Crosslinking of 1,9-Bis[glycidyloxypropyl]penta-(1′H,1′H,2′H,2′H-perfluoroalkylmethylsiloxane)s with α,ω-Diaminoalkanes: The Cure Behavior and Film Properties

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ABSTRACT: A series of nine films were prepared via phenol-catalyzed thermal crosslinking reactions of 1,9-bis-[glycidyloxypropyl]pentasiloxanes {1,9-bis[glycidyloxypropyl]decamethylpentasiloxane (**I**), 1,9-bis[glycidyloxypropyl]-3,5,7-tris(3′,3′,3′-trifluoropropyl)heptamethylpentasiloxane (**II**), and 1,9-bis[glycidyloxypropyl]-3,5,7-tris(1′H,1′H,2′H, 2′H-perfluorooctyl)heptamethylpentasiloxane (**III**)} with α,ω-diaminoalkanes [1,6-diaminohexane (**a**), 1,8-diaminooctane (**b**), and 1,12-diaminododecane (**c**)]. The crosslink density was controlled by the choice of **a–c**. The cure behavior of **I–III** with **a–c** was studied with differential scanning calorimetry. The me-

chanical properties of the films were determined by dynamic mechanical thermal analysis. Their thermal stability was analyzed by thermogravimetric analysis. The surface properties of the films were evaluated with static contact-angle measurements. These films represented a novel class of epoxies with an unusual combination of properties: high flexibility (low glass-transition temperature), good thermal stability, and hydrophobic surfaces. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 203–210, 2004

Key words: crosslinking; films; fluoropolymers

INTRODUCTION

Epoxy resins are used extensively in adhesives, coatings, composites, and packaging for electronics.[1,2] Their high resistance to chemicals, solvents, corrosion, and electricity makes them a useful class of thermosets.[1,2] High modulus, tensile strength, and dimensional stability are valuable mechanical properties found in traditional epoxies. Upon curing, they form highly crosslinked microstructures with high glass-transition temperatures (T_g's). However, contraction during curing generates internal stress, which promotes the loss of the mechanical, thermal, and moisture barrier properties.[3] Brittleness, low thermal stability, flammability, and a tendency to absorb water limit their utility.

The toughening of epoxies through the incorporation of functionally terminated rubber or thermoplastic modifiers has been reported.[4–16] These undergo phase separation during curing to form randomly dispersed particles within the epoxy matrix. Rubber or elastomeric modifiers that have been studied include carboxy- and amine-terminated butadiene–acryloni-

trile copolymers,[4] polyacrylate elastomers,[5] poly(propylene oxide),[6] polysiloxanes,[7–10] and fluoroelastomers.[11] Unfortunately, small amounts of rubbery modifiers dissolved in the matrix cause a decrease in the T_g and modulus values of epoxy resins. Thermoplastic modifiers are ductile engineering polymers that possess high T_g's. These may improve the toughness of epoxies without lowering the modulus or T_g. Among the α,ω-functionalized thermoplastics that have been evaluated as epoxy modifiers are poly(aryl ether sulfone)s,[12,13] poly(aryl ether ketone)s,[14] poly-(ether imide)s,[15] and polycarbonates.[16] The addition of a modifier to an epoxy resin is complicated by the requirement of simultaneously optimizing the solubility, stability, molecular weight, and concentration to achieve efficient toughening without the loss of valuable epoxy resin properties.

Epoxy resins often lack a high level of thermal stability and are quite flammable. Epoxy–imide resins have shown improved thermal stability.[17,18] Several other approaches to obtaining flame retardancy have been tried. These include the incorporation of additive-type or chemically bonded flame retardants to the epoxy resin. In particular, curing agents containing organophosphorous groups,[19–23] organosilicon groups,[24] or both[24,25] have received attention.

Most epoxies absorb between 1 and 7 wt % water with a concomitant loss of physical properties.[26] Wa-

ter absorption is facilitated by polar hydroxyl and amine groups present in amine-cured epoxy resins, which provide sites for hydrogen bonding with water.[26] Such polar groups lead to hydrophilic surfaces, which have both high surface tension and poor release properties.

We have anticipated that the incorporation of silicon- or fluorine-containing groups into epoxies might decrease brittleness (i.e., lower T_g), improve thermal stability, and increase hydrophobicity. Problems typically associated with additive-type modifiers could be avoided by the covalent attachment of siloxane and fluoroalkyl segments to epoxy moieties. Such materials may combine the useful properties of epoxies with those of siloxane and fluoropolymers. Siloxanes exhibit low-temperature flexibility, high thermal stability, flame retardancy, hydrophobicity, and low surface tension.[27] Fluoropolymers also have low surface tension and are stable versus high temperatures, organic solvents, and chemicals.[28] Fluoroalkylsiloxanes, such as poly[(3′,3′,3′-trifluoropropyl)methylsiloxane], possess low T_g's and chemical inertness.[29] In fact, epoxy-type materials containing siloxane or fluoroalkyl moieties have been reported. For example, epoxy-terminated siloxane monomers have been synthesized and crosslinked.[30,31] α,ω-(Glycidyloxypropyl)oligosiloxanes[10] and poly(dimethylsiloxane) copolymers with pendant glycidyloxypropyl groups[32] have also been prepared. Fluorinated epoxy resins have been synthesized and cured with α,ω-(diamino)oligosiloxanes.[33,34]

We have previously reported the synthesis of 1,9-bis[glycidyloxypropyl]decamethylpentasiloxane (**I**), 1,9-bis[glycidyloxypropyl]-3,5,7-tris(3′,3′,3′-trifluoropropyl)heptamethylpentasiloxane (**II**), and 1,9-bis-[glycidyloxypropyl]-3,5,7-tris(1′*H*,1′*H*,2′*H*,2′*H*-perfluorooctyl)heptamethylpentasiloxane (**III**).[35] In contrast to other studies with siloxane or fluorinated modified epoxies,[10,32–34] these have well-defined microstructures. This may be useful in establishing structure–property relationships. We have produced **I–III** through the covalent attachment of siloxane and fluoroalkyl segments to epoxy moieties to reduce the brittleness, thermal instability, and high surface tension associated with conventional epoxies. 3′,3′,3′-Trifluoropropyl and 1′*H*,1′*H*,2′*H*,2′*H*-perfluorooctyl groups have been used for **II** and **III**, respectively, because fluoroalkyl groups in which the fluoro substituents are in the α or β position to silicon are hydrolytically and thermally unstable.[36] Finally, when the epoxy matrix is highly crosslinked, it becomes more brittle.[15] To study the effect of the crosslink density on the film properties, we have varied the molecular distance between the crosslinks through the choice of α,ω-diaminoalkanes [1,6-diaminohexane (**a**), 1,8-diaminooctane (**b**), or 1,12-diaminododecane (**c**)]. These cure reactions represent the most reactive type of epoxy–amine crosslinking systems: terminal epoxy groups, such as glycidyl ethers, and primary aliphatic amines.[37] Phenol has been used to catalyze these cure reactions.

Here we report the phenol-catalyzed cure of 1,9-bis[diglycidyloxypropyl]pentasiloxanes (**I–III**) with α,ω-diaminoalkanes (**a–c**) to form nine films (**Ia–Ic**, **IIa–IIc**, and **IIIa–IIIc**). The curing kinetics of **I–III** with **a–c** have been studied with differential scanning calorimetry (DSC). The mechanical properties of the films have been determined with dynamic mechanical thermal analysis (DMTA), and their thermal stability has been analyzed with thermogravimetric analysis (TGA). The surface properties of the films have been evaluated with static contact-angle measurements.

EXPERIMENTAL

Materials

A platinum–divinyltetramethyldisiloxane complex (Karstedt's catalyst) in xylene (2% Pt) was acquired from United Chemical Technologies, Inc. *1H′,1H′,2H′*-Perfluoro-1-octene and 1,3,5-trimethyl-1,3,5-tris(3′,3′,3′-trifluoropropyl)cyclotrisiloxane were purchased from Lancaster. Methyldichlorosilane, hexamethylcyclotrisiloxane (D₃), tetramethyldisiloxane (TMDS), and hexamethyldisilazane were purchased from Gelest. Toluene, dimethyl sulfoxide (DMSO), tetrahydrofuran, allyl glycidyl ether, triethylamine, triflic acid, **a–c**, and phenol were acquired from Aldrich. The solvents were purified by distillation before use. The synthesis of **I–III** is depicted in Figure 1.

Synthesis of 1,9-Bis[glycidyloxypropyl]-pentasiloxanes (I–III)

1H,1H,2H,2H-Perfluorooctylmethyldichlorosilane was prepared from the platinum-catalyzed (Karstedt) hydrosilylation reaction of methyldichlorosilane and *1H,1H,2H*-perfluoro-1-octene.[38]

1,3,5-Trimethyl-1,3,5-tris(1′*H*,1′*H*,2′*H*,2′*H*-perfluorooctyl)cyclotrisiloxane was prepared by the reaction of *1H,1H,2H,2H*-perfluorooctylmethyldichlorosilane with DMSO in the presence of zinc.[39]

1,9-Dihydridodecamethylpentasiloxane was prepared by the triflic acid catalyzed ring opening of D₃ in TMDS.[40]

1,9-Dihydrido-3,5,7-tris(3′,3′,3′-trifluoropropyl)-heptamethylpentasiloxane was prepared by the triflic acid catalyzed ring opening of 1,3,5-trimethyl-1,3,5-tris-(3′,3′,3′-trifluoropropyl)cyclotrisiloxane in TMDS.[41]

1,9-Dihydrido-3,5,7-tris(1′*H*,1′*H*,2′*H*,2′*H*-perfluorooctyl)heptamethylpentasiloxane was prepared by the triflic acid catalyzed ring opening of 1,3,5-trimethyl-1,3,5-tris(1′*H*,1*H*′,2*H*′,2*H*′-perfluorooctyl)-cyclotrisiloxane in TMDS.[41]
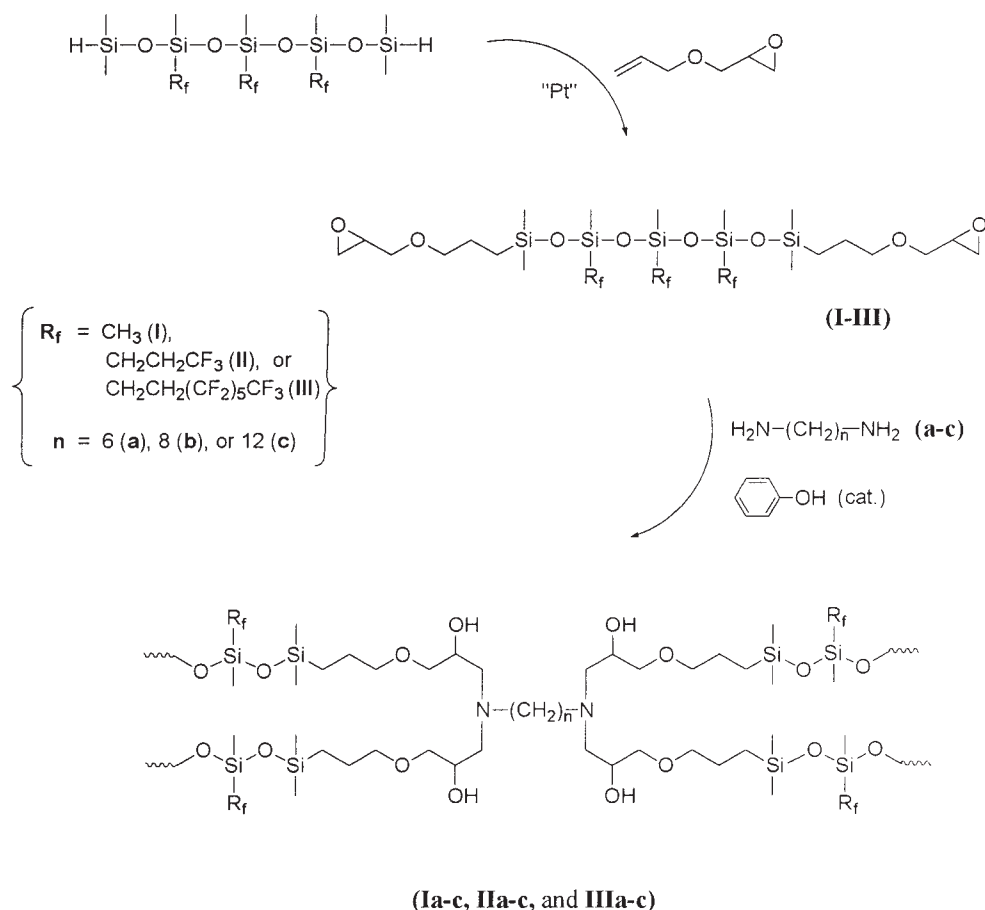
Figure 1 Cure reactions of 1,9-bis[glycidyloxypropyl]pentasiloxanes (**I–III**) with α,ω-diaminoalkanes (**a–c**) used to form films (**Ia–Ic, IIa–IIc,** and **IIIa–IIIc**).

I was prepared by the platinum-catalyzed (Karstedt) hydrosilylation reaction of 1,9-dihydrido-decamethylpentasiloxane with an excess (3.5 equiv) of allyl glycidyl ether in the presence of trace amounts of triethylamine.[35]

II was prepared by the reaction of 1,9-dihydrido-3,5,7-tris(3′,3′,3′-trifluoropropyl)heptamethylpentasiloxane and allyl glycidyl ether as mentioned previously.[35]

III was prepared by the reaction of 1,9-dihydrido-3,5,7-tris(1′H,1′H,2′H,2′H-perfluorooctyl)heptamethylpentasiloxane and allyl glycidyl ether as mentioned previously.[35]

Film preparation

In a typical procedure, **I, II,** or **III** (2 g) was combined with **a, b,** or **c** (0.5 equiv) in a 10-mL, round-bottom flask equipped with a Teflon-covered magnetic stirring bar. The flask and its contents were heated in an oil bath at approximately 80°C to yield a homogeneous solution. Phenol (4 wt %) was then added, and the mixture was allowed to stir for a few minutes. The warm mixture was cast uniformly at 10 mil onto clean glass microscope slides with a Gardner drawdown bar. The coated glass slides were placed in a 110°C oven overnight to cure. The films were removed from the glass slides with a clean single-edge razor blade.

Cure kinetics

DSC scans were recorded on a Shimadzu DSC-50 with a constant flow of helium. For the curing studies, **I, II,** or **III** was combined with a stoichiometric amount of **a, b,** or **c** and phenol (4 wt %), as mentioned previously. Three to four drops of this mixture were placed in an open aluminum pan. Each sample was heated from 25 to 250°C at a rate of 10°C/min.

Film characterization

DMTA was performed with a TA Instruments Q800 DMA 5 in the three-point bending configuration at a frequency of 5 Hz. After equilibration at −130°C for 4 min, the temperature was increased at a rate of 5°C/min to 30°C.

TGA was performed on films with a Shimadzu TGA-50 instrument with a nitrogen or air flow rate of
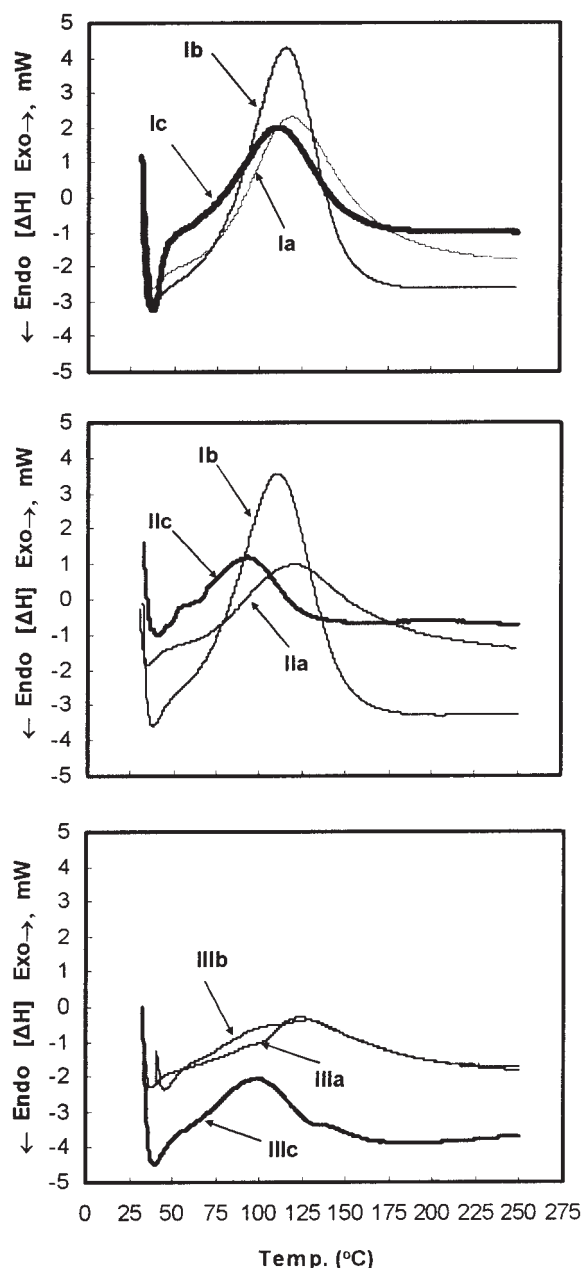
Figure 2 DSC measurements of stoichiometric reactions of I–III and α,ω-diaminoalkanes (**a–c**).

with a fresh water droplet, and the values were averaged.

RESULTS AND DISCUSSION

Film formation

For a nearly complete reaction to be ensured, mixtures of **I–III** with **a–c** need to be homogeneous. Crosslinkers **a–c** all have melting points above room temperature: approximately 43, 51, and 70°C, respectively. For this reason, solutions of **I–III** with **a–c** were prepared at approximately 80°C. The formation of crosslinked networks through reactions of **I–III** with α,ω-diaminoalkanes (**a–c**) is depicted in Figure 1. Four crosslinking points may be generated from each molecule of **a**, **b**, or **c**. However, it is likely that fewer than four crosslinks are formed, and thus the networks are probably nonuniform.

Curing kinetics

DSC was used to study the curing behavior of **I–III** with **a–c**. A thermal sweep of stoichiometric mixtures of **I–III** with **a–c** produced broad exothermic peaks (Fig. 2). The curing behavior parameters of these systems are summarized in Table I. These include the initial temperature (T_i), at which the exotherm starts; the peak temperature of the exotherm (T_p); and the temperature at the end of the exotherm (T_f). The effect of the crosslinker (**a–c**) on the cure behavior is evident. For a given 1,9-bis[glycidyloxypropyl]pentasiloxane (**I–III**), T_i increases in the following order: **c** < **b** < **a**. A lower T_i is associated with a crosslinker that is more reactive.[42] Similar trends have also been observed for T_p and T_f. The curing range ($T_f - T_i$) narrows as the molecular weight of the crosslinker (**a–c**) increases.

The conversion has been calculated as (H_T/H_0) $\times$ 100, where H_T is the area under the peak up to temperature T and H_0 is the total peak area. The rate of cure for **I–III** increases in the following order: **a** < **b** < **c** (Fig. 3). Thus, the highest molecular weight crosslinker (**c**) produces the fastest rates of conversion.

40 cc/min. The temperature was increased at a rate of 4°C/min from 25 to 800°C.

Static contact-angle measurements were made with a First Ten Ångstroms (FTÅ) 4000 optical contact-angle measurement system equipped with a video camera. Approximately 10 μL of distilled and deionized water was placed on the film surface at room temperature, and the contact angle was calculated with the FTÅ system drop-shape-analysis software. Contact-angle measurements were made at the interfaces of air (θ_{Air}) and glass (θ_{Glass}) with the film. Three measurements were performed for each film surface

TABLE I
Cure Behavior Parameters of I, II, or III with a, b, or c by DSC

Film	T_i (°C)	T_p (°C)	T_f (°C)	$T_f - T_i$ (°C)
Ia	73	119	193	120
Ib	60	115	160	100
Ic	58	110	158	100
IIa	64	122	205	141
IIb	61	110	149	88
IIc	52	93	125	73
IIIa	68	124	204	136
IIIb	61	110	190	129
IIIc	52	99	149	97
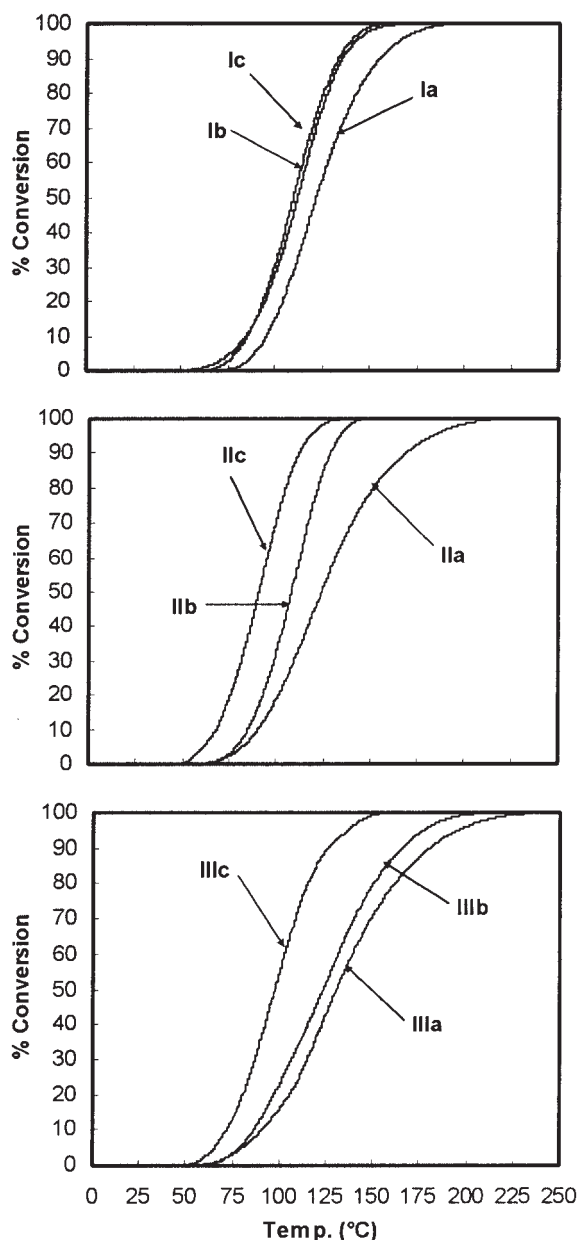
Figure 3 Conversions of stoichiometric reactions of **I–III** and α,ω-diaminoalkanes (**a–c**).

This effect becomes more pronounced in the following order: **I** < **II** < **III**. Thus, **IIIc** shows a significantly higher rate of conversion than **IIIa**. The enhanced reactivity of **c** may reflect its greater conformational mobility, which is due to its longer methylene chain between the two terminal amino groups.

Properties of the films

DMTA

The mechanical properties of the films (**Ia–Ic**, **IIa–IIc**, and **IIIa–IIIc**) have been determined with DMTA. The loss modulus (G'') exhibits maxima at T_g and T_β (beta

transition temperature).[43] The values of T_g and T_β are reported in Table II. For films prepared from **I** and **II**, T_g increases in the following order: **c** < **b** < **a**. Films crosslinked with **a** have the highest crosslink densities, which increase their T_g's.[44] Films based on **III** deviate from this trend and have T_g's between −37 (**IIIc**) and −45°C (**IIIa** and **IIIb**). For films prepared with a specific crosslinker (**a–c**), T_g is expected to increase with the presence of adjacent CF_n groups because of their mutual electronic repulsion, which gives rise to side-chain rigidity.[36] For example, the T_g values of **IIc** (−40°C) and **IIIc** (−37°C) are higher than that of non-fluorinated **Ic** (−50°C). T_g of **IIa** (−31°C) is higher than that of **Ia** (−36°C); however, T_g of **IIIa** (−45°C) is lower. Similarly, T_g of **IIb** (−37°C) is higher than that of nonfluorinated **Ib** (−45°C), but T_g of **IIIb** (−45°C) is equal to that of **Ib**. T_β is often associated with side-chain mobility, which may be related to toughness.[45] The T_β values of **Ia–Ic** (−76 to −70°C) are lower than those of the other films, except for **IIIb** (−77°C). No T_β has been observed for **IIIa**.

The storage modulus (G') is related to the stiffness or resistance to deformation.[46] G' of the films is strongly influenced by the crosslinker (**a–c**; Fig. 4). G' increases from −130 to 30°C in the following order: **c** < **b** < **a**. **IIIa** has the highest overall values of G'. For films prepared with the same crosslinker, G' typically increases with higher levels of fluorination of **I–III**.

Thermal stability

The thermal stabilities of the films (**Ia–Ic**, **IIa–IIc**, and **IIIa–IIIc**) in nitrogen and in air have been determined with TGA. In nitrogen, the thermal stability of films based on **I** is rather dependent on the crosslinker (**a–c**; Fig. 5). The catastrophic decomposition of **Ia**, **Ib**, and **Ic** begins at 200, 275, and 350°C, respectively. Films based on **II** exhibit similar behavior. **IIa** and **IIb** both initially begin to degrade at approximately 275°C, whereas **IIc** begins to decompose at slightly lower temperatures. A significant decrease in the thermal stability of films based on **III** has been observed. **IIIa–IIIc** begins to decompose at approximately 200°C. This

TABLE II
Properties of the Films

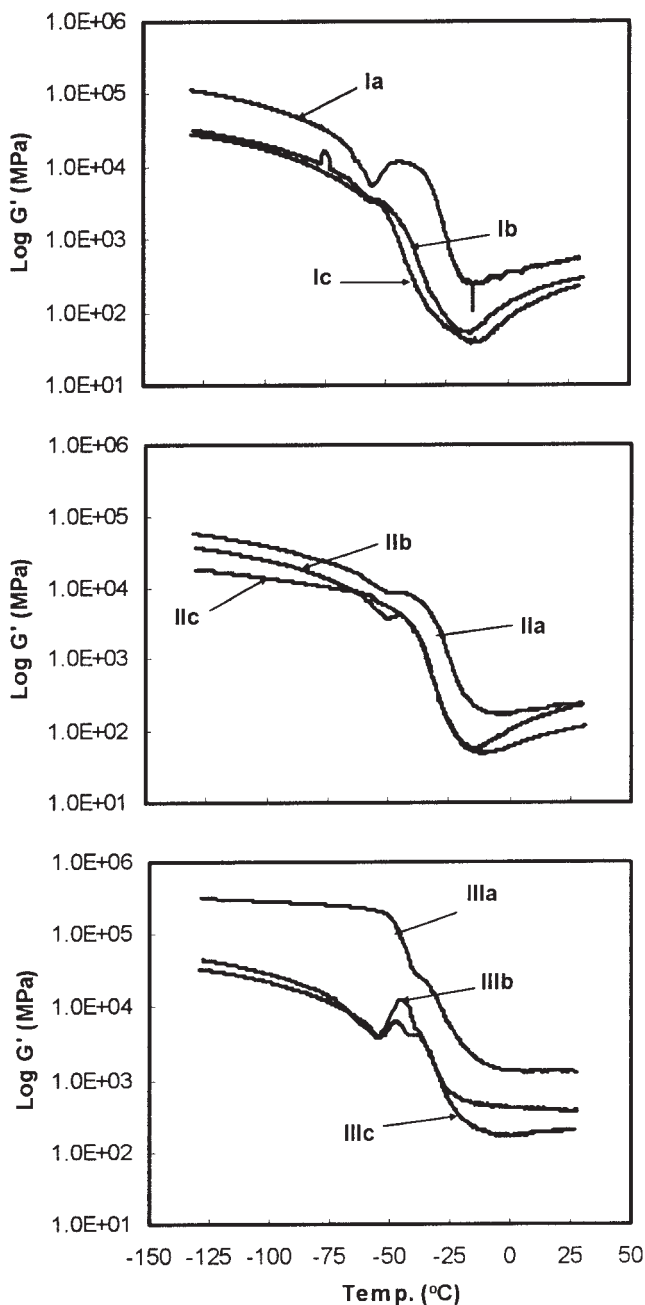| Film	T_g (°C)	T_β (°C)	θ_{Air} (°)	θ_{Glass} (°)
Ia	−36	−76	112	92
Ib	−45	−76	112	95
Ic	−50	−70	102	91
IIa	−31	−61	111	82
IIb	−37	−64	105	85
IIc	−40	−55	112	82
IIIa	−45	—	129	112
IIIb	−45	−77	124	119
IIIc	−37	−66	153	Not applicable

Figure 4 G' of **Ia–Ic**, **IIa–IIc**, and **IIIa–IIIc** films.

is expected, as fluorosilicones typically have lower thermal stability than comparable siloxanes.[47] By 450°C, over 95% of the initial sample weight is lost for all nine films. No further weight loss occurs upon heating to 800°C. The thermooxidative decomposition of the films begins at lower temperatures in air than in nitrogen (Fig. 6). Films of **Ia–Ic** and **IIa–IIc** begin to decompose at approximately 225°C, whereas **IIIa–IIIc** are stable to approximately 175°C. The majority of the sample weight for all nine films is lost by 450°C. By 800°C, the char yields of the nine films are less than approximately 15%.

Contact-angle analysis

Static contact-angle measurements of distilled and deionized water on film surfaces (θ_{Air} and θ_{Glass}) are reported in Table II. At the air interface, all the films are hydrophobic ($\theta_{Air} > 90°$).[48] There is a marked increase in θ_{Air} for films based on **III** (124–153°). Films based on **III** are also hazy. Fluoroalkyl groups are known to undergo surface reorganization, which can lead to increased hydrophobicity and haziness.[49] This effect is most significant for **IIIc** ($\theta_{Air} = 153°$) which is extremely hydrophobic. This may be attributed to its relatively low crosslink density, which allows for enhanced mobility of the fluoroalkyl groups. The θ_{Air}
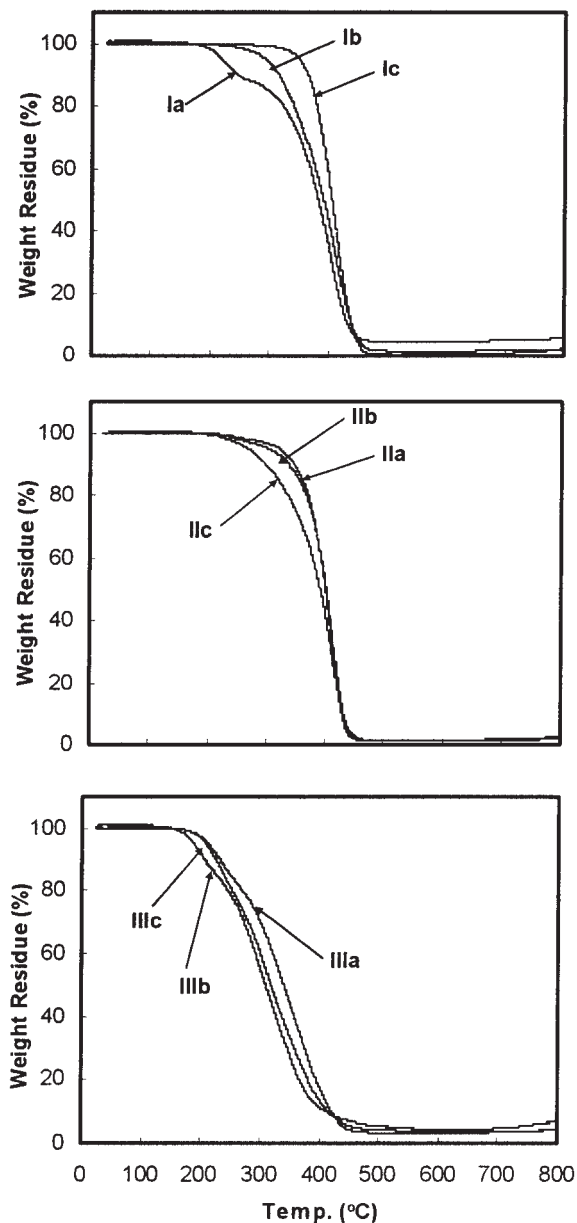

Figure 5   TGA of **Ia–Ic**, **IIa–IIc**, and **IIIa–IIIc** films in nitrogen.
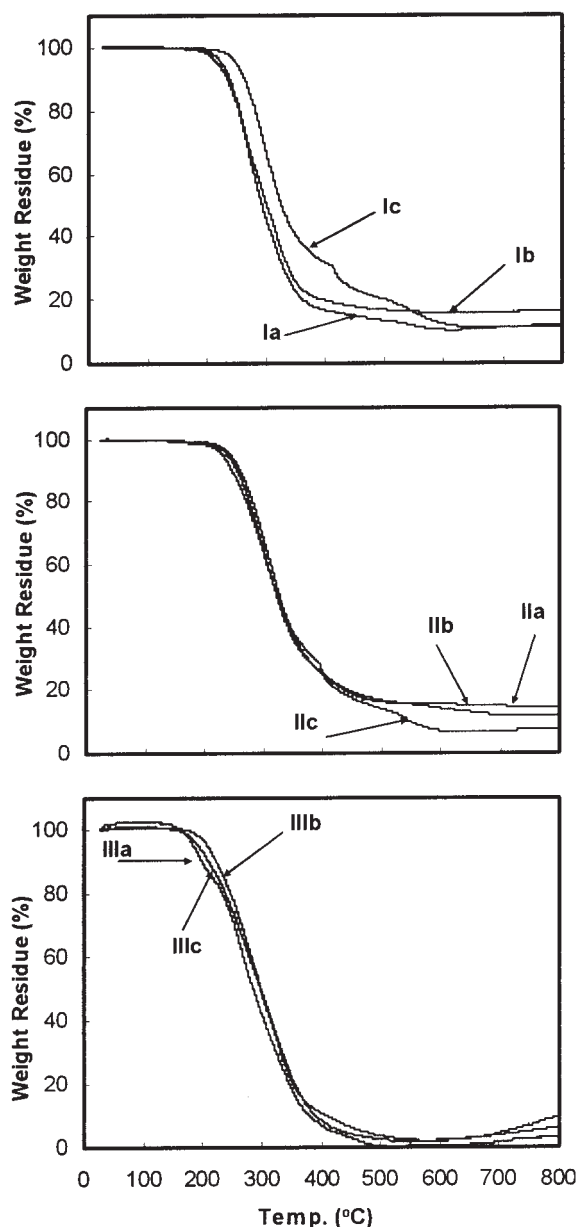
Figure 6 TGA of **Ia–Ic**, **IIa–IIc**, and **IIIa–IIIc** films in air.

values of films based on **I** (102–112°) and **II** (105–112°) are quite similar. For all films, θ_{Glass} is lower than the respective value of θ_{Air}. This effect has been observed for fluoroepoxy films.[47] The θ_{Glass} values of films based on **III** (112–119°) are quite high in comparison with those of films prepared with **I** (91–95°) and **II** (82–85°). Thus, films of **IIa–IIc** display similar θ_{Air} values and lower θ_{Glass} values with respect to those of nonfluorinated films of **Ia–Ic**. Apparently, the 3′,3′,3′-trifluoropropyl groups of films based on **II** are ineffective in producing lowering surface tensions. θ_{Glass} of **IIIc** cannot be determined because the water droplet will not hold its shape long enough to be measured. This may indicate that defects form in the film when it is removed from the glass.

CONCLUSIONS

1,9-Bis[glycidyloxypropyl]pentasiloxanes (**I–III**) have been crosslinked with α,ω-diaminoalkanes (**a–c**) to form nine films (**Ia–Ic, IIa–IIc,** and **IIIa–IIIc**). The curing behavior has been analyzed with DSC. The rate of crosslinking increases with the molecular weight of the crosslinker in the following order: **a** < **b** < **c**. G' increases as the molecular weight of the crosslinker decreases in the following order: **c** < **b** < **a**. The thermal stability increases with a lower fluorine content in the pendant groups in the following order: **III** < **II** < **I**. The highest values of θ_{Air} and θ_{Glass} have been observed for highly fluorinated films based on **III**. The films prepared in this study are an interesting class of epoxies because they are flexible (low T_g), have good thermal stability, and possess hydrophobic surfaces.

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