Hybrid Siloxane Epoxy Coatings Containing Quaternary Ammonium Moieties

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ABSTRACT: An ever increasing concern over bacterial infections caused by consumer products as well as medical devices is obvious from the recent surge in literature documenting the need for novel self-decontaminating coatings. Within, we report a hybrid ionic organic/inorganic siloxane epoxy system containing quaternary ammonium moieties. This novel low surface energy antimicrobial coating is capable of self-decontaminating in a variety of environments. The system is designed to be used as an over-coating, for devices that are prone to come into contact with pathogenic bacteria. These coatings have been synthesized, characterized, and an-alyzed for both physical and antimicrobial properties. Preliminary antimicrobial evaluation indicates a direct correlation between antimicrobial activity and hydrophobicity of the biocidal functional group within the resin matrix. These coatings have demonstrated the ability to eliminate up to 99.9% of pathogenic bacteria on the surface. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3080–3086, 2008

Key words: coatings; synthesis; biological applications of polymers; polysiloxanes; surfaces; structure-property relations; crosslinking; amphiphiles

INTRODUCTION

Recent health concerns about pathogenic bacteria have resulted in an increased demand for effective antimicrobial coatings, especially for medical device applications.[1–4] Bacterial infection is a serious complication associated with the use of internal medical devices, representing an estimated 45% of all hospital infections.[5] The first reported step in the development of an infection is the adhesion of bacteria to a biomaterial/implant followed by subsequent propagation.[6,7] One strategy to prevent bacterial attachment and propagation on surfaces is to lyse the microorganism that come into contact with the substrate before adhesion. Formation of effective biocidal surfaces has been the goal of a number of research groups, and a variety of techniques have been used with varying degrees of success. The vast majority of reported methods incorporate antimicrobial components during manufacturing processes, frequently resulting in complicated processing, a need for reduced processing temperature, and alteration of structural integrity and durability. The lack of an effective general purpose self-decontaminating over-coating is evident in the variety of applications that currently exist in medical facilities, food preparation areas, and in the prevention of biofilm formation in humid/marine environments.[8] Moreover, the concern surrounding bacterial resistance to common therapeutic agents has further driven the search for new antimicrobial coating systems.[9]

Among the various polymer matrices available, epoxy resins remain dominant in the development of high performance materials due to their thermal stability, mechanical properties, and processability.[10] They are frequently used in situations where tough, durable coatings or adhesives are needed, as the chemical structure of epoxy resins impart high chemical resistance against a wide range of severe corrosive conditions.[11] However, brittleness frequently affects the durability and places a constraint on design parameters, which limits their use.[10] In attempts to improve such properties, for increased broad spectra utility, epoxy resins have been modified with flexible polymeric segments such as carboxyl, hydroxyl and amine terminated butadiene, polyurethanes, nitrile rubber, and silicones.[12] Polydimethyl siloxane (PDMS) is a commonly used commercial silicone modifier due to its wetability, film forming properties, low temperature tolerance, flexibility, and hydrophobic behavior.[13] A siloxane component blended into an epoxy resin may provide the needed properties, yet results in the migratory separation of the individual components upon ageing.

This facet would be desirable if biocide leaching was the mode of kill; however, this approach is less attractive in light of current environmental regulations, especially in moist/marine environments. A siloxane/epoxy resin copolymer system can circumvent compatibility issues by covalently bonding the otherwise incompatible polymers together.

The permanent fungicidal and bactericidal properties of polysiloxanes bearing pendant quaternary ammonium salt groups have been reported by Dragan and coworkers.[14–16] Quaternary ammonium compounds belong to the class of cationic disinfectants and have been widely used for half a century. The method of biocidal activity involves an electrostatic interaction with constituents of the cell wall, followed by destabilization of the cytoplasmic membrane via the lipophilic moiety present in the QAS. Because of the very high osmotic pressure, this destabilization leads to a loss of cytoplasmic constituents, resulting in subsequent cell death.[17] In damp or aqueous environments, paints and polymers able to maintain a surface free of microorganism and biofouling is greatly desired. This property is frequently acheived by the linkage of a biocidal moiety that extends out of the matrix to inhibit microorganism growth at the surface of the polymer. Ionic moieties containing quaternary ammonium salts included in the polymer matrix should impart interesting and valuable antimicrobial properties.

Although recent advances concerning antimicrobial agents are impressive, most systems are limited in application by phase separation, leaching, and efficacy. Therefore, a need for novel antimicrobial epoxy coatings remains. Herein, we report the synthesis and characterization of a new series of bioactive material and evaluate their biocidal activity in films against both Gram-positive and Gram-negative bacteria. This work represents the first series of epoxy-quat functionalities crosslinked with diamino siloxane functionalized oligomers, in which various quaternary ammonium salt sequences have been incorporated into the backbone to maximize antimicrobial activity. The presence of covalently bound antimicrobial moieties should impart biocidal activity without risk of leaching and remain active for prolonged periods of time.

EXPERIMENTAL

Materials

All chemicals were reagent grade and used without further purification, except for tetrahydrofuran (THF) and toluene. THF was distilled from sodium/benzophenone, and toluene was distilled from sodium, both under nitrogen. All silicone reagents were purchased from Gelest. Moisture sensitive reactions were conducted in oven-dried glassware under a nitrogen atmosphere. Unless otherwise noted, ^{1}H and ^{13}C NMR were taken in CDCl$_3$ at 300 MHz with a tetramethylsilane (TMS) internal standard. Chemical shifts are reported in units of ppm downfield from TMS. UV/VIS measurements were recorded on an Ocean Optics HR-4000 High Resolution UV–VIS Spectrometer used with Spectrasuite Software. Contact angle measurements were made on a VCA OptimaXE instrument fitted with AST Products. VCA Version 1.90.0.9 for Windows software, which calculated the left and right advancing angles.

Films were prepared from concentrated prepolymer solutions according to the specific testing method reported, but in general, films were drawn onto aluminum Q-panel brand test panels using a #52 draw-down bar wet-film applicator purchased from Paul N. Gardner Company, (Pompano Beach, FL).

Monomer and prepolymer synthesis

General procedure for the synthesis of quaternary diglycidyl phenyl ammonium compounds (3)

Into a 250-mL round-bottomed flask equipped with reflux condenser and stir bar, 20.0 mmol of 4,4'-methylenebis(N,N-diglycidylaniline) (1), 45.0 mmol of alkyl bromide (2), and 50 mL of THF were placed. The resulting solution was allowed to reflux for 24 h under nitrogen. Volatiles were then removed in vacuo to afford the desired product in acceptable purity for subsequent use.

Characterization of 4,4'-methylenebis(N,N-diglycidyl-N-ethylphenylammonium bromide) (3a). FTIR: 3468, 3048, 3002, 2960, 2918, 1616, 1516, 1385, 1335, 1239, 1189, 973, 842 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.09 (d, $J = 7$, 4H), 6.76 (d, $J = 6$, 4H), 3.78–3.67 (m, 10H), 3.50–3.38 (m, 4H), 3.20–3.15 (m, 4H), 2.82–2.78 (m, 4H), 2.60–2.58 (m, 4H), 1.89–1.85 δ (t, $J = 5$, 6H). ^{13}C NMR (CDCl$_3$): 146.6, 130.7, 129.6, 112.7, 112.6, 67.9, 53.1, 50.6, 50.5, 45.4, 45.3, 39.7, 25.6 δ. Product was afforded as a pale yellow viscous liquid in a 87% yield.

Characterization of 4,4'-methylenebis(N-butyl-N,N-diglycidylphenylammonium bromide) (3b). FTIR: 3466, 3047, 3001, 2960, 2918, 1616, 1516, 1385, 1335, 1239, 1191, 973, 842 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.09 (d, $J = 6$, 4H), 6.77 (d, $J = 5$, 4H), 3.81–3.67 (m, 10H), 3.48–3.38 (m, 4H), 3.17–3.16 (m, 4H), 2.81–2.77 (m, 4H), 2.59–2.57 (m, 4H), 1.92–1.83 (m, 4H), 1.49–1.47 (m, 4H), 0.95 δ (t, $J = 3$, 6H). ^{13}C NMR (CDCl$_3$): 146.6, 130.7, 130.6, 129.6, 112.6, 67.9, 53.1, 50.6, 50.5, 45.4, 39.7, 25.6 δ. Product was afforded as a pale yellow viscous liquid in a 95% yield.

Characterization of 4,4'-methylenebis(N,N-diglycidyl-N-hexylphenylammonium bromide) (3c). FTIR: 3463, 3051, 3007, 2962, 2917, 1619, 1513, 1387, 1333, 1236, 1190,

972, 841 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.09 (d, $J = 7$, 4H), 6.77 (d, $J = 6$, 4H), 3.81–3.67 (m, 10H), 3.49–3.38 (m, 4H), 3.17–3.16 (m, 4H), 2.80–2.76 (m, 4H), 2.59–2.57 (m, 4H), 1.89–1.82 (m, 4H), 1.48–1.31 (m, 12H), 0.92 δ (t, $J = 4$, 6H). ^{13}C NMR (CDCl$_3$): 148.2, 133.4, 129.3, 129.1, 115.2, 68.7, 53.1, 52.2, 50.5, 50.2, 47.3, 45.4, 39.7, 38.3, 25.6, 14.6 δ. Product was afforded as a pale yellow viscous liquid in a 92% yield.

Characterization of 4,4′-methylenebis (N,N-diglycidyl-N-octyl phenylammonium bromide) (3d). FTIR: 3467, 3043, 3001, 2958, 2921, 1619, 1512, 1386, 1334, 1243, 1192, 971, 841 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.09 (d, $J = 4$, 4H), 6.76 (d, $J = 4$, 4H), 3.81–3.68 (m, 10H), 3.50–3.38 (m, 4H), 3.17 (m, 4H), 2.80–2.79 (m, 4H), 2.59–2.58 δ (m, 4H), 1.87 (m, 4H), 1.44–1.31 (m, 20H), 0.91 (t, $J = 6$, 6H). ^{13}C NMR (CDCl$_3$): 148.6, 132.2, 129.7, 129.3, 116.7, 68.3, 54.3, 51.1, 50.7, 50.2, 47.3, 45.2, 38.9, 37.5, 25.3, 15.7 δ. Product was afforded as a pale yellow viscous liquid in a 91% yield.

General procedure for the preparation and application of prepolymers **5**, **6** and **7**

Into a 250-mL round-bottom flask equipped with reflux condenser and stir bar, 5.0 mmol of either 4,4′-methylenebis(N,N-diglycidyl aniline) (1) or N-alkyl derivative 4,4′-methylenebis-(N-alkyl-N,N-diglycidyl phenylammonium bromide), (3) 5.0 mmol of diamino PDMS (4) (MW 900-1000), and 50 mL of toluene were placed. The resulting mixture was allowed to reflux for 20 h under nitrogen. The sample was then concentrated *in vacuo*, removing ∼90% of solvent to afford a viscous partially croslinked prepolymer suitable for film application.

The respective prepolymers (**5–7**) were applied onto Q-panels and glass microscope slides using the draw-down bar and subjected to a 4-h curing at 120°C. Faint yellow transparent and visually uniform films were obtained with an average thickness of 50–75 μm. Q-panels were coated for hardness and tack measurements. Quartz slides were coated for UV/VIS and contact angle measurements, and glass slides were prepared for antimicrobial testing. Similarly, 1.5–2.0 g samples were prepared in 2″ aluminum pans for Dynamic Mechanical Analysis (DMA), thermogravimetric analysis (TGA), and gel fraction studies.

In general, UV/VIS spectra of prepared films were characterized as featureless with a strong absorption onset at ∼350 nm. FTIR-ATR analysis of cured samples yields the following spectral data: **5a** FTIR: 2963, 1616, 1512, 1259, 1081, 1021, 788, 691 cm^{-1}; **5b** FTIR: 2960, 1610, 1513, 1256, 1084, 1023, 787, 693 cm^{-1}; **5c** FTIR: 2967, 1617, 1510, 1259, 1086, 1021, 788, 696 cm^{-1}; **5d** FTIR: 2966, 1613, 1514, 1255, 1081, 1022, 785, 697 cm^{-1}; and **6** FTIR: 2969, 1617, 1511, 1251, 1021, 786, 697 cm^{-1}.

Film tack, hardness and contact angle measurements

Film tack and hardness of samples prepared on Q-test panels was monitored using a TA XTplus Texture Analyser (Godelming, Surrey, UK). Using compression test mode, the applied force required to penetrate 10% of the film thickness with a one inch round probe tip at a probe insertion speed of 0.1 mm/s was determined for each sample. In tack measurements the probe tip and applied force was held for 10 s, and then the probe tip was withdrawn at a constant rate of 0.1 mm/s from the film. Force measurements are recorded as grams per unit time, and the highest force point is recorded as the peak force. Pencil hardness tests were also performed—according to ASTM method D 3363 00—where the degree of hardness of a pencil used to scratch the film surface at a 45° angle in a 0.25″ stroke is systematically increased until the pencil visually mars the film surface. The hardest pencil that will not scratch the surface is determined from the scale of 9B (softest) to 9H (hardest). Liquid contact angles were measured at 20°C using a VCA 2500-AST goniometer, equipped with a light source, camera, and flat horizontal support for test slides. Water drops of 5 μL were deposited on samples, and static contact angles were calculated via computer (and manual) analysis of drop images. Reported contact angles are determined as the average of three measurements per slide. Contact angles from both the sides of the drop were compared and found to be equal within the experimental error.

Mechanical, thermal analysis and gel fractions

Glass transition temperatures (T_g) of prepared polymer samples were measured using a TA Instruments #2980 DMA instrument. Cured samples were removed from aluminum pans and cut into rectangular test samples, 30 mm length and 5 mm width. Thickness varied slightly from sample to sample. Samples were tested in tension mode, frequency 1 Hz, amplitude 15 μm, over the temperature range of −70 to 150°C, and at a ramp rate of 2°C/min. T_g was approximated as the peak of the tan delta (δ) plot. Gel fractions of the cured films were obtained by dissolving a known mass of film in toluene, resting the sample for 24 h at room temperature, and recovering the insoluble mass fraction, followed by residual solvent evaporation under reduced pressure.

The thermal stability of cured polymer samples was evaluated by TGA where weight changes in a material are monitored as a function of temperature (or time) under a controlled atmosphere. Using a TA instruments Q500 series TGA instrument, average 5–10 mg samples were analyzed in platinum pans over
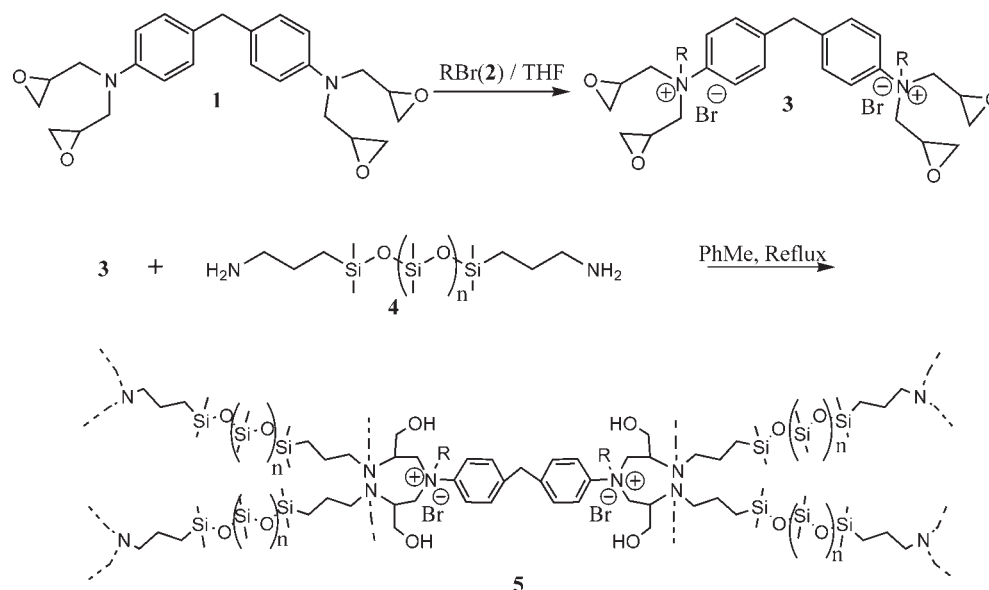
Figure 1 Synthetic scheme of hybrid quaternary ammonium-PDMS epoxy systems.

the temperature range of 0–1000°C at a heating rate of 10°C/min.

Bacterial challenge preparation

Bacteria and Media

Luria-Bertani (LB) media (Difco Laboratories, Detroit, MI) was used as a bacterial growth medium for preparation of bacteria for bacterial challenges, and Letheen Broth (Difco Laboratories, Detroit, MI) was used as a growth medium postchallenge due to its ability to deactivate quaternary ammonium salts. Both were prepared according to the manufacturer's specifications. *Staphylococcus aureus* (ATCC 25923) was used for all Gram-positive bacterial challenges and *Escherichia coli* (ATCC 25922) was used for all Gram-negative bacterial challenges.

Bacterial Challenge

Overnight cultures were grown in LB media, pelleted, and resuspended in 0.5% saline solution. An aliquot of 10^7 CFU/10 µL bacteria was deposited onto a 1 cm^2 area of each coating. The bacteria were exposed under ambient conditions for 2 h. The coatings were then swabbed with a sterile cotton swab which was then placed in 5 mL of Letheen broth. The broth was then serially diluted seven times. The dilutions were incubated at 37°C for 18 h, after which tubes were visually examined and determined to have growth by the presence of turbidity. Controls indicated that no death due to desiccation occurred. Log kill was determined by the following: Log kill = 7—highest dilution exhibiting bacterial growth.

RESULTS AND DISCUSSION

A new homologous series of amphiphilic quaternary ammonium biocides was designed such that they could be easily applied and crosslinked in a single-step to an existing surface as well as ensure active moieties are compatible as an additive into a variety of common commercial resins currently used in manufacturing processes. The amphiphilic nature of the biocides allows adjustment in hydrophilicity–hydrophobicity through variation of the alkyl substituent on the ammonium, while retaining the antimicrobial activity.

The synthesis of the hybrid siloxane epoxy polymer (**5**) was achieved by first quaternizing the tertiary amines of **1**, resulting in the tetra-epoxy di-quaternized moiety (**3**). Subsequent crosslinking of the primary amine functionalities of the PDMS (**4**) resulted in the formation of the desired matrix **5** (Fig. 1). To ensure that the observed biological activity resulted from the quaternary ammoniums present in the backbone of **5**, an analogous system without the quaternary ammoniums was prepared by reacting **1** with **4**, resulting in the formation of **6** (Fig. 2). Furthermore, to determine the effect of the hybrid PDMS component, an alkyl analogue control
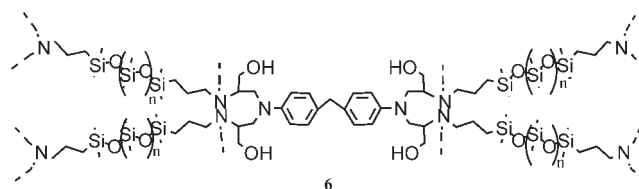

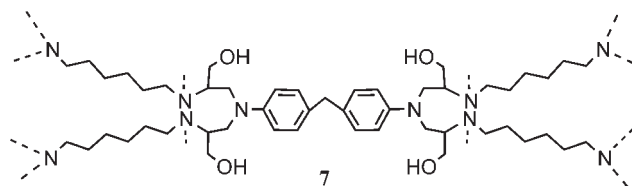**Figure 2** Synthesis of nonquaternized polymer system **6**.

Figure 3 Synthesis of polymer controls without PDMS **7**.

was also prepared by reacting **1** with hexane-1,6-diamine, resulting in the formation of matrix **7** as shown in Figure 3.

Biological results for the analogous control matrices **6** and **7** afforded no biological activity against the two pathogenic bacteria examined in this study, thus indicating that any activity observed from compound **5** is the direct result of the quaternary ammonium functionalities in the matrix, and independent of the PDMS or amine components (Table I). Compounds **5a–5c** all provided 1 log reduction against both Gram-postive and Gram-negative consistently; however, **5d** showed an enhanced antimicrobial effect, resulting in 3-log reduction against *S. aurus*, a Gram-positive bacterium, and a 2-log reduction against *E. coli*, a Gram-negative bacterium. Attempts to further extend the alkyl chain of the quaternary ammonium moiety on **3** resulted in an incompatibility which greatly reduced the ability to react with **4** to afford the corresponding matrix **5**. It was concluded that the steric effects of alkyl pendent groups greater than eight carbons in length prevented the amine from effectively interacting with the resulting epoxy functionalities, yielding a poorly crosslinked material that did not afford a coating suitable for evaluation.

As summarized in Table II, prepared films were found to be medium-hard as determined by texture analysis and pencil hardness tests. Within the experimental error, all films were found to be of similar hardness. Room temperature storage modulus was

TABLE I
Synthesis of 3 and Antimicrobial Evaluation of 5, 6, and 7

Sample ID	(2) R=	Yield 3 (%)	Film testing with *S. aurus* Gram (+)[a]	Film testing with *E. coli* Gram (−)[a]
5a	nC_2H_5—	87	1 log	1 log
5b	nC_4H_9—	95	1 log	1 log
5c	nC_6H_{13}—	92	1 log	1 log
5d	nC_8H_{17}—	91	3 log	2 log
6	–	–	0 log	0 log
7	–	–	0 log	0 log

[a] Reported in log reduction from a starting concentration of 10^7 CFU/cm^2.

obtained from DMA analysis and is also reported in Table II. At use temperature, those samples containing quaternary ammonium functionality are found to possess approximately the same storage modulus as the control sample prepared without alkylation of the phenyl diglycidyl monomer. All samples have rubbery plateau storage modulus and glass transition (T_g) values characteristic of their composition, as determined by DMA analysis in tensile mode from the peak of the tan δ plot (Fig. 4). Glass transitions are generally broad—as measured by full width at [1/2] height of the corresponding tan δ plot—and are comparable among the quaternary ammonium ion samples, suggesting a similar network structure. The tan δ plot also provides an indication of the damping ability of the polymer network, which relates to the material's ability to lose energy to molecular rearrangements and internal friction. There is an interesting correlation between the intensity of the tan δ peak and increasing the alkyl group length on the quaternary ammonium moiety of the phenyl diglycidal monomer (**7** < **6** < **5a** < **5b** < **5c** < **5d**, Fig. 4 insert), suggesting that the presence of longer alkyl chains on the

TABLE II
Film Hardness, Room Temperature Modulus, and Glass Transition Temperatures (T_g)

Sample ID	(5) R=	Texture analysis (g)[a]	Pencil[b]	RT (25°C) modulus (MPa)[c]	Glass transition temperature (T_g) (°C)[d]	Broadening in tan δ plots (FWH)[e]
5a	nC_2H_5—	11 (±3)	H	180	67	53 (±5)
5b	nC_4H_9—	25 (±10)	H	150	68	52 (±5)
5c	nC_6H_{13}—	24 (±7)	H	170	85	58 (±5)
5d	nC_8H_{17}—	19 (±3)	H	230	66	58 (±5)
6	–	19 (±1)	H	150	59	45 (±5)
7	–	–	–	1,500	103	>73

[a] Gram force required to penetrate 10% thickness of coating with stainless steel 1″ probe tip.
[b] According to pencil hardness test: ASTM method D 3363 00.
[c] Room temperature storage modulus from DMA analysis.
[d] T_g recorded as peak maximum of tan δ plot and broadening in loss tangent curve at full width at 1/2 height (FWH), error estimated from multiple runs.
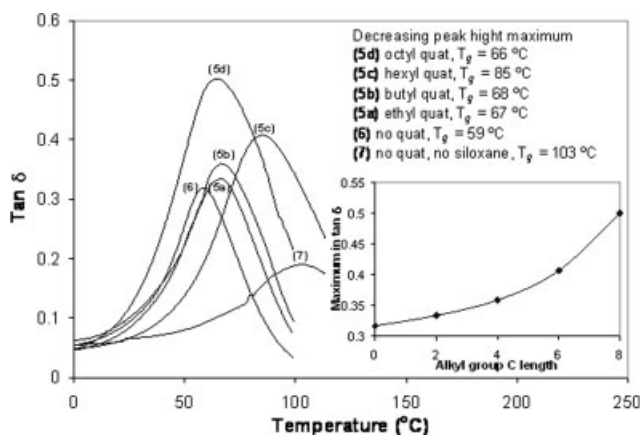
Figure 4 DMA analysis of prepared films, showing glass transition (T_g) as the peak maximum of tan delta plot.

Figure 5 Thermogravimetric analysis of cured coatings as a function of composition.

quaternary ammonium ion may create an internally plasticized network, thereby increasing free volume and damping effect. As expected, control samples prepared without siloxane were brittle, and found to possess a much higher glass transition temperature and RT storage modulus.

Gel fractions and water contact angle measurements were obtained on cured coating samples, key results of which are summarized in Table III. The insoluble fraction remained high in all samples (>90 wt %), supporting the formation of extensive chemically crosslinked networks. Contact angles, measured on coated quartz slides, provide information regarding surface energy and the balance of coating hydrophilicity/hydrophobicity. Contact angles for all samples are large (>90°), indicating a generally hydrophobic surface, and, considering experimental error, possesses no discernable trend with composition. Bulk tack measurements by texture analysis further support a low-surface energy coating, likely from the surface modifying siloxane segments, and samples **5a–5d** give very low tack values indicative

TABLE III
Contact Angle Measurements and Gel Fraction for 5 and 6

Sample ID	Alkyl group	Contact angle[a]	SD[b]	Gel fraction[c] (%)
5a	nC_2H_5-	88.9°	2.9°	93
5b	nC_4H_9-	93.2°	0.7°	93
5c	$nC_6H_{13}-$	101.1°	0.9°	94
5d	$nC_8H_{17}-$	94.4°	3.7°	95
6	No-quat	94.5°	2.2°	95

[a] Average of three measurements on left and right sides of droplet.
[b] Standard deviation.
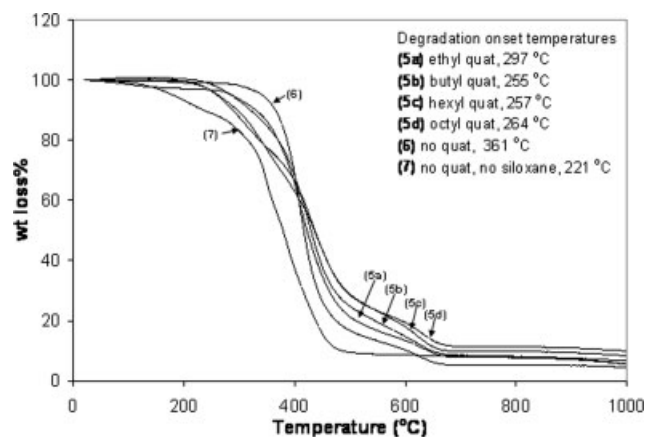[c] Gel fraction quantified as the insoluble fraction recovered after 24-h solvent exposure.

of tack-free films. The hydrophobic/low-surface energy nature of the coating is expected to act as a second line of defense against bacteria, as it will repel water-borne challenges under standard use conditions.

TGA was performed on cured samples **5–7,** and the calculated thermal degradation onset temperatures are summarized in Figure 5. When considering the low-temperature thermal stability, sample compositions **6** and **7** represent the two experimental extremes, 361 and 221°C, respectively, and coatings prepared from alkylated phenyl diglycidyl monomer are characterized by intermediate onset temperatures. Incorporation of the polysiloxane segment imparts additional thermal stability, whereas the alkyl ammonium functionality results in a reduced degradation on-set temperature. Thermal degradation of the alkyl ammonium moiety is predicted to occur through an initial Hoffman elimination reaction, and similarly to the work of Xie et al.,[18] no obvious trend of degradation onset with length of alkyl ammonium ion substituent exists is observed.[18] In a detailed study of several alkyl quaternary ammonium surfactant compounds, Xie et al.[18] found that alkyl architecture and chain length do not significantly affect initial degradation onset temperature, although chain length is understandably expected to affect initial mass loss.

CONCLUSIONS

In this article, we have reported a novel series of hybrid siloxane epoxy coatings which contain quaternary ammonium moieties. The biological efficacy of each coating system containing the antimicrobial functionality has been demonstrated through the reduction of both Gram-positive and Gram-negative pathogenic bacteria by one log (90% reduction), and in one example a 3-log reduction (99.9%) against

Gram-positive *S. aurus* and 2-log reduction (99%) against Gram-negative *E. coli*. Although this data suggests that quaternary ammoniums incorporated into the resin with greater than eight carbons in length would increase the antimicrobial properties, the limitation of synthetic crosslinking prevented a direct comparison. Synthesis and evaluation of the base resin components confirmed that the matrix without the ammonium components was not antimicrobial active and resulted in no reduction of the bacteria subjected to evaluation. Further studies are currently underway to elucidate the mechanism of the biocidal activity displayed by this unique class of compounds.

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