Synthesis of Acrylic Acid Grafted Silicone Rubber via Preirradiation Graft Copolymerization and Its Physical and Dielectric Properties

JIN-SHENG YANG[1] and GING-HO HSIUE[1,2,*]

[1]Department of Chemical Engineering, National Tsing Hua University, Hsinchu 300, and [2]Department of Chemical Engineering, National Chung Hsing University, Taichung 402, Taiwan, Republic of China

SYNOPSIS

The hydrophilic monomer, acrylic acid (AA), has been grafted onto hydrophobic silicone rubber (SR) film via the γ-ray preirradiation graft technique. The AA percent graft in SR-g-AA film increases with increasing irradiation dose rate. The iron powder in monomer solution serves as one source of ferrous ion that is generated by the oxidation reaction with water. The swelling effect shows that the amount of chloroform taken up by an SR-g-AA membrane decreases with the increasing AA grafting, and the amount of water, alcohol, and glycerol taken up by an SR-g-AA film increases with increasing AA percent grafting. The contact angle, ultimate stress, and elongation at break of SR and SR-g-AA copolymers decrease with increasing AA percent grafting. The oxygen/nitrogen selectivity in these films can be enhanced by the graft modification. The thermal behaviors of SR-g-AA copolymers show the characteristics of SR and polyacrylic acid. Finally, the dielectric properties show that the SR-g-AA film has a superior dielectric property than the original SR and poly(AA) matrix. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Silicone rubber (SR) and its copolymers have very interesting properties, such as good elastomeric behavior; good thermal, ultraviolet (UV), and oxidative stability; good biocompatibility; low surface energy; high gas permeability coefficient; and excellent electric resistance properties. Based on these physical characteristics, polysiloxanes are widely used in hundreds of commercial and military applications.[1-5] The most outstanding characteristic of SR is the retention of its many desirable properties over the very wide temperature range from about −100°C to 315°C.

Graft polymerization is a convenient and well-known method to modify the chemical and physical properties of polymeric materials. The technique of radiation grafting has been widely used in the graft modification of polymer surfaces. Graft polymeriza-

tion can be achieved by ionizing radiation, ultraviolet light, or chemical initiators. Of these radiation grafting methods, the γ-ray preirradiation graft technique is one of the most promising methods because of its simple, large penetration grafting in polymer matrices, and could be used for further modification.[6] The hydrophilic monomer can be easily grafted onto hydrophilic substrate by the γ-ray preirradiation method. Under appropriate experimental conditions, the modification of polymer can be accomplished not only at the surface but also throughout the internal phase of a polymer matrix, forming a homogeneous membrane.[7,8]

The hydrophilic acrylic acid grafted polymers could be utilized as (1) biosensors by immobilizing an enzyme, such as glucose oxidase[9]; (2) polymer initiators for radical polymerization by further oxidation to a peracid-type polymer[10]; and (3) separation membranes for olefin/paraffin separation by incorporating with silver ions[8] and separators for alkaline battery uses.[7] The alteration of polymer surface composition brings about the various bioresponses to these foreign polymeric materials in

bioapplications.[11-15] Various hydrogels of grafted SR may influence the protein adsorption and cell interaction in a unique fashion, due to the hydration character of the grafted membrane for biological purposes; these have been studied by Hoffman.[16]

Silicone rubber, due to its rubbery properties, high stability to chemicals, good biocompatabilities, and high gas permeation properties, was selected as the substrate for graft modification. The preparation of acrylic acid grafted SR has been described in a previous study.[14] This article expends that work by describing the effects of AA percent graft to irradiation dose rate, solvent swelling, water contact angles, stress–strain relationships, and gas permeation properties. The effect of increasing percent grafting by the addition of iron powder to the monomer solution was studied. The thermal behaviors, dielectric properties, and conductivity properties of SR and SR-*g*-AA films were also studied.

EXPERIMENTAL

Materials

Commercially available silicone rubber (SR) (Dow Corning HC-595, SR-A, and SR-B) was used as received. The acrylic acid monomer (Aldrich Co.) containing 200 ppm hydroquinone monomethyl ether as a stabilizer was used as received without further purification.

Irradiation Graft Copolymerization

The preparation of SR film and the preirradiation graft of acrylic acid onto SR film were investigated according to previous work.[17] The mixture of SR-A/chloroform and SR-B/chloroform was casted onto a glass plate. After evaporating the solvent chloroform, the SR film was heated to 100°C for 2 h, and the film was obtained by releasing the film from glass plate in water. Rolled SR films were put into glass tubes and then achieved radiation does rates at various distances from the Co-60 radiation source. The sample films were irradiated under air for generating peroxides and hydroperoxides. The graft reaction was carried out in a 50% acrylic acid aqueous solution with 0.25% iron powder under nitrogen. The AA percent grafting was determined by the percentage increase of the weight based on the initial film weight.

Swelling Measurement

The SR and SR-*g*-AA films of known weight (W_s) were immersed in a swelling agent for 48 h at 25°C. The film was then removed and blotted quickly with absorbent paper to remove the liquid attached on the surface. The weight of the swollen film (W_g) was quickly weighed. The degree of swelling was determined as follows:

$$\text{Swelling}(\%) = \frac{W_s - W_g}{W_g} \times 100\% \qquad (1)$$

Contact Angle Measurement

The contact angle of water on SR and SR-*g*-AA films was measured by the contact angle analyzer (ERMA Inc., Model G-1) at 25°C. The film was placed onto the sample stage in sample chamber. A water droplet of about 0.2 μL was carefully placed onto the film surface by a mini-pipette. A liquid drop of about 1 ~ 2 mm in diameter was formed, and the contact angle was read immediately and directly from the microscope.

Mechanical Properties

The mechanical properties of tensile strength and the elongation at break were measured by using an Instron Tensile Tester (Shimadzu DCS-500) with an elongation rate of 10 mm/min. The mechanical test was performed as closely as possible to ASTM standards.[18]

Gas Permeation Measurement

The oxygen/nitrogen gases' permeation properties were measured by a gas permeability analyzer (Yanaco GTR-10).[8] The permeability coefficient P [$(\text{cm}^3(\text{STP})\text{cm})/(\text{cm}^2 \text{ sec cmHg})$] and the oxygen/nitrogen separation factor α were determined using the following equations:

$$P = \frac{Ql}{At(p_1 - p_2)} \qquad (2)$$

$$\alpha = \frac{P_{O_2}}{P_{N_2}} \qquad (3)$$

where Q is the quantity of gas permeated at STP in a time interval t at the steady state of gas flow, A is the effective film area for permeation, l is the average film thickness, and p_1 and p_2 are the upstream and downstream gas pressure, respectively.

Thermal Analysis

The thermal behaviors were measured by a differential scanning calorimeter (DSC, Dupont 2100) in the temperature range of $-160°C$ to $300°C$ with a heating rate of $10°C/min$. Thermogravimetric behaviors of these samples were measured by a thermogravimetric analyzer (TGA, Dupont 910) in the temperature range of $25°C$ to $900°C$ with a heating rate of $10°C/min$ under nitrogen.

Dielectric Measurement

The measurements of the dielectric properties were performed via a dielectric analyzer (Novocontrol GmbH-HP4191A, Germany). The instruments consisted of a Schlumberger SI 1260 (frequency 0.1 to 10^6 Hz) and a Quatro temperature controller. Both measurement systems were fully external computer controlled. A liquid nitrogen gas heating system ranging from 100 K to 500 K was used. The stability of the temperature adjustment is $±0.1$ K. A sample film (0.1–0.15 mm) was held between two gold-plated brass electrodes (sample diameter 10 mm). The conductance (G_s) of the material is a function of specific conductivity (K_s) of the materials and is directly proportional to the area (q) of the sample electrode and inversely proportional to the distance (l) between electrode. The conductivity K_s (unit: Ω^{-1} cm^{-1}) is calculated as follows:

$$K_s = G_s(l/q) \tag{4}$$

RESULTS AND DISCUSSION
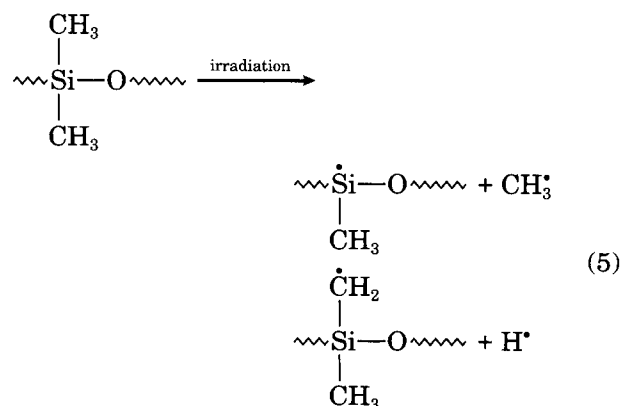
Preirradiation Graft Copolymerization

The acrylic acid (AA) grafted silicone rubber (SR-g-AA) has been described in a previous study via the preirradiation graft method.[17] The AA percent graft versus preirradiation dose rate in air is shown in Figure 1. The AA percent graft increases with increasing preirradiation time and irradiation intensity. In preparing peroxidized polymer by preirradiation method in air for the initiation of grafting reaction, the concentration of polymeric peroxides increases with increasing irradiation dosage and irradiation intensity.[6] In a short irradiation time, the concentration of peroxides increases linearly with irradiation dosage. In a long irradiation time, however, an equilibrium state may be attained in which the rate of peroxide formation equals the rate of peroxide disappearance.[6] Therefore, the AA percent graft proportionally increases with total dosage at
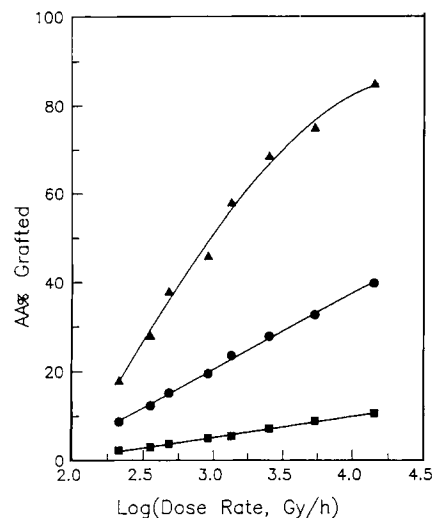
Figure 1 The AA percent grafted vs. preirradiation dose rate in air. Irradiation time: (■) 4 h; (●) 8 h; (▲) 18 h.

shorter irradiation time and would level off at longer irradiation time and higher irradiation dosage. In addition to the formation of peroxides, the crosslinking and the degradation reaction in the radiated sample would occur simultaneously.[19,20] The chain structure of SR would be crosslinked and degraded at high irradiation dose rate as well as high total dosage.[6] Therefore, very high AA percent grafted film could not be obtained at very high irradiation dosage due to the destroyed of the matrix structure.

Irradiation of silicone rubber evolved the release of the gases that mainly constituted of hydrogen (30 $\sim$ 40%) and methane (50 $\sim$ 60%).[19] As a result, the C — H and Si — C bonds are fractured by irradiation, leading to the formation of hydrogen and methyl radical. Two different primary macro radicals could, therefore, be assumed to be formed[19]:

$$
\begin{array}{c}
CH_3 \\
| \\
\text{\textasciitilde Si—O\textasciitilde} \xrightarrow{\text{irradiation}} \\
| \\
CH_3
\end{array}
$$

$$
\begin{array}{c}
\text{\textasciitilde \overset{\bullet}{Si}—O\textasciitilde} + CH_3^{\bullet} \\
| \\
CH_3 \\
\\
\overset{\bullet}{CH_2} \\
| \\
\text{\textasciitilde Si—O\textasciitilde} + H^{\bullet} \\
| \\
CH_3
\end{array}
\tag{5}
$$

The macroradicals, while being under oxygen, would convert into peroxides and hydroperoxides. When the irradiated polymer was subsequently heated in the absence of air, the peroxides (AO_2A) and hydroperoxides (AO_2H) would decompose

$$AO_2A \rightarrow 2AO^{\bullet} \qquad (6)$$

$$AO_2H \rightarrow AO^{\bullet} + HO^{\bullet} \qquad (7)$$

to give the macroradical $AO^{\bullet}$ and $HO^{\bullet}$ radical, which serve as the active sites for graft polymerization and homopolymerization, respectively. The hydroperoxides are more active than the dialkylperoxides that would be decomposed to give macroradicals for graft polymerization at high temperature.[6,19,20] The $HO^{\bullet}$ radical formed from the dissociation of hydroperoxide (AO_2H) could be avoided or reduced in the presence of Mohr's salt (ferrous ammonium sulfate) by the following reaction[21]:

$$AO_2H + Fe^{2+} \rightarrow AO^{\bullet} + Fe^{3+} + OH^- \qquad (8)$$
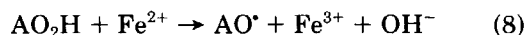
In the preirradiation method, the homopolymerization does not take place so largely as it does in the direct irradiation method.[21] The graft reaction was promoted, and the final AA percent graft could be largely enhanced by the addition of iron powder in the graft reaction system.[17] Table I shows the polymerization of acrylic acid under various conditions catalyzed by benzophenone under nitrogen. Various phenomena could be observed: As compared with run 1 and run 2, the low viscosity of run 2 indicates that the homopolymerization of acrylic acid is inhibited by the addition of iron powder. Additionally, as compared with run 1 and run 3, the water in the monomer solution promotes the homopolymerization reaction since the rate of grafting exhibits a maximum value in an about 50% acrylic acid aqueous solution.[21] Moreover, as compared with run 3 and run 4, the low viscosity of run 4 indicates that the homopolymerization is inhibited by the addition of iron powder in aqueous solution. The

acrylic acid homopolymerizes easily to give a very viscous reaction medium, and the addition of iron powder could effectively depress the AA homopolymerization. As the reaction proceeded, the hydrogen gas was continuously eliminated in run 4, and the monomer solution was neutralized and ceased gradually by the formation of base OH^-. However, no gas is eliminated in a reaction solution without water, as compared with run 2 and run 4. Therefore, a reaction mechanism could be assumed to occur:

$$Fe + 2H_2O \overset{H+}{\rightarrow} Fe^{2+} + H_2 + 2(OH)^- \qquad (9)$$
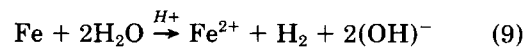
The graft reaction is initiated by $AO^{\bullet}$ radical, and the homopolymerization is initiated by $HO^{\bullet}$ radical. The ferrous ion formed by oxidation of iron in eq. (9) would deactivate the growing chain radical, the monomer radical, and the $HO^{\bullet}$ radical.[21] This resulted in a reduction of the grafting as well as inhibition of homopolymerization. However, the reduction of the grafting reaction is not remarkable in comparison with that of homopolymerization because the concentration of Mohr's salt is much lower in matrix than in monomer solution.[21] Besides, the formation of $HO^{\bullet}$ radical for AA homopolymerization could be avoid by eq. (8). Therefore, the final percent grafting could be increased by the addition of iron that would supply the Fe^{2+} gradually and deactivate the $HO^{\bullet}$ radical by eq. (9).
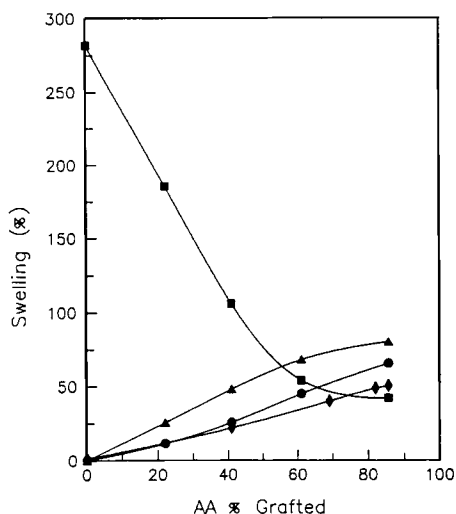
Swelling Effects

The graft of a hydrophilic monomer onto a hydrophobic matrix would lower the interfacial energy in aqueous biological environment and would lower the driving force on the surface for cell attachment in bioapplications.[16,22,23] The hydrophilic acrylic acid (AA) grafted SR membranes give a linear relationship between percent swelling and AA percent grafting. As shown in Figure 2, the percent swelling of water, ethanol, and glycerol in SR-g-AA increases with increasing AA percent grafting and shows in

Table I   Polymerization of Acrylic Acid Initiated by Benzophenone at 70°C for 3 h

No.	System	Bubble (25°C)	Color$_{initial}$	Color$_{final}$	$\eta \times 10^{-3}$ (N s/m^2)^b
1	A	No	No	No	7500
2	AA + Fe	No	Yellow	Brown	≤ 5
3	AA + H$_2$O^a	No	No	No	25,000
4	AA + H$_2$O + Fe^a	Yes	Green	Yellow	140

^{a} AA : H$_2$O = 1 : 1 in volume.
^{b} Measured by Brookfield Viscometer (Model RVT) at 25°C.

Figure 2 Swelling effect of various AA contents SR-*g*-AA in various regents. (■) chloroform; (▲) water; (♦) ethanol; (●) glycerol.

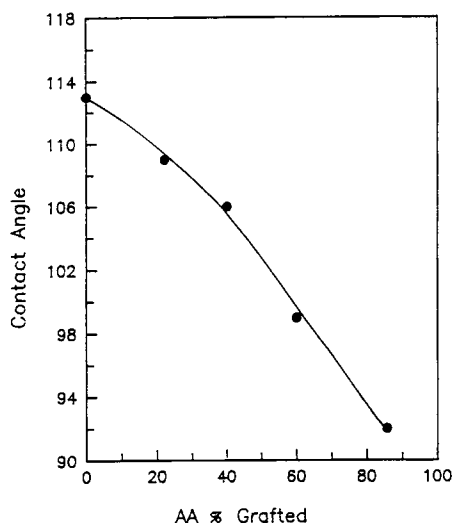**Figure 3** The water contact angle of various AA content SR-*g*-AA samples.

the order water > glycerol > ethanol. The hydrophobic SR film cannot be swelled by water, ethanol, or glycerol. The SR film shows a high swelling behavior in chloroform since it is a solvent for SR in film preparation.[17] The percent swelling of SR-*g*-AA film in chloroform decreases with increasing the grafted acrylic acid since chloroform is a nonsolvent for polyacrylic acid.

Surface Activity of Graft Copolymers

The water contact angle on the surface of a material directly indicates its hydrophilic/hydrophobic properties. Hydrophilic acrylic acid was grafted onto hydrophobic silicone rubber. Various water contact angles on SR-*g*-AA film are shown in Figure 3. As more acrylic acid is grafted, the lower contact angle is obtained. The SR-*g*-AA film is more hydrophilic than the raw SR film. While the SR-*g*-AA film is swelled, the contact angle of the blotted film is lowered to a value of about 65° for the 86% grafted SR-*g*-AA film. The SR-*g*-AA film prepared by the technique of plasma-induced graft copolymerization has a lower water contact angle of about 48° (acrylic acid content 178 μg/cm^2)[24] than that by the irradiation graft method in this study.

Stress–Strain Relationships

The ultimate tensile strength and ultimate elongation of the SR-*g*-AA films depend on AA content. As shown in Figure 4, a maximum stress of about 69 MPa and a strain of about 800% are obtained for

the unmodified SR film. The stress and strain values of SR-*g*-AA films decrease with increasing acrylic acid contents. The chain structure of an SR matrix would be degraded at a high irradiation dosage, which resulted in a high percent grafting and thus a loss of mechanical strength.[6,19,20] Besides, the broad chain-length distribution of the grafted polyacrylic acid, as indicated in the thermal analysis discussed later in this article, may not contribute to the overall mechanical properties. Therefore, the stress and strain values decrease with increasing percent grafting. A stress of about 9.6 MPa and an elongation ratio of about 90% are obtained for the 86% grafted SR-*g*-AA film. The stress and strain values of the
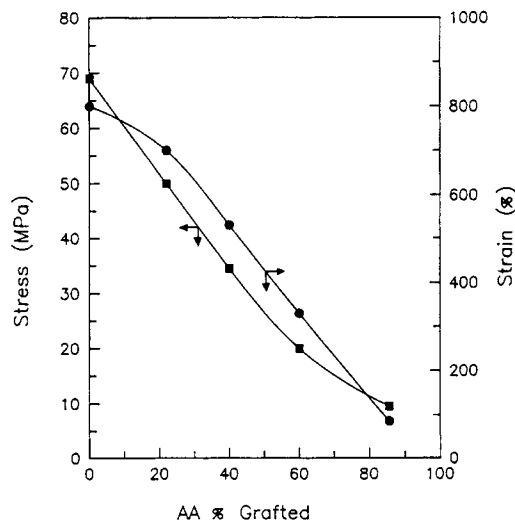
Figure 4 The stress–strain curves of various AA grafted SR-*g*-AA films. (■) stress; (●) strain.

Table II   The Gas Permeation Properties of Oxygen/Nitrogen Gases in Various Samples

Polymer	$P_{O_2} \times 10^{8\,a}$	$P_{N_2} \times 10^{8\,a}$	α^b	$E_{O_2}{}^c$	$E_{N_2}{}^c$
SR	6.01	3.55	1.69	1.0	1.3
SR-g-AA[d]	2.39	1.37	1.75	2.3	2.7
PE[e]	0.034	0.010	3.4	38.7	49.2
PE-g-AA[f]	0.0071	0.0018	3.9	43.9	55.9

[a] Permeability (P): $cm^3(STP)cm/cm^2s$ cmHg.
[b] Selectivity (α): P_{O_2}/P_{N_2}.
[c] Permeation activation energy E: kJ/mol.
[d] 86% AA-grafted.
[e] Linear low-density polyethylene, d: 0.917 g/cm^3.
[f] 90% AA-grafted.

86% grafted SR-g-AA film are close to those of low-density poly(ethylene-g-acrylic acid)[7] and are higher than those of high-density poly(ethylene-g-acrylic acid).[25]

## Gas Permeation Properties

The gas permeation properties of oxygen and nitrogen are listed in Table II. The oxygen/nitrogen separation factor in SR-g-AA film is higher than that in SR film, and the permeability coefficient in SR-g-AA film is lower than that in SR film. The grafted polyacrylic acid is a low-gas-permeable material for gas transport since its polar structure and hydrogen bonding diminish the gas permeation. The activation energies also indicate that gas transport in SR-g-AA films is more difficult than in SR films. As compared with the well-known polyethylene (PE) and its copolymers, the permeability coefficients of SR and SR-g-AA are about two and three orders higher than those of polyethylene and PE-g-AA, respec-

tively. The activation energies also show that permeation in SR and SR-g-AA is much easier than that in PE and PE-g-AA. This is because the highly crystalline PE is difficult for gases to penetrate. As a result, the SR-g-AA can be used instead of PE-g-AA in many applications, such as membrane in battery separation electrolyte and biological uses.[24]

Thermal Behaviors

The thermal behaviors of polymers are the most important property that could be singled out for polymer characterizations since no other class of polymer shows similar characteristic changes as a function of temperature, and most of the end-use applications of polymers take advantage of their unique behavior in processing. The differential scanning calorimetric (DSC) spectra and thermal gravimetric (TGA) spectra of SR, SR-g-AA, and polyacrylic acid are
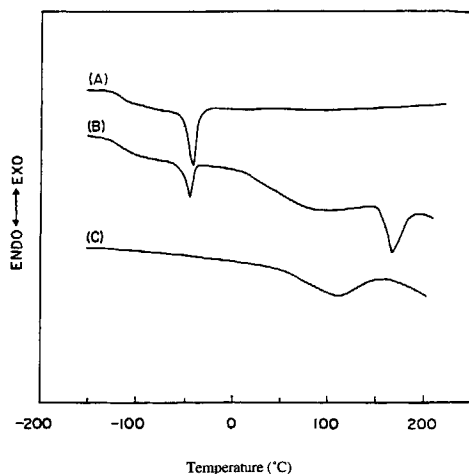
Figure 5   The DSC spectra of (A) SR, (B) SR-g-AA, and (C) polyacrylic acid.
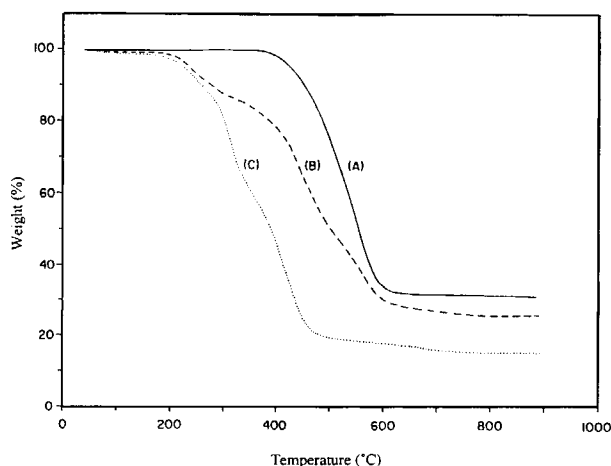
Figure 6   The TGA spectra of (A) SR, (B) SR-g-AA, and (C) polyacrylic acid.

Table III   The Thermal Characteristics of SR, SR-g-AA, and Polyacrylic Acid from DSC and TGA Spectra in Figures 5 and 6

| Sample	T_g (°C)	T_m (°C)	T_d (°C)
SR	−119	−45	375
SR-g-AA (40%)	−107, 56.2	−44.3, 168	305, 190
Polyacrylic acid	98	—	200

shown in Figures 5 and 6, respectively. The characteristics are listed in Table III.

The DSC spectra show that the SR has a T_g point at about −119°C and a T_m point at about −45°C. The T_m point is the melting point of uncrosslinked polysiloxane.[4] The low T_g point of SR indicates a flexible chain with extremely weak interchain forces in the siloxane structure. Silicone rubbers are noted for showing little change over a large temperature range and are an ideal vibration damping material. Silicone rubbers exhibit little change in transmissibility or resonant frequency over the temperature range from −54°C to 149°C.[4] The T_g and T_m of the acrylic acid grafted polysiloxane, respectively, shift to higher and lower temperatures. The SR-g-AA shows a broad T_g transition ranged from −10°C to 65°C since the grafted polyacrylic acid differs in

chain length. The chain motion of the grafted polyacrylic acid can be activated by the adjacent polysiloxane chains, resulting in a lower T_g transition than that of polyacrylic acid. The TGA spectra show that, as compared with the DSC spectra, the SR film is very thermally stable at temperatures below 390°C. The polyacrylic acid decomposed at about 190°C. The TGA curve of SR-g-AA clearly illustrates the decomposition temperatures at 190°C and 350°C for the grafted polyacrylic acid and SR matrix, respectively.
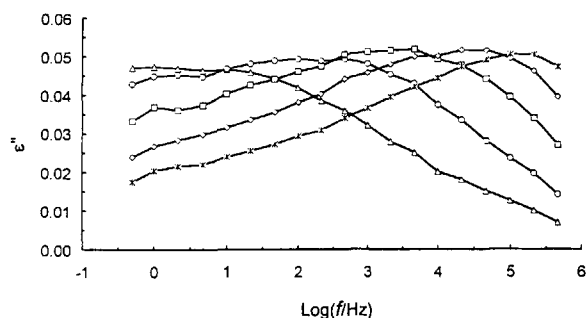
Dielectric Properties

Dielectric analysis is a powerful tool to study the molecular kinetic of a material in order to characterize its chemical, electrical, and physical properties. Figure 7 shows the dielectric constant (ε') and dielectric loss (ε'') for SR, SR-g-AA (40%), and polyacrylic acid films at 10 Hz. One α relaxation (153 K) is revealed as the glass transition temperature (T_g) of SR film. The relaxation curve of polyacrylic acid can be identified as α glass transition relaxation (373 K) as compared with its thermal behaviors. Three dielectric relaxations can be found from the curve of SR-g-AA and are named as α relaxation of SR at 153 K, α relaxation of polyacrylic acid at 383 K, and β relaxation at about 264 K, respectively. The β relaxation of SR-g-AA is revealed as the interaction between polysiloxane chains and the grafted polyacrylic acid. The dielectric constant ε' and dielectric loss constant ε'' at room temperature are listed in Table IV. The ε' of SR-g-AA is higher
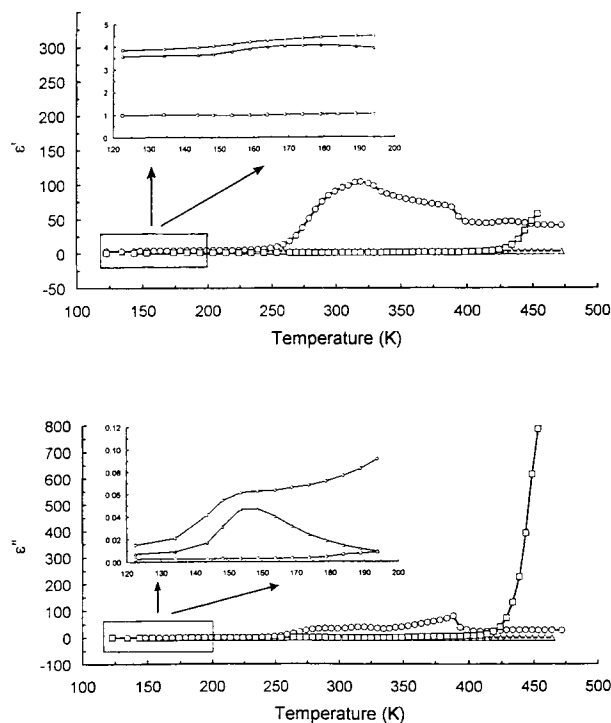
Figure 7   The dielectric constant ε' and loss factor ε'' vs. temperature at 200 Hz. (△) SR blank; (○) SR-g-AA (40%); (□) polyacrylic acid.

Table IV   The Dielectric Properties of SR, SR-g-AA, and Polyacrylic Acid at Room Temperature ($f = 10^5$ Hz)

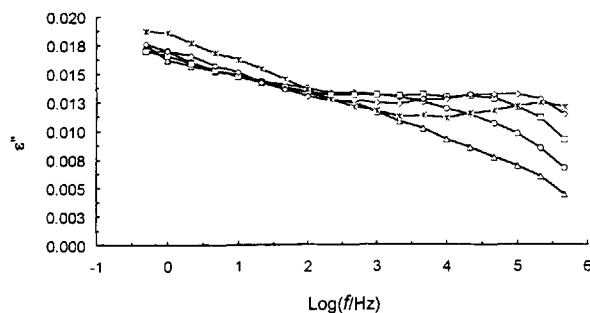| Samples	ε'	ε''
SR	3.19	1.86×10^{-3}
SR-g-AA (40%)	4.56	7.11×10^{-1}
SR-g-AA (86%)	5.51	2.92×10^{-1}
Polyacrylic acid	1.05	1.75×10^{-2}

Figure 8 The dielectric loss constant ε'' vs. frequency of SR. ($\triangle$) 154 K; ($\bigcirc$) 159 K; ($\square$) 164 K; ($\lozenge$) 169 K; (∗) 174 K.
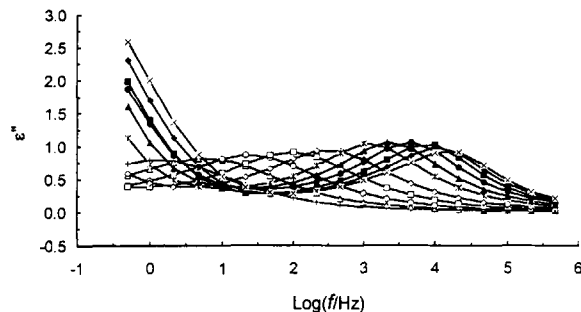
than that of SR and polyacrylic acid, and the ε'' of SR-g-AA is lower than that of SR and polyacrylic acid. The SR-g-AA has superior dielectric properties to the original SR and polyacrylic acid matrix.

The dielectric loss constant (ε'') of SR versus frequencies at various temperatures is shown in Figure 8. The ε'' shifts to higher frequencies at higher temperature. A maximum value of ε'' can be found at each temperature, along with the frequencies at 153 K to approximately 174 K. As the temperature is higher than 180 K, only a little difference can be found for ε''. Therefore, as compared with the thermal behaviors, the SR with a very flexible structure would retain the dielectric strength over both its low- and high-temperature ranges.

The ε'' of SR-g-AA versus frequencies at the temperature range from 154 K to approximately 178 K is shown in Figure 9. The ε'' of SR-g-AA, similar to the ε'' of SR in Figure 8, shifts to a higher temperature at a higher temperature. In addition to the characteristics at low temperature, other specific relaxations are obtained at a higher temperature range (250 K to approximately 350 K), as shown in Figure 10. The loss relaxations shift to higher frequencies,
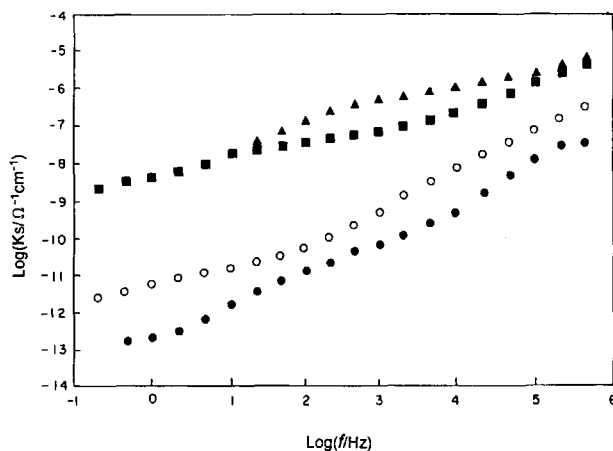

Figure 10 The dielectric loss constant ε'' vs. frequency of SR-g-AA (40%) at the temperature range of α relaxation of polyacrylic acid. (+) 249 K; ($\triangle$) 259 K; ($\bigcirc$) 269 K; ($\square$) 279 K; ($\lozenge$) 289 K; (∗) 303 K; ($\blacktriangle$) 313 K; ($\bullet$) 324 K; ($\blacksquare$) 333 K; ($\blacklozenge$) 343 K; ($\times$) 353 K.

indicating that higher energy is necessary for the local motion of grafted polyacrylic acid. Due to the large differences in chain length of the grafted polyacrylic acid chains, a broad temperature range for relaxation is observed as compared with the DSC spectra in Figure 5.

Figure 11 shows the conductivities of SR, SR-g-AA, and polyacrylic acid at 20°C. The conductivities of SR-g-AA (40% and 86%) are about four orders higher than those of SR and are three orders higher than those of polyacrylic acid at 1 Hz. The differences in conductivities of these samples are smaller at higher frequency range. The sample is held between two gold-plated brass electrodes under an electric field, and the charge carriers may be found in the easiest way by activation of electrons in the unbounded state or in the bonded π state under the applied field.[26] If these electrons are delocalized in

Figure 9 The dielectric loss constant ε'' vs. frequency of SR-g-AA (40%) at the temperature range of α relaxation of SR. ($\triangle$) 154 K; ($\bigcirc$) 159 K; ($\square$) 164 K; ($\lozenge$) 169 K; (∗) 178 K.

Figure 11 The conductivities of ($\bullet$) SR, SR-g-AA ($\blacktriangle$) 40%, ($\blacksquare$) 86%, and ($\bigcirc$) polyacrylic acid at 20°C.

a conjugated state, they form a conductive path of high mobility. Moreover, the packing of polymer molecules may take place due to Van der Waals-type weak forces, and the electronic coupling between molecules is weak and obstructs electronic conduction.[27] Furthermore, in a — (CH)— chain, the delocalization of electron tends to level off all C — C bonds. Thus, the graft of acrylic acid onto SR film resulting in a large increase in conductivity is due to the π electron from grafted carbonyl groups. As compared with SR-g-AA, the polyacrylic acid has a much lower conductivity due to its strong hydrogen bonding structure.

CONCLUSIONS

The hydrophilic monomer, AA, has been grafted onto hydrophobic silicone rubber (SR) film via the γ-ray preirradiation graft technique. The iron in monomer solution serves as one source of ferrous ion that is gradually generated by the oxidation reaction with water. The amount of water, alcohol, and glycerol taken up in SR-g-AA film increase with increasing AA percent grafting. The hydrophilicity of the SR-g-AA films increases with increasing AA content. The values of stress and strain of the SR-g-AA films decrease with increasing AA percent grafting. The thermal behaviors of SR-g-AA copolymers show the characteristics of SR and polyacrylic acid. Two α relaxations are distinguished for the glass transition of SR and polyacrylic acid in SR-g-AA film from the dielectric analysis. The SR-g-AA shows lower electric resistance property than SR and polyacrylic acid.

REFERENCES

1. E. G. Rochow, *Chemistry of the Silicones*, John Wiley & Sons, New York, 1951.
2. J. Y. Corey, E. R. Corey, and P. P. Gaspar, *Silicon Chemistry*, Ellis Horwood, England, 1988.
3. W. Lynch, *Handbook of Silicone Rubber Fabrication*, Van Nostrand Reinhold, New York, 1978, Chap. 1.
4. J. E. Mark, "Silicon-Containing Polymers," in *Silicon-Based Polymer Science: A Comprehensive Resource*, J. M. Ziegler and F. W. Gordon Fearon, Eds., ACS, series 224, Washington, DC, 1990.
5. W. J. Bobear, "Silicone Rubber," in *Rubber Technology*, 2nd ed., M. Morton, Ed., Van Nostrand Reinhold, New York, 1973, Chap. 15.
6. A. Chapiro, *High Polymers, Vol. XV, Radiation Chemistry of Polymeric Systems*, John Wiley & Sons, New York, 1962, Chap. 8.
7. G. H. Hsiue and W. K. Huang, *J. Appl. Polym. Sci.*, **30**, 1023 (1985).
8. G. H. Hsiue and J. S. Yang, *J. Membrane Sci.*, **82**, 117 (1993).
9. G. H. Hsiue and C. C. Wang, *Biotechnol. Bioeng.*, **36**, 811 (1990).
10. G. H. Hsiue, T. L. Perng, and J. M. Yang, *J. Appl. Polym. Sci.*, **42**, 1899 (1991).
11. G. H. Hsiue and P. K. Hsu, *J. Appl. Polym. Sci.*, **32**, 4615 (1986).
12. G. H. Hsiue and Z. L. Yeh, *Angew. Makrom. Chem.*, **153**, 33 (1987).
13. G. H. Hsiue, J. M. Yang, and R. L. Wu, *J. Biomed. Mater. Res.*, **22**, 405 (1988).
14. W. K. Huang and G. H. Hsiue, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 3451 (1989).
15. G. H. Hsiue and C. C. Wang, *J. Appl. Polym. Sci.*, **40**, 235 (1990).
16. S. Uenoyama and A. S. Hoffman, *Radiat. Phys. Chem.*, **32**, 605 (1988).
17. J. S. Yang and G. H. Hsiue, *J. Appl. Polym. Sci.*, **55**, 653 (1995).
18. ASTM D882-79, Standard Test Methods for Tensile Properties of Thin Plastic Sheeting, 1980.
19. R. J. Woods and A. K. Pikaev, *Applied Radiation Chemistry*, John Wiley & Sons, New York, 1994, Chaps. 7–10.
20. J. E. Wilson, *Radiation Chemistry of Monomers, Polymers, and Plastics*, Marcel Dekker Inc., New York, 1974, Chap. 9.
21. I. Ishigaki, T. Sugo, T. Takayama, T. Okada, J. Okamodo, and S. Machi, *J. Appl. Polym. Sci.*, **27**, 1043 (1982).
22. G. H. Hsiue, S. D. Lee, C. C. Wang, and P. C. T. Chang, *J. Biomat. Sci., Polym. Ed.*, **5**, 205 (1993).
23. G. H. Hsiue, S. D. Lee, C. C. Wang, M. H. I. Shiue, and P. C. T. Chang, *Biomaterials*, **15**, 163 (1994).
24. S. D. Lee, G. H. Hsiue, and C. Y. Kao, *J. Polym. Sci., Polym. Chem. Ed.*, **34**, 141 (1996).
25. J. K. Rieke and G. M. Hart, *J. Polym. Sci., Part C*, **1**, 117 (1963).
26. D. W. Van Krevelen, *Properties of Polymers*, Elsevier, Amsterdam, 1976.
27. I. Bunget and M. Popescu, *Physics of Solid Dielectrics*, Elsevier, Amsterdam, 1978.