ELSEVIER

PII: S0032-3861(97)00066-9

Polymer Vol. 38 No. 21, pp. 5301–5306, 1997

0032-3861/97/$17.00 + 0.00

Grafting polyvinylimidazole onto silicon wafers via a copolymer of methacrylate epoxy and methacrylate-functional silane coupling agents

B. Mouanda
LETI (CEA.-Technologie Avancées), D.E.I.N.-S.P.E., Groupe Composants Organiques, Centre d'Etudes de Saclay, F91191 Gif-sur-Yvette, France
(Received 16 April 1996; revised 11 November 1996)

Copolymerization of glycidylmethacrylate (GMA) with γ-methacryloxypropyl trimethoxy silane (γ-MPS) was investigated with the aim of synthesizing a copolymer that could act as an adhesion promoter for polyvinylimidazole (PVI) onto silicon wafers. The copolymer and PVI graftings were investigated by heat curing. The PVI grafting was also examined by use of ultraviolet cured systems involving photosensitizers. The solution of the GMA-γ-MPS copolymer was found to be an effective primer for promoting the adhesion of PVI onto silicon wafers. © 1997 Elsevier Science Ltd.

(Keywords: glycidylmethacrylate-γ-methacryloxypropyl trimethoxy silane copolymers; PVI grafting; photolysis)

INTRODUCTION

Organosilane coupling agents are commonly used to improve adhesion between an organic polymer and an inorganic substrate. These organosilanes have hydrolysable functional groups on the silicon atom, which permit covalent bond formation to the substrate. Trimethoxy silane-modified polymers are also good adhesion promotors. In order to improve the adhesion between polyvinylimidazole (PVI) and a glass surface, copolymers were therefore synthesized.

Kumagai *et al.*[1] have copolymerized vinyl imidazole with γ-methacryloxypropyl trimethoxy silane (γ-MPS) by free radical polymerization. They found that the reactivity of vinyl imidazole (VI) towards γ-MPS was very low: $r_{VI} = 0.079$ and $r_{\gamma-MPS} = 1.39$ in benzene. From their results, they concluded that the imidazole moiety was sandwiched between silane groups in the early stage of copolymerization. A random copolymer is obtained.

In order to obtain imidazole moieties more easily, a copolymer was synthesized as a coupling agent. It was composed by a comonomer with an alkoxysilane group in order to ensure adhesion with silicon oxide surface and a comonomer with an epoxy functional group to form chemical bonds with PVI surface. In this way, PVI was grafted onto silicon wafers, and its properties were unchanged.

It was of interest to study the copolymerization of γ-MPS with glycidylmethacrylate (GMA). The copolymers so obtained were used as adhesion promotors for PVI. The PVI grafting conditions by temperature or ultraviolet (u.v.) irradiation were also studied.

Reagents

γ-MPS, GMA and VI were purchased from Aldrich Chemical Co. and purified by vacuum distillation over hydroquinone for the methacrylate derivatives, and calcium hydride for the last to yield pure and colourless liquids. The purity of monomers was checked by ^1H nuclear magnetic resonance (n.m.r.) and infra-red (i.r.) spectroscopy. The monomers are shown in *Figure 1*. Azobisisobutyronitrile (AIBN) was dissolved in warm methanol (35°C), recrystallized in an ice bath, and then dried in a vacuum oven at room temperature.

Instrumentation

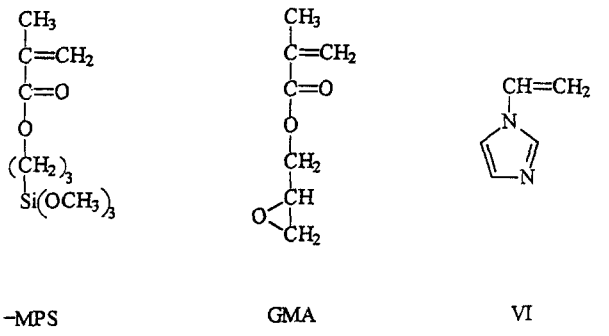
The ^1H n.m.r. spectra of monomers and polymers (copolymers and homopolymers) were recorded on a 60 MHz Hitachi R-1200 n.m.r. instrument, by using CD_3COCD_3 as a solvent. Tetramethylsilane was used as an internal reference.

Polymers were characterized using a Perkin Elmer 1710 Fourier transform i.r. (*FT*i.r.) spectrophotometer with a PC data station, by simple transmission measurements of thin films on double sided polished silicon substrate. Monomers were studied in KBr plates.

The molar masses were determined by means of size exclusion chromatography (s.e.c.) on a Waters 746 apparatus equipped with a set of two columns of Styragel HR calibrated with narrow distribution polystyrene standards and coupled with a differential refractometer. Samples were eluted with THF at a flow rate of 1 ml min^{-1}. Then the molar masses are expressed in equivalent polystyrene. The thermal behaviour of the polymers was studied using a Mettler differential scanning calorimeter (d.s.c.), with a scan speed of 10°C min^{-1}, and a Mettler thermogravimetric analyser (t.g.a.) with a scan speed of 20°C min^{-1}.

Polymerization

Copolymerization of γ-MPS with GMA in argon atmosphere was carried out in dry toluene solution



γ-MPS GMA VI

Figure 1 Monomers used for copolymerizations γ-MPS: γ-methacryloxypropyl trimethoxy silane, GMA: glycidyl methacrylate, and homopolymerization VI: vinyl imidazole

ethanol and pouring it in acetone. The precipited polymer was collected by filtration, washed with acetone and finally dried under vacuum for 16–18 h. The percentage conversion of PVI was around 100%.

Grafting copolymers onto silicon wafers

Silicon wafers with a SiO_2 surface were used as substrates and cleaned as described in the literature[4] before spin coating. The copolymer solution was filtered using a 0.5 μm Millipore filter. Then it was deposited onto the substrate by spin coating and cured at 80°C, for 10 min. The film thicknesses before and after curing, development, were measured with a Sloan Dektak[3] Surface Profiler. Curing in *Table 1* was carried out in an oven at ambient pressure.

Table 1 Effect of copolymer curing conditions

		Copolymer grafted (%) [thickness loss (%)]		
Copolymer	γ-MPS (%)	after 10 min at 80°C	after 2 h at 100°C	after 2 h at 150°C
1	18	0 [100]	11 [a]	46 [53]
2	24	6 [*]	42 [72]	97 [2]
3	42	21 [84]	67 [35]	93 [8]
4	57	49 [49]	96 [8]	100 [1]

[a] Final thickness impossible to measure

Table 2 Influence of copolymer/PVI curing conditions and percentage of grafted PVI

		Grafted PVI at 150°C (%) [thickness loss (%)]		Grafted PVI at 165%C (%) [thickness loss (%)]	
Copolymer	Epoxy (%)	24 h	48 h	24 h	48 h
4	43	4 [45]	12 [40]	57 [14]	65 [13]
3	58	6 [39]	30 [32]	67 [13]	70 [12]
2	76	9 [36]	35 [27]	71 [12]	72 [12]
1	82	10 [35]	36 [23]	72 [10]	73 [10]

Table 3 Influence of salt content and irradiation time on the percentage of PVI grafted

Onium salt (%)	2	2	2	2	5	10	10	10
Time irradiation (s)	60	120	180	300	300	60	180	300
Thickness loss (%)	50	18	9	9	6	50	6	1
PVI grafted (%)	0	43	78	78	88	0	87	100

(0.02 mol in 70 ml) using 0.2 mol% AIBN as an initiator. The solution was stirred at 70°C for 24 h. Next the solution was condensed by rotary evaporation and poured into an excess amount of dry hexane. To purify the polymer, toluene dissolution/hexane precipitation was done twice. Then the precipited copolymers were filtered, washed with hexane and dried at 30°C under vacuum for 16–18 h.

Some polymers were synthesized by taking different molar ratios of γ-MPS and GMA in the initial feed. The corresponding homopolymers were also synthesized. PVI was prepared by radical polymerization of VI withAIBN as a catalyst[2]. The distilled monomer (0.09 mol) was dissolved in 55 ml of methanol and polymerized at 60°C under argon atmosphere for 48 h. A low monomer concentration was used in order to avoid insoluble polymer formation[3]. The polymer was precipited in dioxane. It was purified by dissolving in

PVI was coated by spin coating onto copolymer surface. The grafting was carried out by curing (*Table 2*) in an oven or by ultraviolet (u.v.) irradiation (*Table 3*). The u.v.-visible lamp is a 200 W HBO mercury lamp.

All the coating solutions were kept in a refrigerator at 6°C. After several weeks at ambient temperature and pressure, a gel appeared in the flask. The air humidity modified Si–O–C bonds to Si–OH, and crosslinking reaction began. The copolymer powders were chemically stable and remained soluble even after 1 year.

The adhesion properties of the film obtained after curing and irradiation were determined on different substrate by solvent resistance by solvent jet or in a soxhlet apparatus.

RESULTS AND DISCUSSION

Determination of copolymer composition

The copolymer compositions were determined by ^1H n.m.r. spectra analysis. The characteristic proton resonance signals of copolymer are given in *Figure 2*. The peaks were at $\delta = 3.6$ (CH_3 proton of Si–O–CH_3), $\delta = 3.3$ (CH proton of epoxy group), $\delta = 2.8$ (CH_2

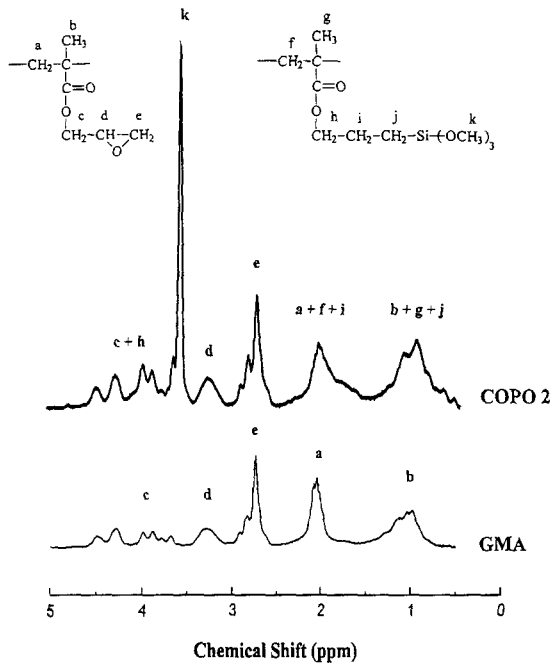


Figure 2 ^{1}H n.m.r. spectra of GMA polymer and copolymer 2

Table 4 Percentage conversion and composition of copolymers

Copolymer	Feed ratio (γ-MPS/GMA)	Yield (%)	Copolymer compositions (n.m.r., γ-MPS/GMA)
1	20/80	14	18/82
2	30/70	48	24/76
3	50/50	62	42/58
4	70/30	60	57/43

The copolymer composition was given by the equation of Alfrey, Mayo and Lewis rearranged by Finemann and Ross where f_1 and f_2 are the mole fractions of the two monomers 1 and 2 in the field, and F_1 and F_2 are the mole fractions in the copolymer. The equation, given in ref. 5, is the following:

$$\frac{f_1}{f_2} \times \frac{F_1 - F_2}{F_1} = \frac{F_2}{F_1} \times \frac{f_1^2}{f_2} \times r_1 - r_2$$

A plot of $f_1(F_1 - F_2)/f_2F_1$ of the above equation vs $F_2f_1^2/F_1f_2$ gives a straight line with a slope. The monomer reactivity ratios were calculated to be $r_1 = 1.57$ for γ-MPS and $r_2 = 1.41$ for GMA. These values are erroneous because of the high conversions. They should be used to estimate the sequence distribution of units in the polymers produced under different molar ratios of monomers. These values of $r_1 > 1$ and $r_2 > 1$ show that these monomers have a tendency to homopolymerize separately, and to give block copolymers.

Thermal behaviour

The thermal behaviour of these copolymers was investigated in a nitrogen atmosphere. The copolymers were stable up to 200°C, and began losing weight above this temperature. The derivative thermogravimetry (d.t.g.) curve showed two maxima, indicating thereby that decomposition takes place in distinct steps. Data are given in *Table 5*. This table shows that the copolymers with γ-MPS content in the range 18–42% have the same behaviour with a weight loss around 20% below 250°C (200–230°C). Jang and Kim[5] explained this result as follows. Below 150°C there is a decrease of Si–O–C bonds due to crosslinking reactions with

Table 5 Results of thermogravimetry analysis of copolymers

		First step			Second step		
Copolymer	γ-MPS (%)	T_{min} (°C)	T_{max} (°C)	Weight loss (%)	T_{min} (°C)	T_{max} (°C)	Weight loss (%)
1	18	31	247	21	247	553	79
2	24	28	256	18	256	594	80
3	42	28	253	20	253	594	82
4	57	28	115	2.5	115	594	79

proton of epoxy group), $\delta = 1.0$ (CH_3 of γ-MPS and GMA) and $\delta = 0.8$ (CH_2 proton of $-CH_2-Si-(OCH_3)_3$). The data are given in *Table 4*. The copolymer compositions were determined from the peak intensities at 3.6 ppm and 2.8 ppm.

The effect of the mole fraction of γ-MPS on percentage conversion was determined by taking different molar ratios of γ-MPS and GMA initial feed and keeping the time and temperature of polymerization constant (24 h at 70°C). The increase in percentage conversion was observed by increasing the fraction of γ-MPS, but at higher mole fractions the increase stopped. The s.e.c. results showed that molecular weight M_w are in the range of 2×10^4 to 7.5×10^4, in equivalent polystyrene. They corroborate the former results, the masses increasing with the Si content in the copolymer.

Although the copolymer polymerizations were taken to very high conversions (60%), we calculated the reactivity ratios of the two monomers.

residual water vaporized by heating. Above 150°C, in the range 150–200°C, a drastic increase of Si–O–Si bonds is attributed to the thermal degradation of the Si–O–C bond.

The d.s.c. thermogram, after a first scan, did not show a change in heat capacity before and after going through a glass transition temperature (T_g). Only after three scans was a T_g measurable. The T_g is 156°C for copolymer 2 (d.s.c. end temperature = 300°C), and its high value was attributed to a crosslinking reaction of the copolymer.

The weight loss in the copolymer below 300°C is attributed to the thermal decomposition of the γ-MPS unit, and thermal stability above 300°C is mainly due to the crosslinking reaction.

However both thermal degradation and crosslinking occur above 150°C for GMA moieties[6]. Copolymer 1 with the high content of GMA was the most stable. It totally decomposed at 370°C, a few degrees higher than the other compounds (350–360°C).

Grafting by thermal baking

Copolymers 1, 2 and 4, were dissolved in MIBK. Copolymer 3 and PVI were dissolved respectively in toluene and MeOH. The solutions were made in order to obtain films with a thickness of about 100 nm after curing during 10 min at 80°C.

We first studied the influence of the curing temperature and time on the copolymer film thickness grafted onto silicon wafers. The results are summarized as the percentage of the copolymer grafted and the thickness loss after spin coating, curing at 80, 100 or 150°C during 10 min or 2 h (initial thickness), and then acetone (copolymer solvent) jet (final thickness). The percentage of copolymer grafted was deduced from the i.r. spectra at the same transition scale from the peak intensity at 1728 cm^{-1} (vibration band of C=O in methacrylate ester groups) before and after development.

The copolymer grafted (%) =

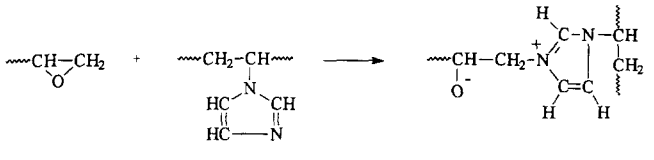
[I_{1728} after development/I_{1728} before development] × 100

The thickness loss (%) =

[initial thickness − final thickness/initial thickness] × 100

The results are shown in *Table 1*.

The results show that the higher the Si content the higher the percentage of copolymer grafted and the smaller the thickness loss are. The temperature increase has a good influence on the adhesion. Except for copolymer 1, less than 10% of the thickness is lost after 2 h at 150°C, even after exposure to acetone vapour in a soxhlet apparatus during 24 h. But baking at elevated temperature (150°C) prevents the further reaction between epoxy groups and tertiary amine from PVI, because the epoxy moieties also crosslink. The epoxy/amine reaction[7] is:



Consequently, the copolymer films were only cured at 80°C, for 10 min before coating the PVI. After the PVI coating, the films (copolymer/PVI) were cured at 150 or 165°C during 24 or 48 h in order to allow the epoxy/amine reaction. After curing they were subject to a MeOH jet, and the final thicknesses measured. The percentage of grafted PVI was estimated from i.r. spectra (*Figure 3*), before and after development from the peak intensities at 3116 cm^{-1} (vibration band of C=CH and N=CH in imidazole cycle)[5] and 1728 cm^{-1} (vibration band of C=O in methacrylate ester groups) from the equation:

$$\text{Grafted PVI\%} = C/C_o \times 100$$

$$\text{with } C_o = I_{3116}/I_{1728} \text{ before development}$$

$$\text{and } C = I_{3116}/I_{1728} \text{ after development.}$$

The results are shown in *Table 2*. The percentage PVI grafted could also be obtained from the weight variations, but the wafers were too small in dimension and too low in weight to obtain precise values.

The results show that an extended curing at elevated temperatures promotes both the copolymer adhesion (*Table 1*), and the percentage of grafted PVI. As we saw before, at 150°C, the thermal degradation and crosslinking reaction occurred, both for the organosilane molecules and the epoxy groups. The temperature also improves the movement of polymer molecules, and their interpenetration. The amine–epoxy reaction is therefore facilitated. However only around 70% of PVI was grafted at 165°C. The amine–epoxy reaction is certainly limited by the crosslinking of the epoxy groups. The reaction was accompanied by a thickness loss. The thickness variation is essentially due to the elimination of ungrafted PVI by the solvent. The bilayer of copolymer/PVI was also exposed to methanol vapour in a soxhlet apparatus during 24 h and the PVI layer remained. The bilayer was unchanged.

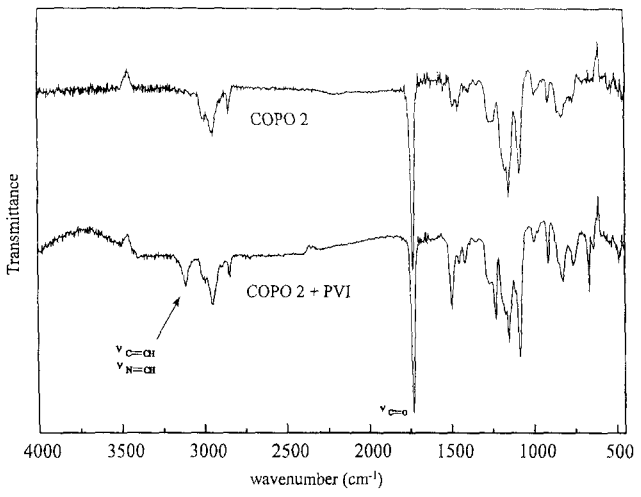


Figure 3 I.r. spectra of copolymer 2 film and copolymer 2-PVI bilayer film

Grafting by u.v. irradiation

For some applications, curing at high temperature (150–165°C) could be a problem, so we studied the PVI grafting by u.v. irradiation. It is well known that onium salts are capable of photoinitiating cationic polymerization of epoxy monomers[8]. On irradiation with u.v. light, the onium salts such as diaryliodonium and triarylsulfonium salts undergo photolysis during which the organic cation is destroyed and a powerful Brönsted acid ($H^+ MXn^-$) is liberated. The strong protonic acid, in subsequent steps, efficiently initiates the polymerization of cationically polymerizable monomers like epoxy monomers. We take advantage of this for the PVI grafting. In order to avoid the epoxy groups reacting together, and to crosslinking the copolymer layer, the onium salt was incorporated into the PVI solution. The salt was added in proportion to the epoxy group content in the copolymer coating solution. We used $\Phi_3SCF_3SO_3$, synthesized as described in the literature[8]. The influence of salt content and irradiation time were examined. The results are summarized in *Table 3*. The experiment was done as follows. Copolymer 2 in MIBK solution was spin coated on the Si wafer. A postbake at 80°C, for 10 min, was done. The spinning solution of PVI and onium salt was coated and baked at 80°C, for 10 min. The photografting was achieved under the u.v.–visible range of the mercury lamp at 80°C during 60, 120, 180 or 300 s, following by a bake at 80°C, for 10 min.

Table 6 Polymer and copolymer remaining after water immersion at 90°C during 1 h

Layer	Treatment before water immersion	Copolymer remaining (%)	PVI remaining (%)
Copolymer 2	150°C, 2 h	87	
Copolymer 2	165°C, 48 h	90	
Copolymer 2 + PVI	150°C, 48 h		77
Copolymer 2 + PVI	165°C, 48 h		90
Copolymer 2 + PVI + 2% salt	u.v. light, 120 s	65	
Copolymer 2 + PVI + 2% salt	u.v. light, 180 s	72	
Copolymer 2 + PVI + 10% salt	u.v. light, 180 s		55
Copolymer 2 + PVI + 10% salt	u.v. light, 300 s		60

The acid molecules generated during irradiation can diffuse to the interlayer to open the epoxy group, and to permit the amine–epoxy reaction. The wafer was at last exposed to the MeOH solvent. One sample (10 mol%, 300 s irradiation) was exposed to methanol vapour in a soxhlet apparatus during 24 h, and the result was the same as a methanol jet. The PVI layer was resistant to the methanol vapour. I.r. spectra and thickness measurements were taken at each step.

The results in *Table 3* show that with only 2 mol% of salt the reaction occurred, and around 80% of PVI was grafted after 300 s of irradiation. The best result is obtained with 10 mol% of salt and 300 s of irradiation. The onium salt examined in these experiments absorbs the u.v. light at a wavelength of 254 nm. However, the amount of u.v. light at 254 nm emitted from the light source is smaller, and so the irradiation time has to be longer.

U.v. grafting is possible when the irradiation dose is sufficient, and the percentage of PVI grafted is high compared to the values reached by thermal curing. The salt present in the PVI layer limited the crosslinking reaction between the epoxy groups and the epoxy–amine reaction is preferential.

Water resistance

Polymer and copolymers with imidazole moieties are generally soluble in water[3]. Therefore, in order to verify the PVI resistance and the stability of the Si–O–Si bonds towards water, some wafers were immersed in hot water without stirring. The experiments were performed at 90°C during 1 h. For comparison, wafers with a monolayer of copolymer 2, a bilayer of copolymer 2 and PVI after thermal curing or u.v. light irradiation were used. The i.r. spectra were realized before and after water treatment. The results are summarized in *Table 6*.

The results show that in all cases a relatively high percentage of copolymer remained on the silicon wafer after water treatment, even when the sample was heated at only 80°C (u.v. irradiation).

Two arguments can be used to explain the copolymer water resistance. Water can be absorbed in adhesive layer resulting in either chemical modification (hydrolysis) or physical damage (microcracking)[9]. The interfacial regions of a bonded joint are usually recognized as a weak link most vulnerable to the effect of moisture. In the case of alkoxysilane compounds, the interfacial weakness is overcome. Indeed, alkoxysilane coupling agents contain chemical functional groups that can react with silanol groups on the silica surface. Attachment to the silica surface can thus be made by covalent bonding. In addition, the coupling agents contain at least one other group, which could co-react with the resin during curing. Assuming that all this occurs, the coupling agent may act as a bridge to bond the silica surface to the resin. This could be expected to lead to the strongest interfacial bond. The formation of such an interface would be expected to provide greater moisture resistance, but a highly polar M–O–Si oxane bond is produced. This bond should be vulnerable to hydrolysis, although the hydrolysis is reversible. Hydrolysis reaction products have the ability to reform and reproduce oxane bonds, as indicated by the following equilibrium reaction[10]:

$$M\text{–}O\text{–}Si\text{–} + H_2O \rightleftharpoons M\text{–}OH + HO\text{–}Si\text{–}$$

With a copolymer joint, the rigidity of the copolymer restricts the movement of silanol groups away from the surface. The system would remain in equilibrium because the silanol groups resulting from the hydrolysis would not be physically removed from the interface.

The second argument is the following. We have seen previously that higher temperatures enhance the density of copolymer grafting and facilitate the condensation reactions. Condensation reactions can occur between the organosilane group and the silanol function at the surface and between the $Si\text{–}OCH_3$ from the neighbouring monomers. The number of silanol groups available for water adsorption decreases. The presence of water at the interface between the wafer and the organic coating led to the loss of adhesion of the protective coating[11].

For u.v. irradiation results at relatively low temperature (80°C), the generated Brönsted acid also attacks the alkoxy group of silane coupling agent[12] and facilitates the condensation reactions. Both curing at high temperature and u.v. irradiation decrease the number of silanol groups available for water adsorption, and thus increase the copolymer water resistance.

Better results were obtained for both the copolymer and the copolymer/PVI bilayer cured at 165°C, 48 h. For the grafted PVI by u.v. light irradiation, the best results are obtained with 10 mol% of salt. However, the values are smaller than that obtained by thermal curing. The salt content is an important parameter, because the salt could react both with the epoxy moieties and the alkoxy groups. In all cases, the PVI layer was resistant to cold water during 15 h at room temperature.

CONCLUSION

The results of the investigations of the PVI grafted onto silicon wafers via a copolymer coupling agent are promising. PVI was grafted both by thermal curing and irradiation. By irradiation the grafting was improved because the epoxy groups crosslinking was

limited by the relatively low temperature used. The polymeric coupling agent was effective in enhancing adhesion for PVI, even after water immersion, during 1 h at 90°C. The performance of the polymeric coupling agent is now evaluated using a pullout test in order to determine its efficiency.

REFERENCES

1. Kumagai, M., Tsuchida, K., Ogino, Y., Hansen, J. and Ishida, H., *Polymer*, 1995, **26**(3), 535.
2. Lemque, R., Vidal-Madjar, C., Racine, M., Piquion H. and Sebille, B., *J. Chromatogr.*, 1991, **553**, 165.
3. Chapiro, A. and Mankowski, Z., *Eur. Polym. J.*, 1988, **24**, 1019.
4. Roscoe, S. B., Yitzchaik, S., Kakkar, A. K. and Marks, T., *J. Polym. Prep.*, 1994, **35**(2), 178.
5. Jang, J. and Kim, H., *J. Appl. Polym. Sci.*, 1995, **56**, 1495.
6. Ueno, T., Shiraishi, H. and Naraoka, K., in *Proceedings of Conference on Radiation Curing Asia (CRCA'88)*, Sankei Kaikan, Tokyo, Japan, 1988, p. 56.
7. Boisde, G., Biatry, B., Magny, B., Dureault, B., Blanc, F. and Sebille, B., *Chemical, Biochemical and Environmental Sensors, SPIE*, 1989, **1172**, 239.
8. Crivello, J. V. and Lam, J. H. W., *J. Appl. Polym. Sci., Polym. Chem. Edn*, 1979, **17**, 977.
9. Shaw, S. J., *Polym. Int.*, 1996, **41**, 193.
10. Pluddemann, E. P., *Silane Coupling Agents*. Plenum, New York, 1991.
11. Angst, D. L. and Simmons, G. W., *Langmuir*, 1991, **7**, 2236.
12. Maruno, T. and Murata, N., *J. Adhesion Science and Technology*, 1995, **9**(10), 1343.