rpm, for 3 h and then degassed for 10 or 30 min. After adding a stoichiometric amount of the curing agent, the mixture was cured at 80°C for 2 h, 150°C for 2 h, and finally at 190°C for 4 h. It was confirmed by FTIR 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).

A dynamic mechanical analysis of the cured system was completed using a nonresonance forced vibration viscoelastometer (Rheogel-E-4000, UBM) in the tension mode. The frequency and amplitude of

the vibration were adjusted to 10 Hz and $\pm 5 \mu\text{m}$, respectively. The heating rate was 2°C/min and the measured temperature range was from -150 to 250°C. The sample dimensions were approximately $4.5 \times 30.0 \times 0.4 \text{ mm}^3$.

A thermal gravimetric analysis was carried out using TG (TG-DTA6200, SII Nanotechnology). The sample weight was 20 mg and the atmosphere was air. The heating rate was 20°C/min and the measured temperature range was from 100 to 800°C.

The morphology of the phase structure was observed using a transmission electron microscope (TEM, JEM-1210, JEOL). An ultrathin 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 approximately $127 \times 12.7 \times 4 \text{ mm}^3$. The height from the top of the Bunsen burner to the bottom of the test specimen was always maintained 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. Optical photographs showed the state of the test specimens 20 s after the second ignition.

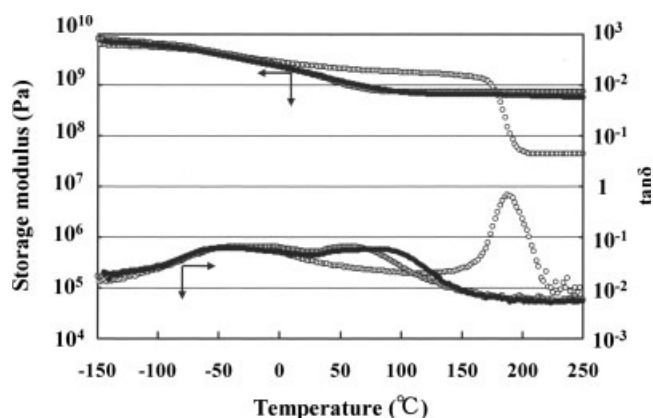


Figure 1 Dynamic mechanical properties of the DGEBA (open circles), PGSQ (gray circles), and PGPSQ/DDM (black circles) systems.

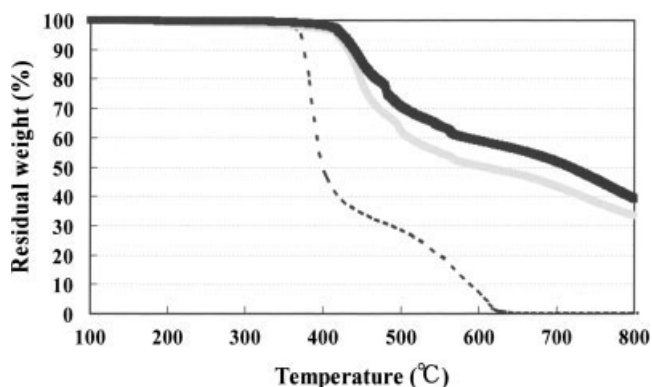


Figure 2 TGA curves of the DGEBA (- - -), and PGSQ (gray circles), and PGPSQ (black circles) systems.

The fracture toughness was measured according to ASTM E-813-89 using the three-point bending method. The sample dimensions were $6.0 \times 40.0 \times 3.0 \text{ mm}^3$. The precrack was formed by tapping with a new razor blade. The ratio of the precrack length ranged from 0.5 to 0.75 for the sample width. The specimen was mounted in an Instron-type tensile machine (AG-2000E, Shimadzu) and loaded at a constant crosshead speed (0.5 mm/min).

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

RESULTS AND DISCUSSION

Thermal properties of PGSQ and PGPSQ systems

The temperature dependence of the dynamic mechanical properties of the DGEBA, PGSQ, and

PGPSQ systems are shown in Figure 1. The storage modulus of the DGEBA system showed a significant decrease. This phenomenon is due to the glass-rubbery transition around 180°C and the storage modulus in the rubbery plateau region over 200°C was $4.4 \times 10^7 \text{ Pa}$. In the PGSQ and PGPSQ system, it retained a 10 times higher modulus than that of the DGEBA system in the same high temperature region, though the relaxation peak predicted as a molecular motion of the aliphatic chains between the inorganic moiety and epoxy group was observed between 30 and 100°C. In the PGPSQ system, a shift in this relaxation peak was observed in a slightly higher temperature region. This result is derived from the introduction of the phenyl group, which has a low mobility compared to the glycidylpropyl group. Generally, it is known that the phenyl groups form π - π stacking structure and this super molecular structure shows thermal stability.¹⁰ However, the large differences were not totally observed.

The thermal decomposition properties of DGEBA, PGSQ, and PGPSQ are shown in Figure 2. For the initial decomposition temperature, at which a 5 wt % mass loss occurs, the PGSQ system (418°C) was about 30°C higher than the DGEBA system (390°C). Though the decomposition temperature of the PGPSQ system (425°C) was similar to that of the former system, the slope of the weight loss curve is quite gentle compared to the PGSQ system. Moreover, the yield at 800°C in the PGPSQ system (39.0 wt %) was considerably higher than the theoretically calculated $\text{SiO}_{3/2}$ content (27.4 wt %). As mentioned in a previous paper,⁷ this result means that the PGPSQ prevents the epoxy matrix from thermal decomposition as well as the PGSQ system (the experimental yield at 800°C: 33.3 wt %, the theoretical yield: 23.6 wt %). In addition to this prevention, the introduced phenyl groups, which can easily form a

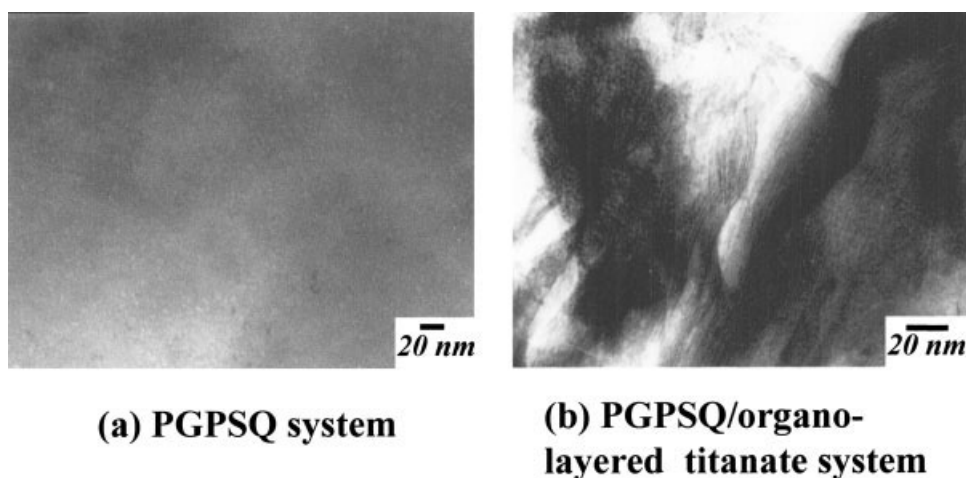


Figure 3 TEM photographs of PGPSQ and PGPSQ/organo-layered titanate (10 wt %) systems.

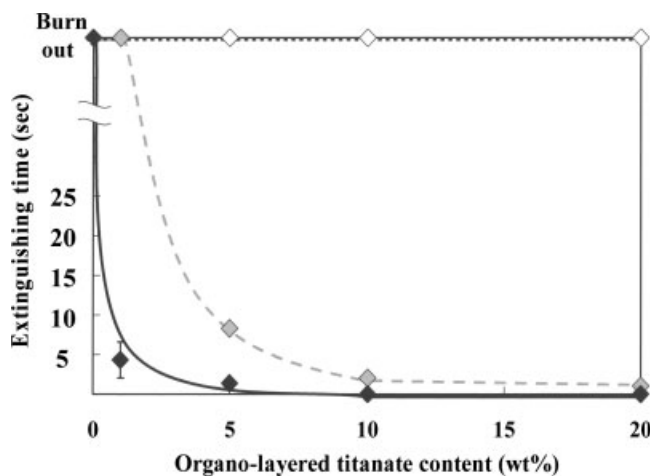


Figure 4 Extinguishing time of the epoxy/organo-layered titanate systems. DGEBA (open diamonds), PGSQ (gray diamonds), PGPSQ (black diamonds).

noncombustible char, contribute to the high yield at 800°C.

Morphology and flame retardancy of PGPSQ/layered titanate systems

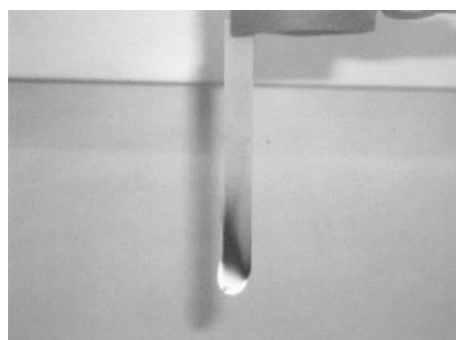
The morphology of the PGPSQ/organo-layered titanate system is shown in Figure 3. The nanocomposite system showed many dark and bright spots. The dark spots indicate the inorganic components in this system, which are the siloxane network structure and layered titanate, because of their difference in the transmitted electronic density between the organic component and inorganic component. This result means that the PGPSQ system forms a microscopic phase separation structure. Moreover, the layered titanate combined with the PGPSQ resin was laminated to the thin titanate layers in the composite. Namely, though they do not perfectly disperse as a sheet of titanate, it appears that their interlayer

spacing in the nanocomposite was certainly enlarged. Based on the X-ray diffraction pattern of the composites, the basal spacing was considerably expanded to about 3.5 nm. However, the layered structure was not always observed in the entire field of view. This means that the stacked layered titanate disperses as an aggregated structure.

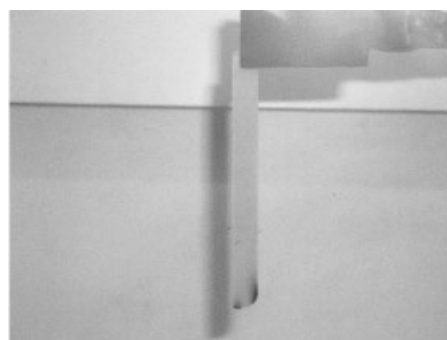
The relationship between the titanate contents and extinguishing times of the DGEBA, PGSQ, and PGPSQ/organo-layered titanate systems are shown in Figure 4. The DGEBA/organo-layered titanate system burned without self-extinguishing, regardless of the change of the titanate content. On the other hand, the PGSQ showed the self-extinguishing property for greater than a 5 wt % titanate content system. These results suggest that the sheet-like structure of the organo-layered titanate having a large scale surface area affects the self-extinguishing property of the PGSQ system.⁷ Marvelously, self-extinguishing of the PGPSQ system was achieved even in the 1 wt % titanate containing system and the system was classified UL V-0. It is considered that the system easily forms a char during burning, because the PGPSQ contains many phenyl groups compared to the PGSQ. Generally, it is known that the theoretical char residue (CR) is related to the char-forming tendency (CFT), which is due to the chemical structure of the polymers.¹¹

$$CR = \{\Sigma(CFT)/M_{\text{unit}}\} \times 1200 \quad (1)$$

CR is a very important value which closely affects the flame retardancy. The calculated CR value of the glycidylxypropyl group is 3.96 after the ring opening reaction of the epoxy groups. On the other hand, that of the phenyl group is 15.6. Thus, the CR value shows that the char-forming ability of the PGPSQ completely differs from that of the PGSQ. Corresponding to the CR value, the flame retardancy of the PGPSQ system was actually improved over than



(a) PGSQ / organo-layered titanate



(b) PGPSQ / organo-layered titanate

Figure 5 Test specimen of the (a) PGSQ and (b) PGPSQ/organo-layered titanate systems after ignition (organo-layered titanate content: 1 wt %).

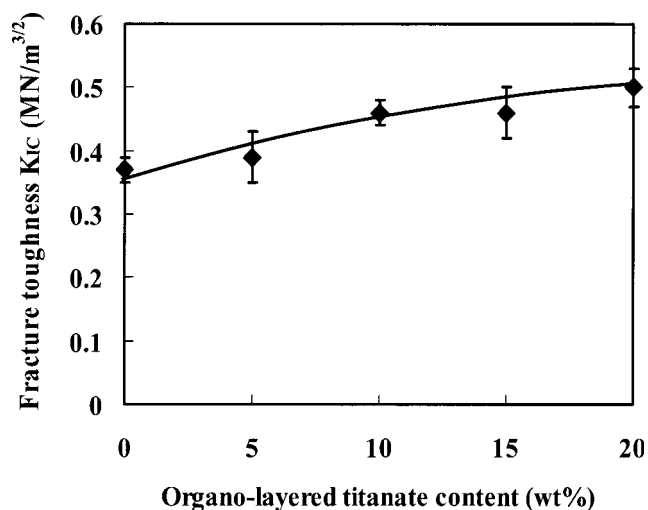


Figure 6 Fracture toughness of the PGPSQ/organo-layered titanate nanocomposites.

that of the PGSQ system. These results are also supported by the TGA data (Fig. 2) as previously mentioned.

The state of the test specimen (1 wt % organo-layered titanate content system) after the second ignition was observed and shown in Figure 5. The pictures show their flammability after ignition for 10 s. The PGSQ/organo-layered titanate system showed a moderate blazing. On the other hand, the test specimen of the (b) PGPSQ/organo-layered titanate system showed rapid self-extinguishing just after ignition and some nonflamed drippings of the species were observed. As shown in Figure 4, the unmodified PGPSQ system finally blazed up. From the difference in the burning behavior due to the existence of the layered titanate, it is considered that the flame resistance of the PGPSQ/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 layered titanate. Based on these results, it is considered that the combination of the

high heat resistance matrix and gas barrier filler was required to achieve the self-extinguishing property.

Mechanical property of the PGPSQ/organo-layered titanate nanocomposites

The PGPSQ system has a theoretical 27.4 wt % $\text{SiO}_3/2$ content. Therefore, the ductility of the system is a very serious problem for practical use. On the other hand, there are many reports about an improvement in the fracture toughness by the addition of clay.^{12–15} They suggested that in the prevention of crack growth is based on the clay as a high aspect ratio filler. Layered titanate used in this study has a considerably high aspect ratio compared to ordinary clays.⁷ Therefore, there is high possibility of a ductility improvement of the silsesquioxane. The fracture toughness values of the PGPSQ/organo-layered titanate systems are shown in Figure 6. The neat PGPSQ system showed considerably low K_{Ic} value. It is well known that the ordinary epoxy resin DGEBA ($n = 0.1$) has an approximate $0.7 \text{ MN}/\text{m}^{3/2}$ value. From this result, it is shown that the PGPSQ system has a poor fracture toughness. With a change in the organo-layered titanate content, the value of K_{Ic} gradually increased and the 20 wt % content system achieved a 1.3 times higher K_{Ic} value than the neat resin. This result suggests that the toughness of PGPSQ can be improved by the addition of a layered titanate filler. These results suggest that the layered titanate as a filler partly works on the flame retardancy and partly for the toughening.

The fracture surfaces of their systems were observed by SEM and are shown in Figure 7. The fracture surface of the neat PGPSQ system showed relatively flat and some shear deformation traces. This means that the PGPSQ system has ductility. On the other hand, the 10 wt % layered titanate system contained submicron particles as the likely aggregated layered titanate and many shear traces around the particles are observed. These results suggest that

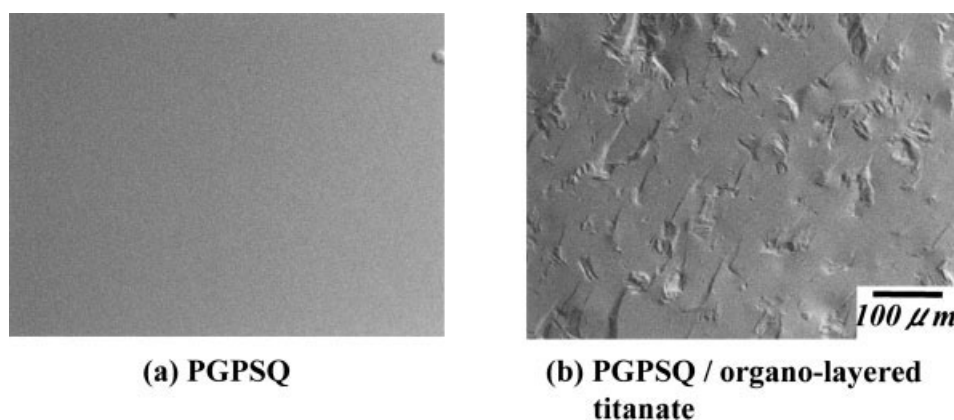


Figure 7 SEM photographs of PGPSQ system and PGPSQ/organo-layered titanate (10 wt %) nanocomposites.

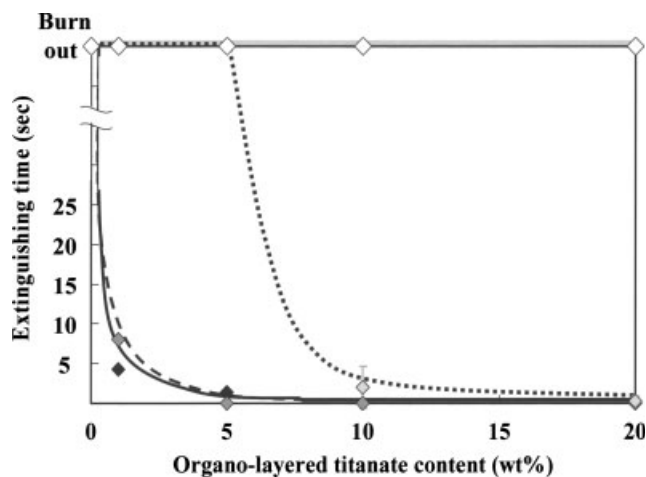


Figure 8 Extinguishing time of the PGPSQ/DGEBA/organo-layered titanate systems. DGEBA content: (—) 0 wt %, (PGPSQ), (---) 10 wt %, (···) 20 wt %, (— · —) 30 wt %.

the dispersed layered titanate prevents crack growth during the fracture process. It is consistent with the improvement in the fracture toughness.

Flame retardancy of PGPSQ/titanate systems with the addition of DGEBA

To minimize the PGPSQ content as a matrix resin, DGEBA was added to the PGPSQ. As previously mentioned, the PGPSQ has a high flame retardancy

and achieved self-extinguishing even for the 1 wt % layered titanate content. However, a more realistic method would be needed for consideration of ordinary uses as high flame retardant compounds in the industrial field. Generally, expensive materials are mixed with inexpensive ones. Therefore, we tried adding DGEBA to the PGPSQ to reduce the PGPSQ contents of the composites and investigated the most suitable content in the state which maintains a high flame retardancy. The relationship between the titanate content and extinguishing time of the PGPSQ/organo-layered titanate added DGEBA system is shown in Figure 8. As a result, in the 10–20 wt % DGEBA added PGPSQ systems, though the burning time gradually increased, the high content organo-layered titanate systems were classified to UL V-0. However, in the 30 wt % DGEBA added PGPSQ system, no self-extinguishing was achieved for any layered-titanate content (Fig. 9).

CONCLUSIONS

PGPSQ, which partially contains a phenyl group as side chains, showed a higher flame retardancy than the PGSQ system. With only the 1 wt % addition of the organo-layered titanate, self-extinguishing of the PGPSQ system was achieved and classified UL V-0. This result is due to the multiplication effect of the high thermal stability of PGPSQ and the gas barrier

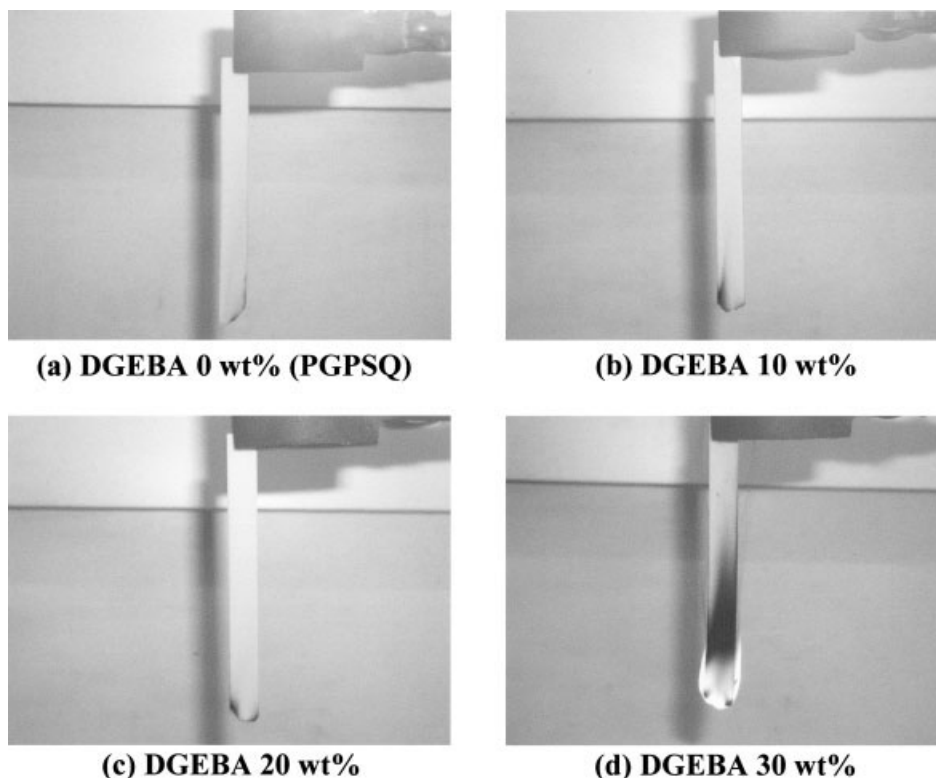


Figure 9 Test specimen of the PGPSQ/DGEBA/organo-layered titanate (10 wt %) systems after ignition.

property of the layered titanate. Moreover, the ductility of PGPSQ was improved by combination with the layered titanate.

The PGSQ, PGPSQ, and layered titanate were provided by Nippon Kayaku Co., Ltd., and Otsuka Chemical Co., Ltd.

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