Electron Beam Effects on Polymers. II. Surface Modification of Bis-GMA Substrates by Functionalized Siloxane Oligomers

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Synopsis

   Surface modification of polymer films via electron beam irradiation was studied using the methacrylic acid derivative of the diglycidyl ether of bisphenol A, commonly called bis-GMA, as a curable substrate. Functionalized polydimethylsiloxane (PDMS) oligomers were utilized as surface modifiers. Considerable changes in the wetting characteristics were observed for the siloxane modified bis-GMA surfaces by critical surface tension measurement. For dosages up to 5 Mrads, the dosage level strongly affects the critical surface tension of the polymer. This result implies differences in the concentration of the attached PDMS oligomers to the bis-GMA substrate. The methacrylate-terminated PDMS was observed to be more effective in lowering the critical surface tension than a similar vinyl-terminated PDMS. Higher molecular weight and multifunctional PDMS coatings resulted in somewhat lower critical surface tensions in the dosage range applied in this study. The surface thickness of the functionalized PDMS coatings which were bonded to the substrate surface depended on the molecular weight of the surface modifiers as obtained by XPS analysis. Peel tests of the uncoated and PDMS coated bis-GMA clearly resulted in agreement with the critical surface tension data. Chemical inertness and poor wettability of PDMS provided the PDMS coatings with enhanced resistance to chemical degradation caused by a 24-h exposure to aqueous nitric and acetic acid.

INTRODUCTION

   Electron beam (EB) curing offers a solvent- and initiator-free process for coating and film applications which may consume less energy than conventional thermal processes. Recently, pollution standards and increasing energy costs have accelerated the utility of the EB radiation process and the number of available EB radiation curable materials.

   EB techniques usually involve the use of reactive formulations composed of an unsaturated monomer or oligomer, either by itself, or by compounding with other reactive components which will bring about improvements of system properties. Relatively low-energy EB radiation generated from a linear filament (electrocurtain) can easily polymerize materials containing reactive "double bonds" by electronic and ionic excitation. The penetration capability of this low energy EB depends on the electron energy (beam kV) and

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properties of the material which is to be irradiated. The thickness of the coating material, which is applied on a substrate, is often of the order of a few mils, and the curing process is initiated and often completed within seconds. Hence, EB processes are generating a number of industrial applications such as pressure sensitive adhesives,[1] coatings for metallic and polymeric substrates,[2] optical fibers,[3] coatings and laminates of paper, electrical printed circuits,[4] sterilization, and food packaging.

Of the newer areas for EB applications, surface modification of organic polymer films is now receiving attention. This is due to the importance of surface properties of organic polymer films in a variety of applications such as protective coating processes and paper release coatings, etc. Many physical or chemical methods have been employed for the purpose of altering wetting characteristics, resistance to abrasion, and chemical inertness.[5] The utility of a polymer coating may depend critically on surface free energy which is related to wettability or will depend on the abrasion and adhesion properties. Low surface free energy reduces the wettability and frictional force and hence often lengthens the lifetime of the coatings. With regard to these concerns, silicone-based materials offer unique chemical and physical properties which are brought about by their inorganic characteristics and surface properties. Much effort has been concentrated on the utilization of a compatible polysiloxane as a second component in EB curable systems.[6] Also silicone-containing graft copolymers and block copolymers have been employed for the purpose of being used as additives in a polymer film, and considerable changes of surface properties have been reported even when they were used with a composition less than 1 wt %.[7,8]

As an alternative to the methods using organic compatible siloxane materials, relatively low molecular weight polydimethylsiloxane (PDMS) having radiation-curable functional groups were utilized in this study in an attempt to chemically attach these species onto the surface of the curable substrate for altering surface properties through EB irradiation. This method possibly possesses potential merits with regard to lower cost and *in situ* processabilities for altering surface properties.

In this study, monofunctionally end-capped PDMS as well as multifunctionalized siloxanes were investigated as surface modifiers in conjunction with radiation variables.

EXPERIMENTAL

Materials

Shown in Figure 1 is the methacrylic acid derivative of the diglycidyl ether of bisphenol A, 2,2-bis-[4(2-hydroxy-3-methacryloxy-propyloxy)-phenyl]-propane, commonly referred to as bis-GMA (Freeman Chemical, Nupol 46-4005).
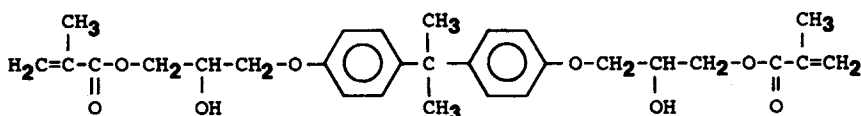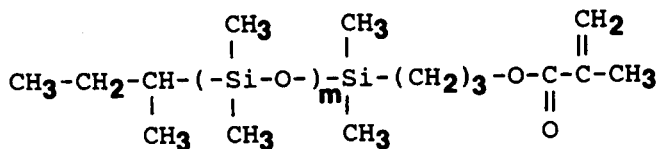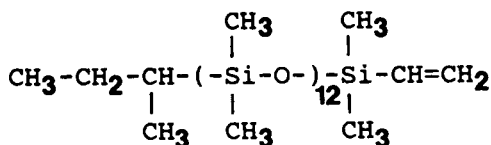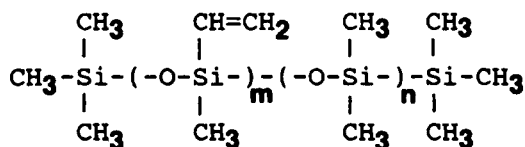

Fig. 1.   Chemical structure of bis-GMA.

$$CH_3-CH_2-CH-(-Si-O-)_m-Si-(CH_2)_3-O-C-C-CH_3$$

with CH₃, CH₃, CH₂ branches, and CH₃, CH₃, CH₃, O branches

(a)

$$CH_3-CH_2-CH-(-Si-O-)_{12}-Si-CH=CH_2$$

with CH₃, CH₃ branches and CH₃, CH₃, CH₃ branches

(b)

$$CH_3-Si-(-O-Si-)_m-(-O-Si-)_n-Si-CH_3$$

with CH₃, CH₃, CH=CH₂, CH₃, CH₃ and CH₃, CH₃, CH₃, CH₃ branches

(c)

Fig. 2. Chemical structures of functionalized siloxane surface modifiers: (a) PDMS-M ($m = 10$ for MW 1000, $m = 64$ for MW 5000, $m = 132$ for MW 10,000); (b) PDMS-V; (c) DMS–VMS (1, 7.5, 19% VMS).

This material served as the substrate upon which the PDMS modifiers were placed. Figure 2 shows the chemical structures of the PDMS containing surface modifiers. One was monofunctionally end-capped with a methacrylate (PDMS-M) [MW 1000 (1K), 5000 (5K), 10,000 (10K)], while a second possessed a vinyl(allyl) functional group (PDMS-V). These were synthesized and characterized as described elsewhere.[9,10] The reaction scheme to achieve these different structures is shown in Figure 3. A low molecular weight multifunctional dimethylsiloxane vinylmethylsiloxane copolymer (DMS–VMS) was purchased from Petrarch System Inc. and utilized as the third surface modifier. This system had 1, 7.5, and 19 wt % content of vinylmethylsiloxane and a viscosity of 1000 cS at room temperature.

Sample Preparation

A liquid bis-GMA coating (ca. 5 mil thickness) was applied on steel plate coupons (0.75 × 0.75 in.). Thermal heating (50°C) was used to promote a smooth liquid surface by lowering the resin viscosity. A 10 wt % solution of one of the siloxane oligomeric modifiers in n-hexane was then spray-coated on the surface of the bis-GMA liquid substrate film. A coating thickness (dried) of the siloxane material deposited on bis-GMA was controlled to less than 2 μm. EB irradiation of this two-layered liquid system was then performed. Any remaining unreacted PDMS oligomers were then removed using n-hexane via Soxhlet extraction for 24 h. After extraction, the samples were dried at

BuLi   +   (IN CYCLOHEXANE)

(ROOM TEMPERATURE)

(TETRAHYDROFURAN)

PDMS-M   PDMS-V
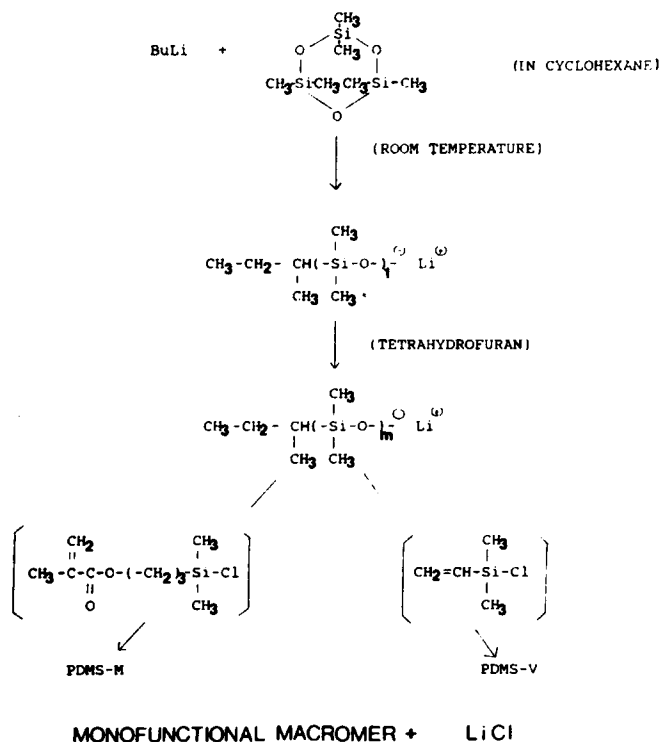
MONOFUNCTIONAL MACROMER +   LiCl

Fig. 3.   Reaction scheme for monofunctional end capping.

atmospheric conditions for 24 h before further testing. Uncoated bis-GMA materials were treated similarly as a "control." For the samples utilized for later peel tests, the same procedures were performed except that the bis-GMA was first applied on a titanium coupon (1 × 5.2 in.).

Irradiation and EB Apparatus

An Electrocurtain CB/150/15/180 (Energy Science Inc.) equipped with a linear tungsten filament was used to irradiate the samples. A diagram of the instrument is shown in Figure 4. It can operate at a voltage between 150 and 175 (kV) with an electron beam current up to 10 mA. Penetration depths at these voltages limit sample thicknesses to ca. 5 mils. A constant voltage of 175 kV was utilized throughout this study. A conveyor speed of 40 feet per minute (fpm) was used for single pass dosages up to 10 Mrads. A dosage of 20 Mrads/pass was obtained at a line speed of 20 fpm such that the current requirement (half of that for the 40 fpm treatment) was within the operating range. Operating parameters were set according to

$$D = KI/S \tag{1}$$

where $K = 66.1$ (Mrad ft/mA/min). The K value was determined by the calibration of the dosage received by the sample and the other variables in above equation. The line speed is given by S (fpm), and I is the electron beam
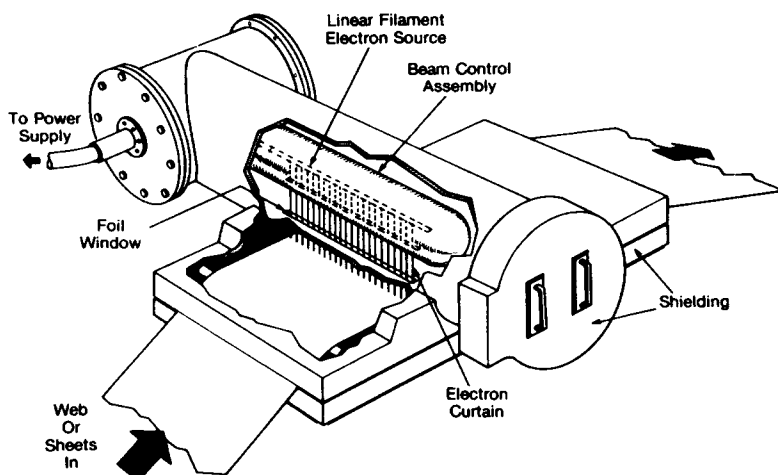
Fig. 4.   General schematic of electrocurtain instrument utilized in this study.

current (mA). Samples were placed on wood inserts in aluminium trays and passed through the conveyor system of the EB instrument.

Surface Tension Determination

Contact angle measurements were performed using a Rame-Hart (100-00) goniometer. In analyzing the contact angles, Zisman's critical surface tension method was utilized.[11] This method provides estimates of the surface free energy of the sample. Using the values of the liquid surface tensions which were reported by Dann,[12] as shown in Table I, the critical surface tension of the bis-GMA, and functionalized PDMS coatings on bis-GMA substrates were determined.

X-Ray Photoelectron Spectroscopy (XPS) Analysis

XPS take-off-angle studies were conducted to detect the degree of surface enrichment of the siloxane surface modifiers. The measured photopeak areas were obtained using a Kratos XSAM 800 spectrometer and used to calculate

TABLE I
Surface Tensions of Zisman Liquid Series Reported by Dann[12]

Liquid	Γ (dyn/cm)
Water	72.2
Glycerol	63.4
Formamide	58.2
Methylene iodide	50.6
1-Bromonaphthalene	44.6
Hexadecane	26.5
Decane	23.8
Octane	21.6
Hexane	18.3

atomic concentrations.[13] Both 90° and 10° take-off angles were utilized for the surface analysis investigations.

Peel Tests

Samples of 10 Mrads radiation cured bis-GMA samples with and without the methacrylate-terminated PDMS coating (MW 1000) were prepared on rectangular titanium coupons (1 × 5.2 in.). A masking tape (Permacel-Avery Int. Co.) was applied with a rolling 2 kg weight at a speed of 50 mm/min. The controlled rolling weight was reapplied twice more for each sample to ensure contact of the tape to the substrate. Peeling force was measured as a function of peel rate using a Model 1122 Instron testing machine according to the 180° peel adhesion testing method (ASTM D1000-78).

Tests for Chemical Resistance

Hexane-extracted samples of bis-GMA with and without PDMS-M (MW 1000, 10 Mrads) coatings were treated with aqueous nitric acid (70%) and acetic acid (99%) by placing each acid on the sample surface for 24 h. After the acid treatment, each sample was washed with deionized water and dried for 24 h. Scanning electron microscopy (SEM) pictures were taken of these acid-treated sample surfaces to allow comparisons between the uncoated bis-GMA and siloxane-coated bis-GMA surfaces.

RESULTS AND DISCUSSION

Surface Tension Measurements

Contact angle measurements of the uncoated bis-GMA, PDMS-M (MW 1000) coatings, and PDMS-V (MW 1000) coatings were performed as summarized in Table II. Critical surface tensions of these samples were determined as a function of the EB irradiation dosage as shown in Figure 5. In each case, for dosages up to 5 Mrads, dosage level strongly affects the critical surface tension, which implies a difference in the concentration of the attached PDMS oligomers to the bis-GMA surface. The dosage effect levels off above 5 Mrads. It is important to note that the methacrylate end group is observed to be more effective in lowering the critical surface tension than the vinyl end group. This may be due to a greater reactivity or possibly a greater copolymerizability of the methacrylate terminal group with bis-GMA relative to the vinyl terminal group.[14] These features would facilitate the reaction at the time of irradiation.

Contact angle measurements of unmodified bis-GMA as well as those treated with PDMS-M (MW 1000), PDMS-M (MW 5000), and PDMS-M (MW 10,000) were performed with the results listed in Table III. The critical surface tensions of these samples were determined as a function of EB irradiation dosage (Fig. 6). Differences in critical surface tension between the uncoated bis-GMA and PDMS-coated bis-GMA surfaces ranged from 10 to 20 dyn/cm. Changing the molecular weights of PDMS also resulted in noticeable differences of the critical surface tension in the dosage range above 5 Mrads, whereas it resulted in scattered data below 5 Mrads. As shown previously in

TABLE II
Contact Angles of Uncoated Bis-GMA, PDMS-M (MW 1000) Coatings and PDMS-V (MW 1000) Coatings[a]

| Sample	Water	Hexadecane	Glycerol	Bromonaphthalene	Formamide
Bis-GMA (0.5 Mrad)	79.3[a]		68.0	20.3	62.4
Bis-GMA (2 Mrads)	78.9		69.9	23.8	62.2
Bis-GMA (5 Mrads)	84.2		75.1	24.9	67.3
Bis-GMA (10 Mrads)	82.3		74.3	26.5	65.0
Bis-GMA (20 Mrads)	83.9		78.0	32.8	66.2
PDMS-M (MW 1000 at 0.5 Mrad)	86.3	12.9	78.8	42.0	69.5
PDMS-M (MW 1000 at 2 Mrads)	87.2	16.9	91.9	61.2	84.5
PDMS-M (MW 1000 at 5 Mrads)	90.2	22.5	91.4	62.2	88.4
PDMS-M (MW 1000 at 10 Mrads)	91.9	22.1	92.4	66.4	88.2
PDMS-M (MW 1000 at 20 Mrads)	93.2	22.4	94.3	67.2	89.2
PDMS-V (MW 1000 at 0.5 Mrad)	80.8	5.7	71.1	32.7	64.9
PDMS-V (MW 1000 at 2 Mrads)	84.5	7.9	78.8	43.1	72.3
PDMS-V (MW 1000 at 5 Mrads)	86.2	10.0	80.7	51.3	74.0
PDMS-V (MW 1000 at 10 Mrads)	93.3	16.1	82.2	53.1	74.0
PDMS-V (MW 1000 at 20 Mrads)	95.0	18.7	92.7	61.7	87.0

[a] Each contact angle was averaged over 10 measurements.
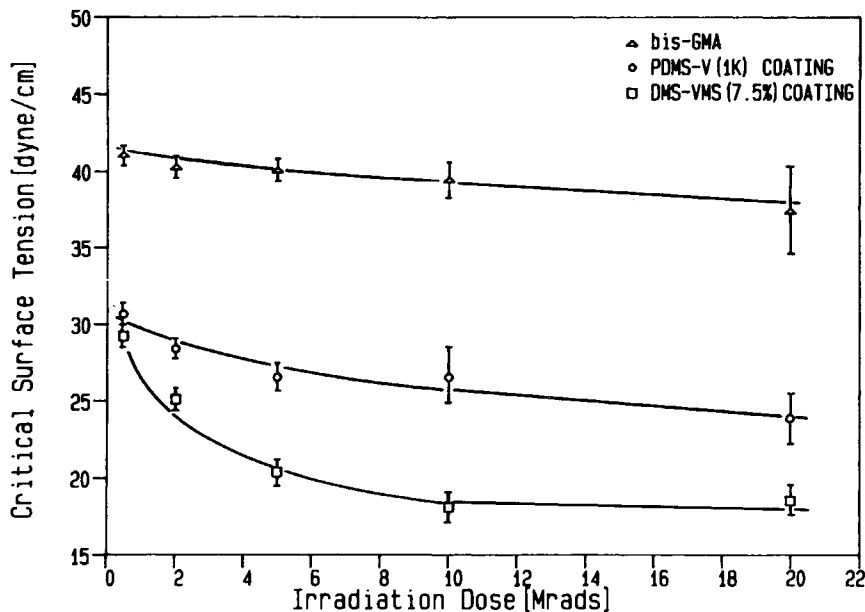
Fig. 5. Irradiation dose vs. critical surface tension for uncoated bis-GMA (△), methacrylate-terminated PDMS-M (MW 1000) coated bis-GMA (□), and vinyl-terminated PDMS-V (MW 1000) coated bis-GMA (○).

Figure 5, the effect of dosage on the critical surface tension levels off above 5 Mrads, and hence the differences in critical surface tension in this dosage range as shown in Figure 6 are believed to be due to the difference in molecular weight of the PDMS materials. PDMS coatings of higher molecular weight resulted in a greater final thickness on the surface of the bis-GMA layer. This will be proven by XPS analysis later in this paper. Therefore, a thicker PDMS coating gives a greater distance between the surface of the bis-GMA substrate and the free "air-side" surface of the PDMS coating. We believe these "final" thicker coatings assist in promoting a lower critical surface tension.

It was reported by LeGrand and Gaines[15] that higher molecular weight of polymer liquid resulted in a higher surface tension based on the free volume theory. However, in our study, the monofunctionalized PDMS-M and PDMS-V possess a very low probability to be crosslinked by our relatively low-energy EB irradiation, although they can be dimerized or possibly trimerized. Therefore, once the oligomers are attached to the bis-GMA surface through their monofunctionality, the other EB-polymerized species on the surface are expected to be removed by the solvent extraction. Hence, no matter what molecular weight the chemically attached PDMS oligomers have, there should be a relatively low dependence on the free volume for the range of molecular weight addressed here, i.e., rather limited and has little bearing on our results. In the dosage range below 5 Mrads, the concentration of the functional end group in addition to EB irradiation dosage can be regarded as the important process variables. For a higher molecular weight of PDMS in the dosage range below 5 Mrads, these two variables appear to somewhat counterbalance each

TABLE III
Contact Angles of Uncoated Bis-GMA, PDMS-M (MW 1000) Coatings,
PDMS-M (MW 5000) Coatings and PDMS-M (MW 10,000) Coatings

| Sample	Water	Hexadecane	Glycerol	Bromonaphthalene	Formamide
Bis-GMA (0.5 Mrad)	79.3[a]		68.0	20.3	62.4
Bis-GMA (2 Mrads)	78.9		69.9	23.8	62.2
Bis-GMA (5 Mrads)	84.2		75.1	24.9	67.3
Bis-GMA (10 Mrads)	82.3		74.3	26.5	65.0
Bis-GMA (20 Mrads)	83.9		78.0	32.8	66.2
PDMS-M (MW 1000 at 0.5 Mrad)	86.3	12.9	78.8	42.0	69.5
PDMS-M (MW 1000 at 2 Mrads)	87.2	16.9	91.9	61.2	84.5
PDMS-M (MW 1000 at 5 Mrads)	90.2	22.5	91.4	62.2	88.4
PDMS-M (MW 1000 at 10 Mrads)	91.9	22.1	92.4	66.4	88.2
PDMS-M (MW 1000 at 20 Mrads)	93.2	22.4	94.3	67.2	89.2
PDMS-M (MW 5000 at 0.5 Mrad)	78.3	17.2	74.6	34.0	68.3
PDMS-M (MW 5000 at 2 Mrads)	91.0	26.8	82.9	39.9	69.6
PDMS-M (MW 5000 at 5 Mrads)	95.3	28.1	90.9	61.0	75.2
PDMS-M (MW 5000 at 10 Mrads)	101.8	35.5	95.2	63.9	87.2
PDMS-M (MW 5000 at 20 Mrads)	104.5	34.5	95.4	69.3	88.2
PDMS-M (MW 10,000 at 0.5 Mrad)	84.0	10.0	73.9	43.4	64.8
PDMS-M (MW 10,000 at 2 Mrads)	86.6	29.0	88.0	47.9	77.2
PDMS-M (MW 10,000 at 5 Mrads)	105.6	31.4	96.6	60.3	91.1
PDMS-M (MW 10,000 at 10 Mrads)	108.0	33.3	99.4	68.5	93.3
PDMS-M (MW 10,000 at 20 Mrads)	101.5	43.4	103.0	73.2	97.2

[a] Each contact angle was averaged over 10 measurements.
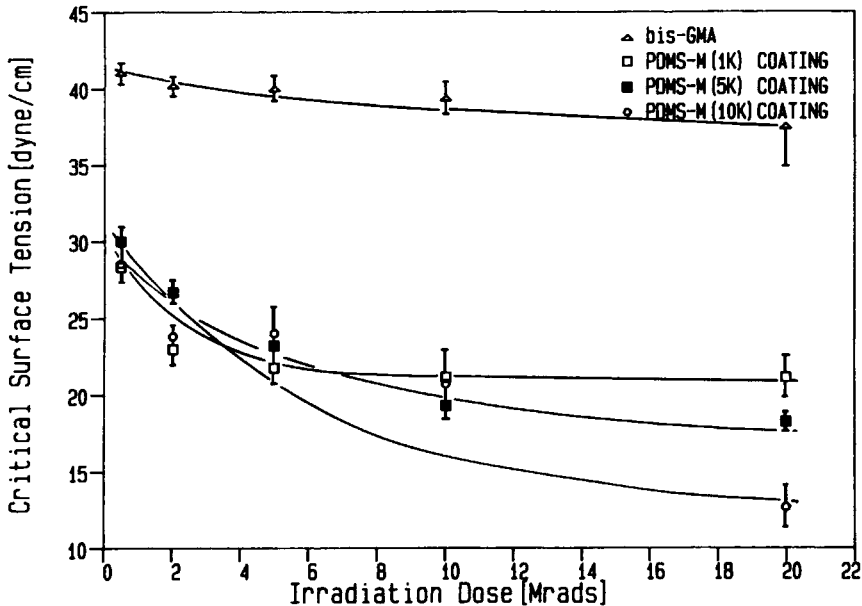
Fig. 6.   Irradiation dosage vs. critical surface tension for uncoated bis-GMA (△) and methacryl-ate-terminated PDMS-M (MW 1000) (□), PDMS-M (MW 5000) (■), and PDMS-M (MW 10,000) coated (○) bis-GMA.

other in the final critical surface tension data. First, a higher molecular weight PDMS has a tendency to form a greater coating thickness which results in a lower critical surface tension (see later discussion). However, a higher molecular weight PDMS offers a lower concentration of the functional end group, which is of importance at dosage levels below 5 Mrads. For lower molecular weight of PDMS in this same dosage range, the critical surface tensions as influenced by these same variables were expected to be somewhat reversed.

Contact angle measurements of bis-GMA, monofunctional PDMS-V coatings, and multifunctional DMS-VMS copolymer coatings were performed—the results being summarized in Table IV. Figure 7 also shows the critical surface tensions determined as a function of EB irradiation dosage. The molecular weight was 1000 for PDMS-V and about 28,000 for the DMS–VMS copolymer. In the dosage range both above and below 5 Mrads, the multifunctional DMS–VMS material resulted in lower critical surface tensions and showed a greater sensitivity of the critical surface tension on EB dosage in the lower dosage range. This behavior again is in agreement with the earlier considerations based on the concentration of the functional groups and molecular weight in the PDMS system. First, in the dosage range below 5 Mrads, both higher molecular weight and higher concentration of functional groups of the DMS–VMS material in comparison with the PDMS-V material contributes to lower the critical surface tension. However, in the previous data of Figure 6, these two variables appear to counterbalance each other in the critical surface tension data. Secondly, in the dosage range above 5 Mrads, the concentration of functional groups becomes insensitive to EB dosage since the bis-GMA surface portion unattached by PDMS materials decreases and vanishes as the

TABLE IV
Contact Angles of Uncoated Bis-GMA, PDMS-V (MW 1000) Coatings and
DMS-VMS (MW 28000, VMS 7.5%) Coatings[a]

| Sample	Water	Hexadecane	Glycerol	Bromonaphthalene	Formamide
Bis-GMA (0.5 Mrad)	79.3[a]		68.0	20.3	62.4
Bis-GMA (2 Mrads)	78.9		69.9	23.8	62.2
Bis-GMA (5 Mrads)	84.2		75.1	24.9	67.3
Bis-GMA (10 Mrads)	82.3		74.3	26.5	65.0
Bis-GMA (20 Mrads)	83.9		78.0	32.8	66.2
PDMS-V (MW 1000 at 0.5 Mrad)	80.8	5.7	71.1	32.7	64.9
PDMS-V (MW 1000 at 2 Mrads)	84.5	7.9	78.8	43.1	72.3
PDMS-V (MW 1000 at 5 Mrads)	86.2	10.0	80.7	51.3	74.0
PDMS-V (MW 1000 at 10 Mrads)	93.3	16.1	82.2	53.1	74.0
PDMS-V (MW 1000 at 20 Mrads)	95.0	18.7	92.7	61.7	87.0
			Methylene iodide		
DMS-VMS (0.5 Mrad)		13.5	50.8	32.0	66.7
DMS-VMS (2 Mrads)		21.5	63.7	57.2	81.2
DMS-VMS (5 Mrads)		40.1	79.3	59.7	93.3
DMS-VMS (10 Mrads)		47.3	103.2	82.3	111.8
DMS-VMS (20 Mrads)		44.1	109.9	89.4	112.7

[a]Each contact angle was averaged over 10 measurements.
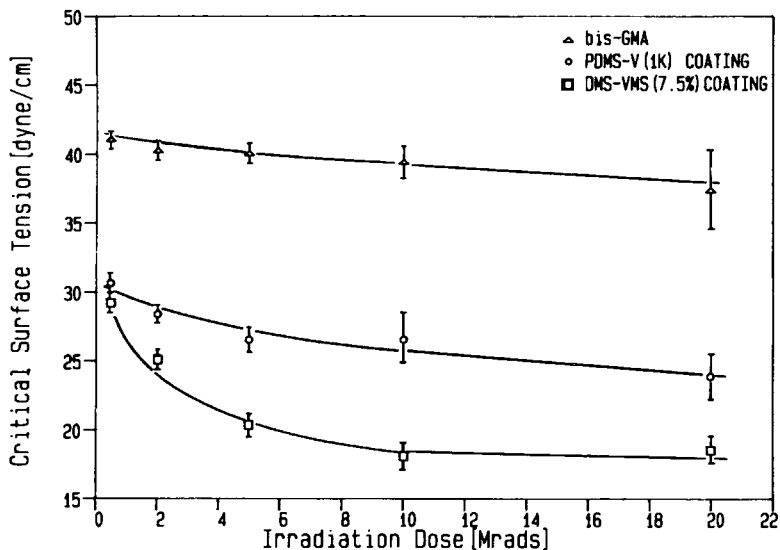
Fig. 7. Irradiation dosage vs. critical surface tension for uncoated bis-GMA (△), vinyl-terminated PDMS-V (MW 1000) coated bis-GMA (○), and DMS–VMS (MW 28,000) (7.5%) coated bis-GMA (□).

EB dosage increases further in this higher dosage range. Therefore, the molecular weight becomes the major variable as discussed in the previous data.

It should be stated that, while high molecular weight PDMS will crosslink with sufficient radiation treatment irrelevant of functional end groups, no gelation occurred for any of the PDMS materials except that of the high molecular weight PDMS with multifunctional groups, i.e., DMS–VMS. These multifunctional DMS–VMS copolymers were found to form a gel in the dosage range above 10 Mrads. Using this knowledge regarding gelation, bis-GMA substrates spray-coated with this DMS–VMS copolymer (19 wt % VMS) and given a 20-Mrad cure were then fractured in the direction perpendicular to the surface at room temperature. An example of a SEM micrograph taken on this gel-coated system is shown in Figure 8. From the SEM results, the thickness of the initial siloxane layer (ca. 2 μm) applied (sprayed) on the liquid bis-GMA substrate could be easily determined.

XPS Analysis

As discussed by the critical surface tension measurement, the thickness of final extracted monofunctionalized PDMS coating was suggested to vary with its molecular weight. In order to approximate the "size" of the PDMS coil which is attached to the substrate surface by a chemical bonding between the functional end-group and the bis-GMA, the radius of gyration of the PDMS coil was approximated by using Gaussian chain statistics.[16] High molecular weight PDMS is known to display Gaussian behavior. However, due to the relatively low molecular weights of the PDMS utilized in this study, they were not expected to be truly Gaussian especially with an attached end to the bis-GMA substrate. Nevertheless, as indicated above, the radius of gyration of

Fig. 8. Scanning electron micrograph showing the thickness (see the region indicated between the arrows) of DMS–VMS (MW 28,000, 19% VMS) gel coating (20 Mrads) on bis-GMA.

PDMS (MW 1000, MW 10,000) was calculated for the purpose of estimating coil dimensions and using these results to compare with the information obtained from XPS take-off-angle experiments.

Figure 9 shows the schematic of XPS take-off-angle analysis which incorporates the thickness dependence upon molecular weight of PDMS in conjunction with the approximate radius of gyration. Figure 10 shows the XPS spectra of the PDMS-M (MW 1000 at 10 Mrads) coating with a 90° take-off angle, the PDMS-M (MW 10,000 at 10 Mrads) coating with a 90° take-off angle, and the PDMS-M (MW 10,000 at 10 Mrads) coating with a 10° take-off angle. In each XPS spectrum, four major signals were detected as a function of core binding energy—these signals being the carbon atom C (1s) at 284 (eV), the oxygen atom O (1s) at 532 (eV), the silicone atom Si (2s) at 149
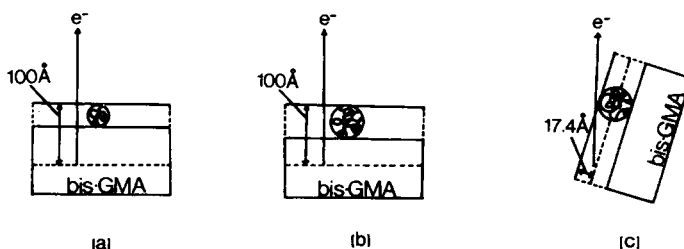

Fig. 9. Schematic diagram of XPS analysis using different take-off angles and molecular weights of PDMS: (a) PDMS-M (MW 1000 at 10 Mrads) coating with 90° take-off angle; (b) PDMS-M (MW 10,000 at 10 Mrads) coating with 90° take-off angle; (c) PDMS-M (MW 10,000 at 10 Mrads) coating with 10° take-off angle.
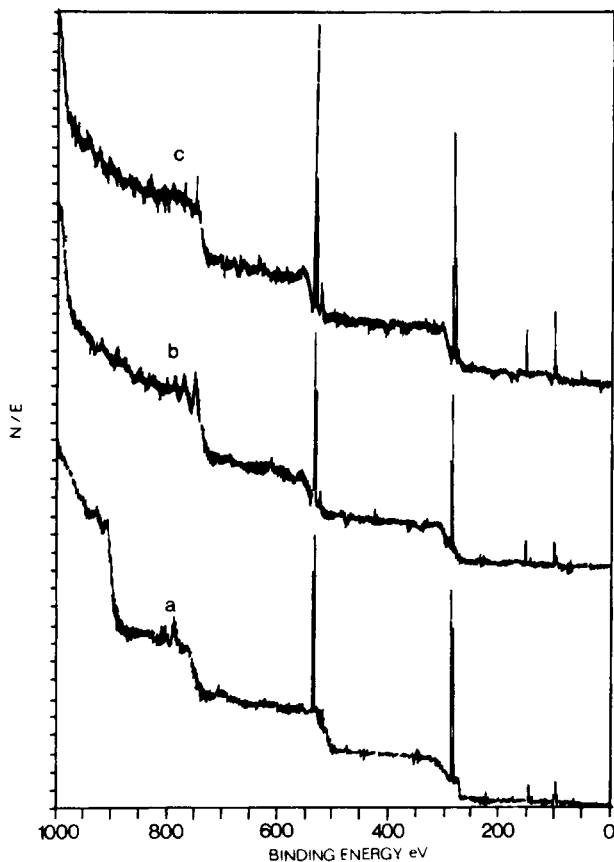
Fig. 10. X-ray photoelectron spectra: (a) PDMS-M (MW 1000 at 10 Mrads) coating with 90° take-off angle; (b) PDMS-M (MW 10,000 at 10 Mrads) coating with 90° take-off angle; (c) PDMS-M (MW 10,000 at 10 Mrads) coating with 10° take-off angle.

(eV) and Si (2p²) at 100 (eV).[17] To test for the consistency of the signals, the peak areas were taken as ratios and compared as shown in Table V.

By increasing the molecular weight of PDMS-M from 1000 to 10,000 but with a constant 90° take-off angle, the C/Si ratio decreased from 13.2 to 9.6. By decreasing the take-off angle from 90° to 10° with a constant 10,000 molecular weight, the C/Si ratio decreased further from 9.6 to 3.9. This C/Si ratio of PDMS-M (MW 10,000 at 10 Mrads) with the 10° take-off angle approached the C/Si ratio of pure PDMS-M (MW 10,000) material since the

TABLE V
XPS Take-Off-Angle Dependence Study

Sample	Radius of gyration (Å)	Take-off angle	Sampling depth (Å)	C/Si ratio
PDMS-M (MW 1000 at 10 Mrads)	7	90	100	13.2
PDMS-M (MW 10,000 at 10 Mrads)	20	90	100	9.6
PDMS-M (MW 10,000 at 10 Mrads)	20	10	17	3.9

analyzed depth was smaller than the diameter of the 10,000 molecular weight PDMS-M coil obtained from the Gaussian approximation of the radius of gyration. Therefore, these XPS data at least support the relative dependence of surface thickness of the functional PDMS on its molecular weight and the speculation that *a monomolecular thickness* of the PDMS component is obtained as would be expected. It should be mentioned that, in the case of the 10° take-off-angle analysis of the PDMS-M (MW 10,000) coating as shown in Table V, the electrons should escape from a depth of about 20 Å. However, actual XPS data indicate that some electrons were escaping from the bis-GMA substrate. This result can be rationalized as follows. The general sampling depth of XPS analysis with a conventional X-ray source for organic materials is known to be approximately 100 Å. However, it can deviate from this value depending on the type of the material to be analyzed. The accurate determinations of atomic density and mean free paths of the photoemitted electrons are therefore of importance if quantitative results are to be extracted from analytical sampling depth profiling experiments.[18] For our investigation it is believed that there should be a significant difference in the atomic density between the PDMS layer and the crosslinked bis-GMA substrate, thereby affecting the magnitude of electron mean free paths. We also believe that the siloxane layer could have lower density than that of crosslinked bis-GMA substrate, even though the precise estimation of the magnitude of electron mean free path has been known to be difficult.[18] If this is true, the sampling depth may be greater than that expected analytically as the thickness of PDMS increases and the take-off angle decreases in consideration of the atomic density difference. From this point of view, it is possible for some of electrons to escape from the bis-GMA layer, although the sampling depth was smaller than the approximated thickness of the PDMS layer. Whatever the case may be, the XPS results still clearly support the conclusions reached above.

In another XPS experiment, bis-GMA *without* a PDMS coating was EB irradiated and then *completely thermal cured (150°C for 2 h)*, the latter of which completes the polymerization, leading to a high degree of a network formation and eliminating any remaining free radicals. PDMS-M (MW 1,000) was then spray-coated on this *previously cured* bis-GMA and aged for 24 h followed by the same extraction procedure. The XPS spectrum of this sample surface is shown in Figure 11 and resulted in a signal which shows *no existence of the Si component*. This result very strongly supports at least two important premises of this study. First, PDMS oligomers are able to be attached onto the surface of bis-GMA only by chemical bonding between the EB reactive functional end groups of PDMS and the bis-GMA through EB irradiation. Second, there is no possibility for PDMS to remain on the substrate following extraction unless chemical bonding occurs.

Adhesion-Peel Tests

Figure 12 shows the peeling forces for the uncoated bis-GMA and for methacrylate-terminated PDMS (MW 10,000) coatings. Both samples had been irradiated with 10 Mrads. As expected,[19] peeling force increased with increasing peel rate reflecting the viscoelastic behavior of the adhesive. This is
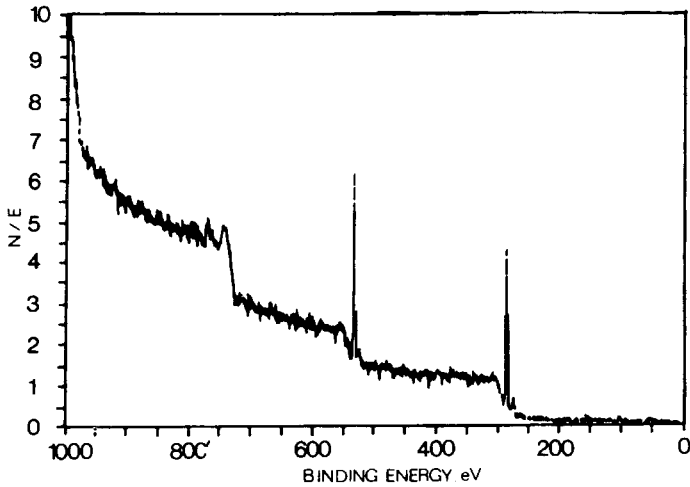
Fig. 11. X-ray photoelectron spectrum of completely cured (EB irradiation and thermal curing) bis-GMA and then followed by siloxane coating and extraction.

not the major issue here. At a lower peel rate of 0.1 cm/s, the peeling forces were about 0.11 N/cm for the uncoated bis-GMA (10 Mrads) and 0.01 N/cm for the methacrylate-terminated PDMS (MW 10,000 at 10 Mrads) coatings. These results show a nearly 90% peel force *reduction* for the siloxane-coated bis-GMA when compared to the uncoated material. At the higher peel rate of 10 cm/s, peeling forces were approximately 0.34 N/cm for the uncoated bis-GMA and 0.14 N/cm for the same methacrylated PDMS (MW 10,000) coatings, which gives a nearly 60% peel force reduction for the PDMS-mod-
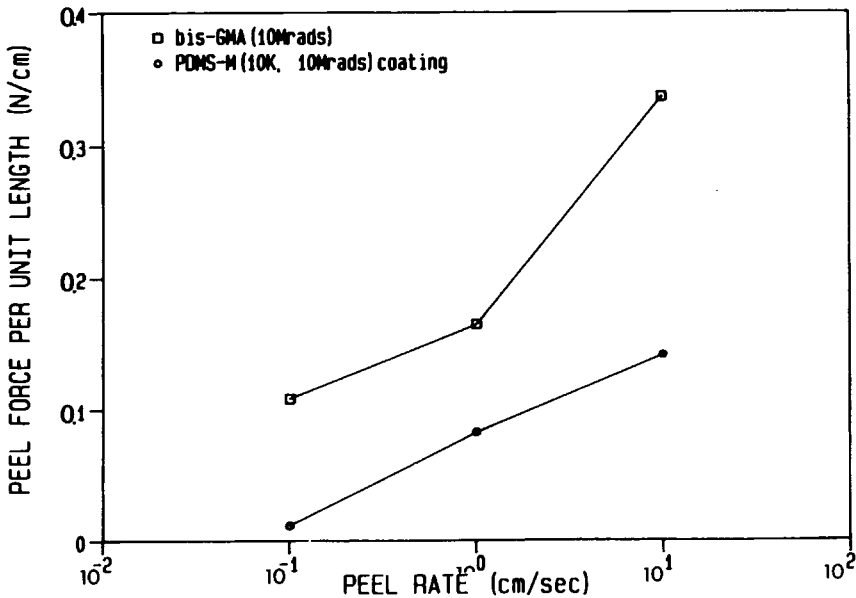

Fig. 12. Peel test results (10 Mrads) for uncoated bis-GMA (□) and methacrylate-terminated PDMS-M (MW 10,000) coated bis-GMA (○).

ified surface. Clearly, the peel force behavior is in direct agreement with the surface tension measurements.

Tests for Chemical Resistance

Polysiloxanes are relatively inert to many hostile chemicals. Also, aqueous solutions of any kind generally have little effect on polysiloxanes. This behavior is principally due to the poor wetting characteristics of silicone. Thus dilute aqueous acids, metal salt solutions, dilute hydrogen peroxide, etc. have little effect on silicone polymers.[20]

Aqueous nitric acid and acetic acid were used as an indicators in a brief test of the chemical resistance of the modified and unmodified bis-GMA surfaces as investigated by SEM. Nitric-acid-treated surfaces of the uncoated bis-GMA and PDMS coated bis-GMA are shown in Figures 13(a) and 13(b), respectively. Acetic-acid-treated surfaces of the uncoated bis-GMA and PDMS coated bis-GMA are also shown in Figures 13(c) and 13(d), respectively.

After being contacted with these acids at the surface for 24 h, uncoated bis-GMA surfaces in Figure 13(a) (treated by nitric acid) and Figure 13(c) (treated by acetic acid) resulted in severe degradation by nitric acid and a somewhat roughened surface by acetic acid. The uncoated bis-GMA is suspected to be oxidized by nitric acid from the fact that the uncured bis-GMA monomer showed high reactivity with nitric acid in a short time period. Therefore, it can be deduced by the reactivity between nitric acid and the bis-GMA monomer and Figures 13(a) and 13(c) that nitric acid is a hostile
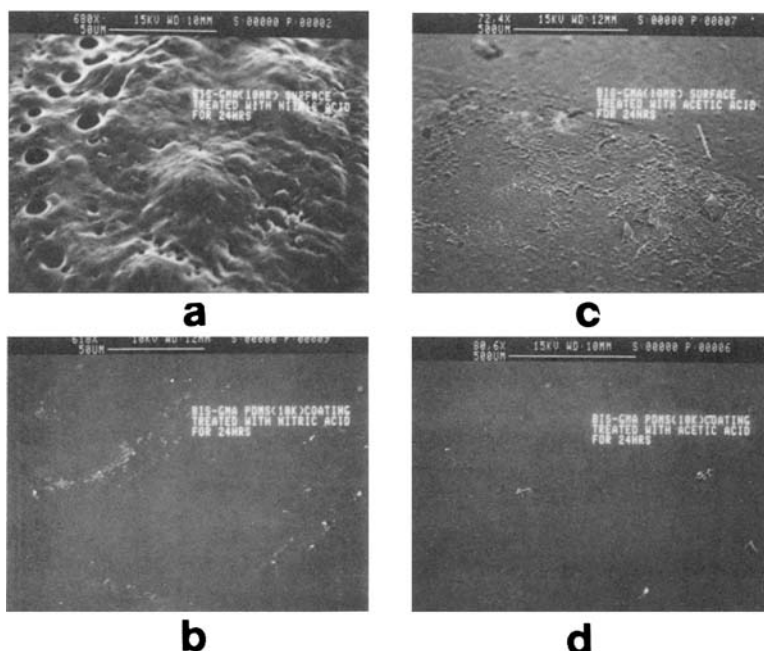

Fig. 13. Scanning electron micrographs: (a) uncoated bis-GMA treated with nitric acid; (b) PDMS (MW 10,000 at 10 Mrads) coated bis-GMA treated with nitric acid; (c) uncoated bis-GMA treated with acetic acid; (d) PDMS (MW 10,000 at 10 Mrads) coated bis-GMA treated with acetic acid.

chemical with regard to bis-GMA. Aromatic substituent groups in organic polymers are known to be susceptible to bond cleavage by strong acids.[20] It is important to add that bis-GMA monomer forms a gel in nitric acid within 1 h when they are brought into contact with each other.

In contrast to the uncoated bis-GMA, the methacrylate-terminated PDMS coated bis-GMA offers extremely low wettability that could repel many organic chemicals as well as aqueous-based systems. Therefore, aqueous acid is not able to contact the bis-GMA layer since the PDMS coating serves as a blocking layer between acid and substrate. Secondly, the chemical inertness of siloxane resists chemical changes by acids at least in the relatively low temperature range.[21] Acetic acid was utilized as a weak acid for the test of chemical resistance. Similar comparisons between uncoated bis-GMA and PDMS coated bis-GMA resulted in the SEM observation given in Figures 13(c) and 13(d).

CONCLUSIONS

A number of conclusions can be made from this study on the topic of surface modification of bis-GMA substrates using siloxane surface modifiers. The degree of chemical attachment of the EB reactive functionalized siloxanes onto the substrate surface increases with dosage up to 5 Mrads and shows nearly constant values above this irradiation dosage level. The methacrylate functional end group was observed to be more effective in bonding to the substrate than the vinyl end group, which might be due to the reactivity of these two functional groups to the bis-GMA liquid substrate. Molecular weight of the monofunctionalized PDMS also played an important role in this study. Increasing molecular weight induces a greater thickness of the PDMS coating on the bis-GMA substrate but lowers the concentration of functional end groups. In the lower EB dosage range, these two variables counterbalanced each other with regard to the final critical surface tension data. Only the molecular weight becomes a variable at higher EB dosage in which the concentration of functional group became insensitive to changing dosage above about 5 Mrads. This tendency to provide a greater "coating thickness" from the higher molecular weight PDMS was also proven by XPS analysis. As expected, an increased number of functional groups in PDMS resulted in a higher sensitivity of bond attachment capability in the lower dosage range and showed lower critical surface tensions in all dosage ranges. Reductions of peeling forces by introducing these surfaces modifiers provided a strong agreement with the critical surface tension data. Inertness and poor wettability of siloxane provided the PDMS coatings with a strong resistance to chemical degradation by nitric and acetic acid in contrast to the uncoated bis-GMA.

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