

Adhesion Properties and Thermal Degradation of Silicone Rubber

Eung-Soo Kim, Hun-Sik Kim, Seong-Hun Jung, Jin-San Yoon

Department of Polymer Science and Engineering, Inha University, Incheon 402-751, South Korea

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ABSTRACT: Silicone rubber is suitable for the thermal insulator of the rocket motors owing to its heat resisting properties as well as its excellent elasticity and restoring force. However, the adhesion properties of the silicone rubber should be improved greatly to be used as the thermal insulator because of its poor adhesiveness coming from the low surface tension. Functional groups were incorporated through copolymerization to the silicone rubber to induce chemical reaction with the functional groups in the propellant/liner components to enhance the adhesion properties. Peeling tests results disclosed that the incorporation of amine groups was the most efficient for the adhesiveness

enhancement and that addition of carbon black improved the adhesiveness still more. Stability against thermal degradation of the silicone rubber was examined by measuring the activation energy through the thermogravimetric analysis. The results revealed that the compounding of the Cloisite[®] clays boosted up the thermal stability of the silicone rubber much more greatly than that of carbon black. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2782–2787, 2007

Key words: silicone rubber; activation energy; clay nanocomposites; adhesion property

INTRODUCTION

Flexible properties and excellent restoring force are required for the thermal insulator, because it should prevent the rocket motor case from deformation and protect the propellant against any external impacts.¹ Heated gas may circulate through the crack, if any, between the thermal insulator and the propellant/liner. It may increase explosively the combustion rate of the propellant so that the combustion becomes uncontrollable. The operation temperature of the rocket motors goes well over 2000–4000 K. Therefore the thermal insulator should be ablated and thermally degraded to protect the motor case by absorbing the combustion heat.^{2,3} In these regards, the thermal insulators should exhibit good adhesion properties as well as thermal stability and ablative characteristics.

Silicone is used as releasing agent due to its poor adhesive properties coming from the low surface tension.^{4,5} Therefore, in spite of the more excellent elasticity and restoring force together with thermal stability of silicone rubber in comparison to other elastomers, its adhesive properties should be improved

greatly to be used as a thermal insulator for the rocket motors.^{6,7}

Incorporation of functional groups, which are capable of reacting with the functional groups in the propellant/liner components, to silicone rubber either through copolymerization or through surface treatment is required for the improvement of the adhesion strength of the silicone rubber.

In this study, amine groups were introduced by way of copolymerization to silicone rubber to enhance the adhesion between the silicone rubber and the propellant/liner by inducing reaction between the amine groups and the isocyanate groups in the propellant/liner components. The isocyanate substances are used for chain extension and crosslinking of hydroxy-terminated polybutadiene to shape the propellant/liner properly.

Thermal stability of the silicone rubber as a function of the amine content was examined by way of the activation energy determined from the weight loss during the thermogravimetric analysis (TGA).^{8,9} Effect of incorporation of the Cloisite[®] series clays and carbon black to the silicone rubber on its thermal stability was also explored.

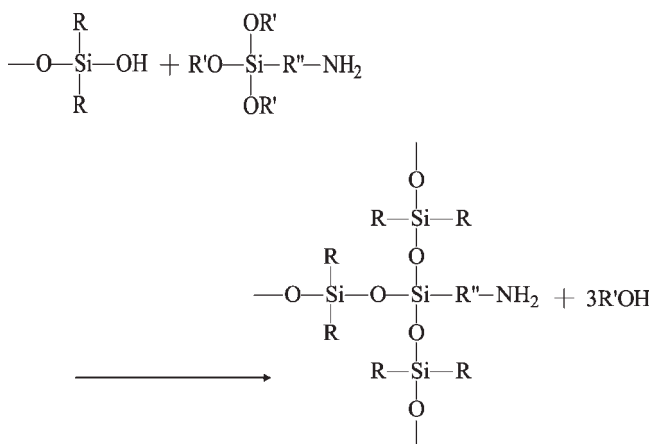
MATERIALS AND METHODS

Materials

Hydroxyl-terminated polydimethylsiloxane (PDMS) was purchased from DongYang Silicone (Iksan,

Correspondence to: J.-S. Yoon (jsyoon@inha.ac.kr).

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Scheme 1 Introduction of amine functional group into hydroxyl-terminated PDMS.

Korea). Tetrapropoxysilane (TPOS, Aldrich) and γ -aminopropyltriethoxysilane (APTES, Aldrich) was used as a crosslinker and adhesion promoter of silicone rubber, respectively. Carbon black (MA100, Mitsubishi, Japan) was supplied by DongYang Silicone. Since the viscosity of PDMS was much higher than TPOS, the carbon black (12 wt %) was premixed into TPOS (88 wt %) to prepare a master batch, which was then mixed with PDMS to obtain well dispersed mixture.

Liner components were composed of hydroxyl-terminated polybutadiene (HTPB) and dimeric diisocyanate (DDI) as a crosslinker, and ferric acetyl acetonate (FeAA) as a catalyst. HTPB contained dioctyl adipate (DOA) as a plasticizer and N-991 carbon black as a filler. The liner components were supplied by ADD (Daejeon, Korea).

The organically modified clays, Cloisite[®]30B, Cloisite[®]25A, and Cloisite[®]20A (C30B, C25A, C20A), were purchased from Southern Clay Product (Gonzales, TX).

Synthesis of silicone rubber

Silicone rubber sheet was prepared from hydroxyl-terminated PDMS and TPOS in bulk state, using dibutyl tin dilaurate (Aldrich) as a catalyst. PDMS was completely dissolved in toluene (1 : 3 weight ratio) at room temperature, and then was mixed with 10% of the crosslinker and 0, 0.7, 1.4, and 2.0 wt % of APTES. Clay (2 wt %) was also added in the mixture when needed, together with dibutyl tin dilaurate (0.1 wt %). The mixture was dried at room temperature for 48 h and then cured in a convection oven at 60°C for 72 h.

Preparation of liner

Poly(butadiene) rubber sheet was prepared by using the mixture composed of hydroxyl-terminated poly-

butadiene (HTPB), dimeric diisocyanate, and ferric acetyl acetonate (FeAA) with 88.73 : 11.27 : 0.05 weight ratio, respectively. The mixture was spread to about 3 mm thickness on the silicone rubber sheet prepared as described above and cured at room temperature for different times to prepare specimens for the peeling test.

Measurements

The thermal analysis of the silicone rubber and the silicone rubber/clay composites was performed by using TGA (TA instruments, Q50). The samples were heated at variable heating rates of 5, 10, and 15°C/min from 25 to 800°C under dry nitrogen flow at 60 cm³/min.

The adhesiveness between the silicone rubber sheet and the cured liner was quantified by using the peeling strength test. The dimension of the specimen was 20 mm × 100 mm × 3 mm and the peel tests were operated at 50 mm/min by universal testing machine (UTM, LLOYD Instruments, Model No. LR10K).

X-ray measurements (XRD) were carried out by using Rigaku DMAX 2500 X-ray diffractometer (Rigaku, Japan) with reflection geometry and CuK α radiation operated at 40 kV and 100 mA. Data were collected within the range of scattering angles (2 θ) of 2–10°.

Transmission electron microscopy (TEM) images were obtained by TEM 2000 EX-II instrument (JEOL, Tokyo, Japan) operated at an accelerating voltage of 100 kV to observe the nanoscale structures of the various composites. All the ultrathin sections (less than 100 nm) were microtomed using a Super NOVA 655001 instrument (Leica, Swiss) with a glass

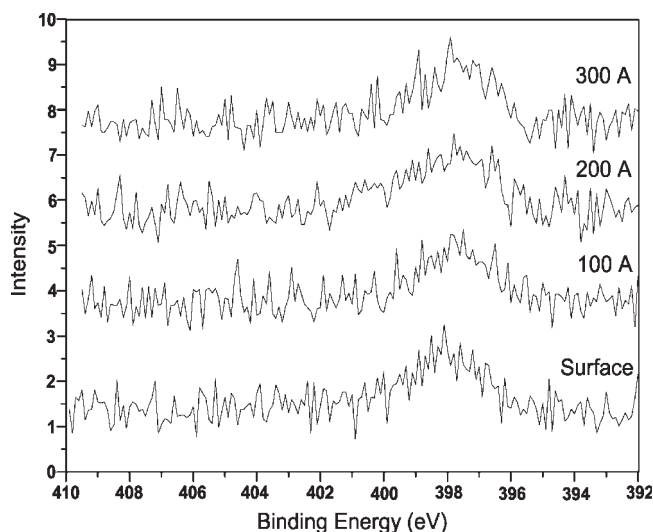


Figure 1 XPS analysis of N element as a function of the depth of the silicone rubber sheet.

TABLE I
Peel Strength (g/cm) of the Silicone Rubber with
Different Contents of APTES

APTES content (wt %)	Silicone rubber with 2 wt % of carbon black	Silicone rubber without carbon black
2.0	Break ($\gg 450$)	27
2.0 ^a	–	182
1.4	302	68
0.7	30	34
0.0	0	0

^a Peel strength of silicone rubber containing 2.0 wt % of APTES after annealing at 60°C for 5 months.

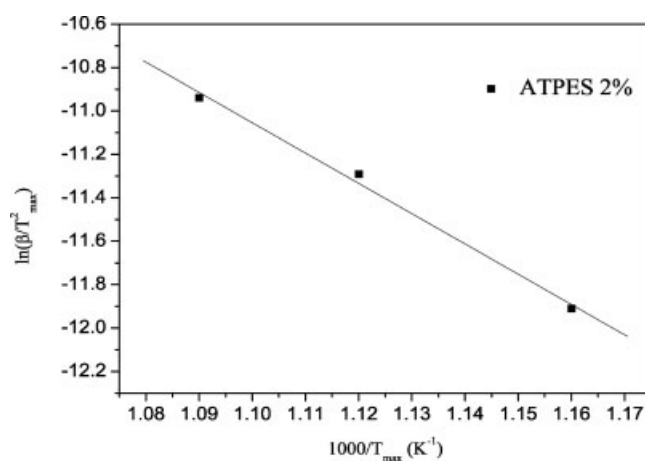
knife and were then subjected to TEM observation without staining.

Determination of activation energy

Various methods have been developed to evaluate activation energy of thermal degradation. The Kissinger equation^{10,11} is one of them and only overall activation energy can be calculated from the Kissinger equation as shown in eq. (1). The relationship among activation energy E , the heating rate β , and the temperature T_{\max} can be described as

$$\frac{d(\ln(\beta/T_{\max}^2))}{d(1/T_{\max})} = -\frac{E}{R} \quad (1)$$

T_{\max} corresponds to the temperature at which the differential of degradation peak has its maximum. The activation energy E can be calculated from the slope of $\ln(\beta/T_{\max}^2)$ as a function of $1/T_{\max}$.



(a) The Kissinger method

The other method useful for the determination of the activation energy is the Flynn–Wall–Ozawa^{12–14} method. It can be described as

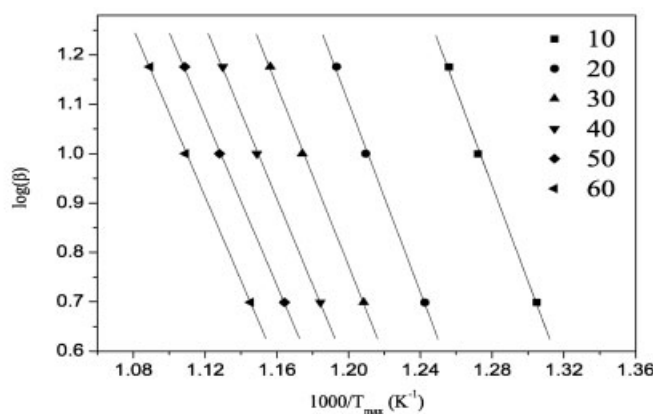
$$\log \beta = \left[\log \left(\frac{AE}{R} \right) - \log f(c) - 2.315 \right] - 0.4567 \frac{E}{RT} \quad (2)$$

From the nonisothermal TGA experiments carried out at different constant heating rates β , the activation energy at any particular value of conversion can be determined.

RESULTS AND DISCUSSION

Silicone rubber sheets with amine groups were prepared by casting the reaction mixture containing aminopropyltriethoxysilane (APTES) on a teflon mold as schematized in Scheme 1. The XPS analysis was carried out as shown in Figure 1 to measure the variation of the N element content to observe the content of APTES residue as a function of the depth of the silicone rubber sheet. The main component of the silicone rubber and APTES should be different in hydrophobicity. However, Figure 1 demonstrates that the APTES content was nearly independent of the depth of the silicone rubber sheet.

The mixture of the liner components were spread and cured on the silicone rubber sheet and then the peeling tests were performed as summarized in Table I. In the absence of APTES, the adhesion force between the silicone rubber and the liner was zero. However, the adhesion force went up with increase in the APTES content. The adhesion force between the silicone rubber and the liner was raised significantly by compounding the silicone rubber with



(b) The Ozawa method

Figure 2 Representation of the TGA analysis results by (a) the Kissinger method and (b) the Flynn–Wall–Ozawa method for the silicone rubber containing 2.0 wt % of APTES without carbon black.

TABLE II
Activation Energy (kJ/mole) of Thermal Degradation of Silicone Rubber with Different Contents of APTES

APTES content (wt %)	Control silicone rubber		Silicone rubber with 2 wt % of C30B		Silicone rubber with 2 wt % of carbon black	
	Ozawa	Kissinger	Ozawa	Kissinger	Ozawa	Kissinger
2.0	164	136	197	162	130	111
1.4	161	133	179	159	131	115
0.7	150	128	167	144	–	–
0.0	101	90	153	140	–	–

2 wt % of carbon black. The silicone rubber containing 2 wt % of APTES together with 2 wt % of carbon black adhered to the liner so strongly that the silicone rubber sheet was torn off during the peeling test. It is to be noted that the silicone rubber without APTES possessed zero adhesion force to the liner even though 2 wt % of carbon black was incorporated. In contrast, the silicone rubber without carbon black but with 2 wt % of APTES adhered more strongly to the liner when the mixture of the liner components was annealed at 60°C for 5 months after being spread on the silicone rubber sheet, in spite of the fact that initially, the same silicone rubber showed relatively poor adhesion force.

Therefore, the enhancement of the adhesion force of the silicone rubber containing APTES is attributed to the interfacial chemical reaction between the amine groups and the isocyanate groups of the liner components. The positive effect of carbon black on the adhesion force of the silicone rubber originates from the fact that the incorporation of carbon black contributed wetting of silicone rubber to the liner to have the liner components spread on the silicone rubber sheet more easily and thereby to facilitate the contact between the two functional groups.

Thermal stability of the silicone rubber as a function of the content of the adhesion promotor and

other additives was explored by determining the activation energy of thermal degradation from the weight loss during the TGA.¹⁵

Equations proposed by Kissinger and Flynn–Wall–Ozawa were employed to determine the activation energy. The activation energy from the Kissinger's equation is determined from the slope of the linear plot of $\ln(\beta/T_{\max}^2)$ as a function of $1/T_{\max}$. The equation proposed by Flynn–Wall–Ozawa yields the activation energy from the linear plot of $\log \beta$ versus $1/T$.^{10–13}

Representation of the results from the TGA by the equations developed by Kissinger and Flynn–Wall–Ozawa is exemplified in Figure 2. The activation energies of the silicone rubbers compounded with Cloisite®30B (C30B) and carbon black are listed in Table II.

Figure 3 shows the time derivative of the weight loss from the TGA clearly exhibiting T_{\max} . However, sometimes T_{\max} and thereby the activation energy could not be determined clearly, because the peak of the time derivative curve of the weight loss was either too broad or multiple, as exhibited in Figure 4, depending on the composition of the silicone rubber components.

The silicone rubber prepared in this study by condensation reaction using tetrapropoxysilane was cured more rapidly when APTES was incorporated.

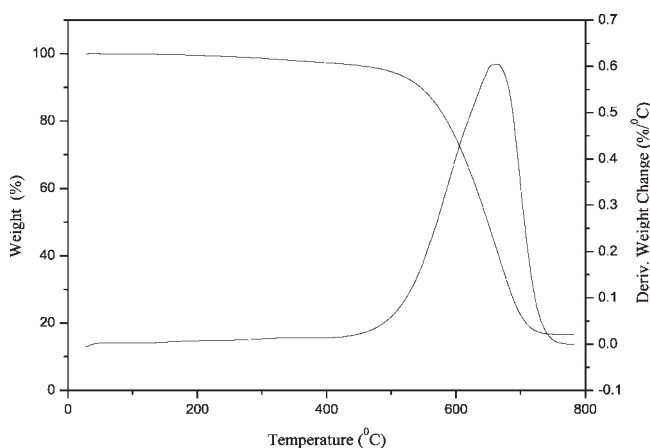


Figure 3 Weight loss and time derivative of the weight loss from the TGA of PDMS with 0.7 wt % of aminopropyltriethoxysilane.

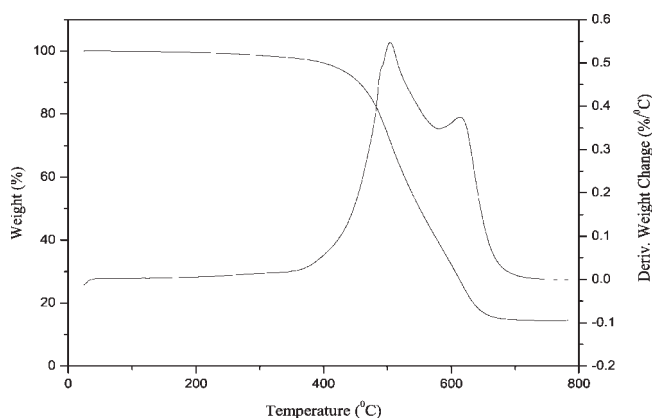


Figure 4 Weight loss and time derivative of the weight loss from the TGA of PDMS with 0.7 wt % of aminopropyltriethoxysilane and 2 wt % of carbon black.

Addition of Cloisite[®]30B (C30B) raised the curing rate further.

The multiple peak of the time derivative curve of the weight loss was observed when the silicone rubber with low content of APTES was compounded with carbon black. The multiple peaks showed a tendency to become a single peak as the curing time increased. Nevertheless, the peak was not completely unimodal even when the curing was continued for more than 1 month (data not shown). The reason why the multiple T_{\max} peaks appeared is not clear at present, but the uneven crosslinking in the silicone rubber is thought to be partly responsible for the multiple T_{\max} peaks.

According to Table II, the activation energy of the thermal degradation of the silicone rubber went up as the amine content increased, contrary to the expectation. The equations proposed by Kissinger and Flynn–Wall–Ozawa gave different values of the activation energy, but both the two equations predicted similarly that the activation energy rose fast initially and then increased monotonously with further increase in the amine content.

The activation energy was raised significantly when 2 wt % of C30B was compounded. The enhancement of the activation energy as a result of the incorporation of C30B appeared more significant when the silicone rubber was free from APTES. In sharp contrast, introduction of carbon black reduced the activation energy and therefore decreased the thermal stability of the silicone rubber.

Figures 5 and 6 demonstrate XRD spectrum and TEM image of the silicone rubber compounded with Cloisite[®]30B (C30B). The characteristic peaks corresponding to the clay layers are not observed in the XRD spectrum. Moreover, the TEM image reveals a morphology with well exfoliated clay layers. A driving force for the exfoliation of the clay layers should come at least partly from the increased interaction

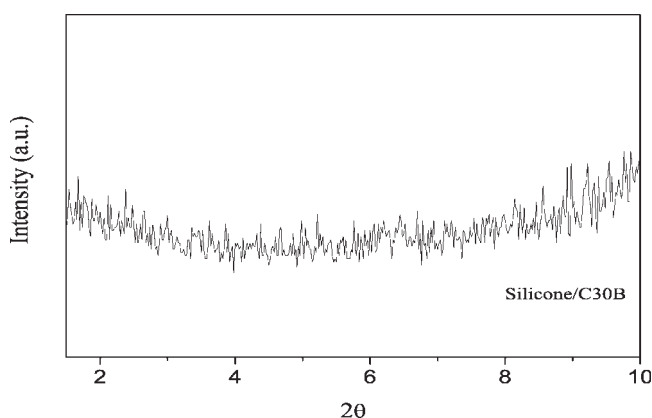


Figure 5 XRD of silicone rubber/clay composites with 2.0 wt % of APTES containing 2 wt % C30B.

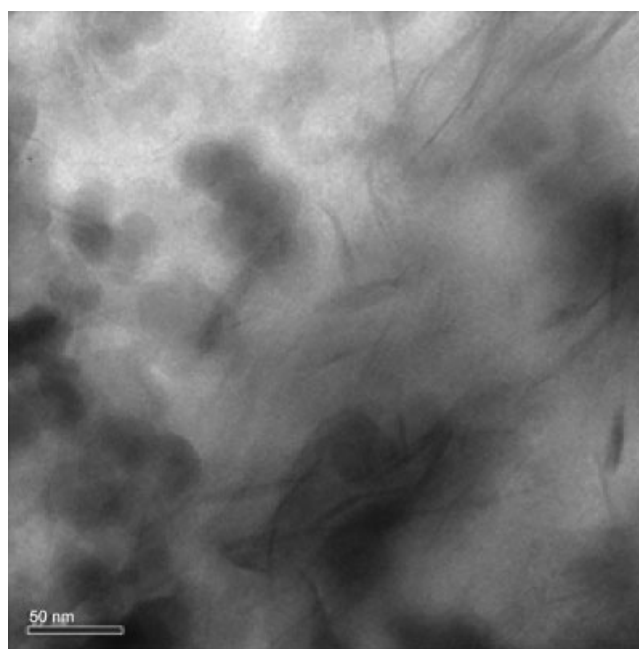


Figure 6 TEM image of silicone rubber/clay composites with 2.0 wt % of APTES containing 2 wt % C30B.

between the clay layers and the silicone rubber matrix, due to the participation of the silanol groups of Cloisite[®]30B (C30B) in the condensation reaction during the preparation of the Silicone/Cloisite[®]30B (C30B) composite and to the hybrid formation of Cloisite[®]30B (C30B) tethered with silicone rubber molecules. If the silanol groups of Cloisite[®]30B (C30B) participated in the condensation reaction, it is natural to admit that Cloisite[®]30B (C30B) assumed the role of the crosslinking sites to boost the thermal stability of the silicone rubber.

CONCLUSIONS

Incorporation of aminopropyltriethoxysilane (APTES) to silicone rubber by way of copolymerization enhanced the adhesion between the silicone rubber and the liner components composed of hydroxyl-terminated polybutadiene and isocyanate substances. Addition of carbon black to the silicone rubber increased further the adhesion force significantly. The activation energy of thermal degradation of the silicone rubber, measured from the weight loss profile of the thermogravimetric analysis, went up as the APTES content increased. Introduction of Cloisite[®]30B (C30B) to the reaction mixture for the preparation of the silicone rubber produced Silicone/Cloisite[®]30B (C30B) with fully exfoliated clay layers. This is attributed to the fact that the silanol groups of Cloisite[®]30B (C30B) participated in the condensation reaction to raise the interaction between the silicone rubber and Cloisite[®]30B (C30B). The layers of Cloisite[®]30B (C30B) tethered with sev-

eral silicone rubber molecules acted as the crosslinking sites and thereby increased the thermal stability of the silicone rubber.

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