Fluorination of Epoxy Surfaces by a Physical Method

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ABSTRACT: To enhance the surface hydrophobicity of epoxy polymers, a simple physical method for the simultaneous surface fluorination during curing of epoxy resins was proposed and evaluated. Curing of epoxy resins against a polytetrafluoroethylene (PTFE) mold gave rise to fluorinated epoxy polymer surfaces due to the anchorage of PTFE molecules on the epoxy polymer surface. The modified epoxy surfaces were characterized using contact-angle measurements and X-ray photoelectron spectroscopy (XPS). The fluorinated epoxy resin surfaces are highly hydrophobic, exhibiting contact angles of similar magnitude to that of the pristine PTFE film surface. The PTFE mold can be used repeatedly to give fluorinated epoxy surfaces with large contact angles. Aging and solvent extraction tests indicated that the fluorinated epoxy surfaces were very stable. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 296–304, 2000

Key words: surface fluorination; epoxy resin; PTFE; XPS; contact angle

INTRODUCTION

Epoxy resins have been used extensively in coatings, electronic parts, and matrices of composite materials and as adhesives because they offer an excellent combination of desirable physical, mechanical and electrical properties.^{1,2} As an established packaging materials for electronic and microelectronic components, one of the most important functions of epoxy resin is to serve as a sealant for electronic and microelectronic components against exposure to moisture and other contaminants. Moisture is probably the most deleterious single factor in the electronics industry, causing electrical or electronic failure in components. Unfortunately, epoxy resins readily absorb water because they possess hydroxyl groups in their molecular structure. A film of moisture, once absorbed on the insulating material, is difficult to remove.¹ Moisture films degrade the performance of electrical and electronic components by increasing their surface conductivity. Moisture also causes an increase in the mobility of the ionic

contaminants that are involved in the electrochemical processes. As a consequence, corrosion, which can result in (1) the disappearance of metallic thin films, (2) the electrical opening of the wire-wound resistors, and (c) the etching and dissolution of metal from anodic areas, occurs readily.¹ Recently a number of studies have been carried out on the interaction of epoxy resins with water,^{3,4} on water absorption in epoxy resins,^{5–11} on the effect of adsorbed water on the properties of epoxy resins,^{11–16} and on the moisture degradation of epoxy resins^{4,17–19} and epoxy composites.²⁰

Surface modification of polymer is a potentially useful method for reducing the moisture absorption in polymers, since the modification will enhance the surface and barrier properties of polymers.^{21–23} A variety of techniques have been proposed for improving the surface properties of polymers. Almost all surface modification processes reported involve chemical reactions.^{21–23} Fluorination of a polymer surface by implantation is an attractive method, as the process can give rise to a highly hydrophobic surface. It has been reported that direct fluorination with fluorine gas can result in a marked decrease in the total surface tension of high-density polyethylene.²⁴ To improve

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the water repellency of polymer surfaces, highly fluorinated compounds, such as CF_4 , C_2F_6 , and SF_6 , have been used as plasma gases in the implantation of fluorine functionalities on the polymer surfaces.^{25–29} Fluorine-containing block copolymers, which are composed of methacrylate, glycidyl methacrylate and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10heptadecafluorodecyl acrylate, have also been blended with an epoxy resin to improve water repellency of the latter. The low surface energy fluorocarbon segments orient toward the exterior surface of the blend to give rise to a fluorinated surface.³⁰

It is well known that fluorine-containing polymers, such as polytetrafluoroethylene (PTFE), have low surface free energy, low tendency for water uptake, and high water repellence.^{24–26} In the present work we report on a simple physical method for surface fluorination of epoxy polymer by curing the epoxy resin against a PTFE surface. X-ray photoelectron spectroscopy (XPS) and contact-angle measurement were used for the characterization of the modified epoxy resin surfaces. Evaluated was the validity of this physical modification method to fluorinate epoxy polymer surfaces and to render epoxy surfaces highly hydrophobic.

EXPERIMENTAL

Materials and Sample Preparations

Poly(tetrafluoroethylene) (PTFE) sheets having a thickness of about 0.5 cm and a density of 2.18 g/cm³ were purchased from Goodfellow, Inc. (Cambridge, England). The surface of the PTFE sheet was thoroughly washed with acetone before being used as the substrate surface. Glycidyl end-capped poly(bisphenol A-co-epichlorohydrin) (number-average molecular weight 377), 4,4'methylenedianiline, 1,3-phenylenediamine, hexamethylenediamine, N,N'-diphenyl-1,4-phenylene diamine, and itaconic anhydride (95%) were purchased from Aldrich Chemical Co. (Milwaukee, WI). The Araldite[®] standard slow-setting epoxy adhesive (resin and hardener) was purchased from Ciba-Geigy AG (Switzerland). Chloroform and toluene (both of 99.5% in purity) were purchased from Merck & Co., Inc. (New Jersey). Acetone was of reagent grade and was purchased from Mallinckrodt Baker, Inc. (Kentucky). Ethanol (99.9%) was purchased from Hayman, Ltd. (Witham Essex, England), while dioxane (99.8%) was purchased from Lab-scan Asia Ltd. (Bangkok, Thailand). Double-distilled water was prepared in our laboratory and was used for the Soxhlet extraction and for water contact-angle measurements.

Glycidyl end-capped poly(bisphenol A-co-epichlorohydrin) (100 parts by weight) and a curing agent—such as, powdered 4,4'-methylenedianiline (27 parts by weight), hexamethylenediamine (16 parts by weight), '-diphenyl-1,4-phenylene diamine (71 parts by weight), 1,3-phenylenediamine (14.7 parts by weight), or itaconic anhydride (30.5 parts by weight)-were mixed to a homogeneous paste by stirring. The Araldite® resin and hardener (1:1 by weight) were also thoroughly mixed in accordance with the manufacturer's instructions. Each epoxy mixture was cast onto the PTFE sheet and then cured in a constant temperature oven. The curing condition was set at 150°C for 1 h unless stated otherwise. After thermal curing, the epoxy-PTFE composite was allowed to return to room temperature over a period of about 6 h in the well-insulated oven. The PTFE sheet used as the mold substrate was separated from the cured epoxy polymer by mechanical delamination at room temperature. The resulting epoxy polymer sheets were stored for a period up to 1 year in a desiccator for subsequent experiments.

Materials Characterization

Static contact angles of water on the pristine and fluorinated epoxy resins and on PTFE sheets were measured with the sessile drop method at 25°C and 65% relative humidity using a contactangle goniometer [Model 100-00-(230)], manufactured by the Ramé-Hart, Inc. (New Jersey). The telescope with a magnification power of $23 \times$ was equipped with a protractor of 1° graduation. For each contact angle reported, 10 readings from different parts of the film surface were averaged.

XPS measurements were made on a VG ES-CALAB MKII spectrometer with a MgK α X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The PTFE and epoxy sheets were mounted on the standard sample studs by means of double-sided adhesive tapes. The core-level signals were obtained at a photoelectron takeoff angle of 75°. The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). The pressure in the analysis chamber was maintained at 7.5 $\times 10^{-9}$ torr or lower during each measurement. All binding energies (BEs) were referenced to neutral carbon C1s peak at 284.6 eV. Surface elemental stoichiometries were determined from XPS peak area ratios, after correcting with the experimentally determined sensitivity factors, and were reliable to $\pm 10\%$. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

Surface microhardness was measured using a DUH-202 Dynamic Ultra Micro Hardness Tester manufactured by Shimadzu Corp. (Kyoto, Japan). The dynamic hardness (H) was obtained from a load (P) applied to the sheet surface through a triangular microindenter with an apex angle of 115° to the resulting indent depth (D). During the measurements the indenter is pressed against the sample surface by an electromagnetic force. The pressing force is increased linearly from zero to the preset point. Although the indenter penetrates into the specimen, the indentation depth is continuously measured. The dynamic hardness is calculated from the formula $H = P/\alpha D$, where α is a constant associated with the shape of the indenter and αD represents the projected contact area of the indenter under the load P. The maximum load applied on the epoxy samples was 400 mN, while the maximum load on the PTFE surfaces was 50 mN. All the hardness values reported in this work are the average of 10 readings measured at different locations on the sheet surface.

The tensile strengths of the PTFE and epoxy samples were determined on an Instron 5544 tensile tester. All measurements were carried out at a crosshead speed of 10 mm/min. For each tensile strength reported, at least three sample measurements were averaged.

Differential scanning calorimetry (DSC) measurements were carried out on a Netzsch STA 409 thermal analyzer. About 20 mg of the mixture of glycidyl end-capped poly(bisphenol A-*co*-epichlorohydrin) (100 parts by weight) and 4,4'-methylenedianiline (27 parts by weight) was used for the DSC measurement. The heating rate was set at 2°C/min.

RESULTS AND DISCUSSION

The useful properties of an epoxy resin appear only after curing. The curing process transforms the epoxy material from a viscous low-molecularweight compound into a highly crosslinked solid network of great hardness. It is known that the surfaces of polymers tend to reconstruct or reorient in response to different environments in order to minimize interfacial energy.²¹ In earlier studies^{34,35} it was suggested that polymer molds, such as poly(ethylene terephthalate) and perfluorinated ethylene propylene copolymer molds, can decrease and increase, respectively, the water contact angles of epoxy resins or ethylene copolymers. The surfaces of the molds exert their influence through the enrichment of polar or nonpolar functional groups in the surface region of the epoxy resins or the ethylene copolymers. However, in the present study it was found that the increase in water contact angles of the epoxy resins cured against a PTFE surface arises mainly from contamination by the PTFE molecules. Molding the epoxy resin against a PTFE surface contaminates or, in fact, fluorinates the cured epoxy surface. In the following study the epoxy resin system comprised of glycidyl end-capped poly-(bisphenol A-co-epichlorohydrin) and 4,4'-methylenedianiline was investigated first.

The C1s, F1s, and N1s core-level spectra of the epoxy surface exposed to air (i.e., the pristine epoxy resin surface) and the corresponding spectra of the surface molded against PTFE during the curing process are shown in Figure 1. The pristine epoxy resin surface is completely free of the F1s core-level signal [Fig. 1(a)]. The presence of a weak N1s core-level signal at the binding energy (BE) of 399 eV is attributable to contribution from the amine curing agent of the epoxy resin. However, a strong and distinctive F1s corelevel signal appears at about 689.2 eV for the epoxy resin surface, which has been molded against the PTFE surface, as shown in Figure 1(b). The appearance of the F1s core-level signal is consistent with the simultaneous appearance of a high-BE C1s component at 291.4 eV, attributable to the \underline{CF}_2 species.^{36,37} Almost identical surface composition and characteristics are observed for the delaminated epoxy resin surface even after the 20th molding cycles on the same PTFE surface [Fig. 1(c)].

Figures 2(a) to 2(c) show the respective widescan spectra, the C1s and N1s core-level spectra of the pristine PTFE substrate surface, and the PTFE surfaces that have been subjected to one and 20 cycles of epoxy molding. It can be seen from the wide-scan spectra and C1s core-level spectra of the PTFE substrate surfaces that even after 20 cycles of epoxy molding, the PTFE surface remains almost identical to that of the pristine PTFE [compare Figs/ 2(b,c) with Fig. 2(a)]. It is observed that for the pristine PTFE surface, the



Figure 1 The C1s, F1s, and N1s core-level spectra of (a) the pristine epoxy resin surface and the surfaces of epoxy resins that were molded against the PTFE mold surface during the curing process for (b) the first time and (c) the 20th time.(Epoxy resin composition: Glycidyl end-capped poly(bisphenol A-*co*-epichlorohydrin) at 100 parts by weight and 4,4'-methylenedianiline at 27 parts by weight).

C1s core-level spectrum consists of a main component peak at the BE of about 291.4 eV, attributable to the \underline{CF}_2 species,^{36,37} and a broad minor



Figure 2 The C1s and N1s core-level spectra of (a) the pristine PTFE mold surface and the PTFE mold surfaces that are used (b) for the first time and (c) for the 20th time.

Table ISurface Microhardness and TensileStrength of the Cured Epoxy Resin and PTFESheets

	Epoxy Resin	PTFE	
Microhardness (GPa) Tensile strength (MPa)	$\begin{array}{c} 1.5\\72\end{array}$	$\begin{array}{c} 0.2\\ 28\end{array}$	

peak component at about 8 eV lower in BE. The low-BE peak component is attributable to the combined contribution of the X-ray satellite peaks of the $\underline{C}F_2$ species arising from MgK $\alpha_{3,4}$ radiation and the adventitious hydrocarbon species present on the PTFE surface.^{36,37} As also shown in Figures 2(a-c), no N1s signal was discernible on any of the three types of PTFE surfaces. That the epoxy resin-PTFE interface is delaminated by cohesive failure inside the PTFE substrate is readily suggested by the wide-scan and C1s spectra of the delaminated PTFE surfaces resembling those of the pristine PTFE surface, together with the absence of the N1s signal on the delaminated PTFE surface [see Figs. 2(b,c)] and the appearance of the strong F1s and $\underline{C}F_2$ signals on the epoxy resin surfaces, which have been molded against the PTFE surfaces [see Figs. 1(b,c)]. That is to say, once a cured epoxy resin-PTFE interface is mechanically delaminated, a quantity of PTFE chains are drawn to and anchored on the epoxy resin surface. The failure mode of the cured epoxy resin-PTFE interfaces is consistent with the results of the surface-hardness and tensile-strength measurements. Table I lists the surface microhardnesses and tensile strengths of the cured epoxy resin and the PTFE sheets. Since PTFE has a much lower surface hardness and a much smaller tensile strength than the cured epoxy resin, the bulk structure of PTFE is more susceptible to rupture than the epoxy resin.

The average water contact angle of the epoxy resin cured against air was measured to be about 72°. The static water contact angle of the pristine PTFE surface was measured to be about 120°. It was found that the molding of epoxy resin against a PTFE surface enhanced the water contact angles of the resulting epoxy resin surfaces to about the same as that of the pristine PTFE surface, 120°. It can be inferred from this observation that the epoxy resin surface is completely covered by the PTFE molecules to a depth greater than the sensitivity of the technique. The contact-angle technique is sensitive to the chemical composition of 1 nm or less of the outermost molecular laver.^{38,39} The values of the contact angles reported in the present work are representative of the advancing contact angles, which reveal mainly the physical characteristics at the anchored PTFE chain-air interfaces. The XPS data are not contradictory to the contact-angle measurement, although the lower BE C1s component (attributable to C-H species) and the N1s corelevel signals (attributable to epoxy resin) were detected on the surface-fluorinated epoxy resin (see Fig. 1). At the photoelectron takeoff angle of 75°, the probing depth of the XPS technique in the organic polymer matrix is about 7.5 nm,³⁷ which is much greater than the sampling depth of the contact-angle measurement.

The water contact angle of the molded epoxy resin surface is independent of the history of the PTFE substrate surface, as shown in Figure 3. It can been seen that after being subjected to 20 casting cycles, the PTFE surface still imparts the epoxy resin surface with the same degree of hydrophobicity. Thus, a PTFE mold can be used repeatedly to give rise to a highly hydrophobic epoxy polymer surface. The contact-angle results are in agreement with the XPS measurements. The C1s, F1s, and N1s core-level spectra of the epoxy resin surface delaminated from the PTFE



Figure 3 The water contact angle of the molded epoxy resin surface as a function of molding cycle on the PTFE surface.(Epoxy resin composition: Glycidyl end-capped poly(bisphenol A-co-epichlorohydrin) at 100 parts by weight and 4,4'-methylenedianiline at 27 parts by weight).



Figure 4 Effect of the curing time on the water contact angle and on the surface composition of the epoxy resin cured on the PTFE surface.(Epoxy resin composition: Glycidyl end-capped poly(bisphenol A-*co*-epichlorohydrin) at 100 parts by weight and 4,4'-methylenedianiline at 27 parts by weight).

surface after the 20th molding cycle is almost identical to those of the epoxy resin surface from the first molding. The [F]/[C] molar ratios of the two epoxy resin surfaces are also identical [compare Fig. 1(b) with Fig. 1(c)]. These results suggest the consistency of the PTFE substrate as a mold surface. The XPS spectra in Figure 2 further confirm hardly any change in the chemical composition of the PTFE surface when the mold was used repeatedly. From looking at the data in Figure 1 and Figure 2, it can thus be concluded that if the cured epoxy resin-PTFE interface is delaminated mechanically, the delaminated epoxy surface will always be contaminated by PTFE chains, and the delaminated PTFE surface is almost free of the epoxy resin.

At a high curing temperature, the mixture of glycidyl end-capped poly(bisphenol A-co-epichlorohydrin) (100 parts by weight) and 4,4'-methylenedianiline (27 parts by weight) is less viscous than at room temperature. The low viscosity of the mixture is advantageous to the intimate contact between the mixture and the PTFE substrate. Upon thermal curing, the mixture gradually loses its fluidity and becomes a hardened solid. Figure 4 shows the effect of the curing time on the water contact angle and on the surface composition of the cured epoxy resin. When the curing temperature was set at 150°C, the [F]/[C]



200

300

250

Figure 5 The DSC curve of the epoxy resin cured at 2°C/min.(Epoxy resin composition: Glycidyl end-capped poly(bisphenol A-*co*-epichlorohydrin) at 100 parts by weight and 4,4'-methylenedianiline at 27 parts by weight).

Temperature (°C)

150

50

100

ratio and the water contact angle of the molded epoxy resin surface increased sharply with curing time before leveling off after 30 min of curing. It is conceivable that the extent of fluorination of the epoxy resin surface is determined to a large extent by the degree of crosslinking of the epoxy resin and the rate of diffusion of the PTFE chains during the curing process. Once the epoxy resin is fully crosslinked, prolonging the curing time will not result in an increase in the degree of fluorination, and thus there's no further increase in water contact angle. The differential scanning calorimetry (DSC) scan of the epoxy resin cured at 2°C/min is shown in Figure 5. The curing process of the epoxy resin, during which the epoxy resin is crosslinked to form a network, is exothermic in nature. The peak of exothermic temperature is at about 158°C. The DSC curve also indicates that a significant extent of the crosslinking reaction is initiated at 120°C. Figure 6 shows the effect of the curing temperature on the microhardness and water contact angle of the cured epoxy resin. The microhardness values of the epoxy resin cured at different temperatures for 3 h or 1 h, respectively, are all high and close to one another. In addition, the surfaces of the epoxy resin cured at different temperatures are all highly hydrophobic. The data in Figure 4 and Figure 6 thus suggest that after curing under appropriate conditions, the epoxy resin delaminated from the PTFE surface will be physically fluorinated by the PTFE mold surface.

Figure 7 shows that under atmospheric conditions and at room temperature (about 25°C), the hydrophobicity of the PTFE-molded epoxy resin



Figure 6 Relationship between curing temperature and the water contact angle of the epoxy resin cured on the PTFE surface.(Epoxy resin composition: Glycidyl end-capped poly(bisphenol A-co-epichlorohydrin at 100 parts by weight and 4,4'-methylenedianiline at 27 parts by weight).

surface remains practically unchanged over an extended period of time. The epoxy resin surface molded on PTFE still retains its hydrophobicity



Figure 7 Effect of time on the water contact angle of the epoxy resin surface molded against the PTFE substrate. (Epoxy resin composition: Glycidyl end-capped poly(bisphenol A-co-epichlorohydrin at 100 parts by weight and 4,4'-methylenedianiline at 27 parts by weight).

after one year of aging in the atmosphere. To examine further the stability of the epoxy resin surface with the PTFE implants, the epoxy resin samples cured on PTFE were extracted with various solvents in a Soxhlet extractor for 30 min. The results are shown in Table II. The extraction by various solvents does not have a significant effect on the surface composition, as illustrated by the approximately constant [F]/[C] ratio and the water contact angle of the surface. Thus, the PTFE chains must have been anchored or entrapped within the epoxy resin to give rise to this good stability in surface composition and hydrophobicity. The retention of the hydrophobic PTFE chains at the epoxy surface is favored, as the configuration helps to minimize the free energy of the surface. Nevertheless, it should be pointed out that the anchoring or entrapment of the PTFE chains at the epoxy surface is mainly a physical phenomenon arising from the interdiffusion of the molecular chains. It is unlikely that the inert PTFE molecules have become covalently attached to the epoxy surface.

Besides epoxy resin derived from glycidyl endcapped poly(bisphenol A-co-epichlorohydrin) and 4,4'-methylenedianiline, surface fluorination of other epoxy systems by the present physical method has also been examined. The C1s and F1s core-level spectra of the various epoxy resin surfaces molded against the PTFE sheets during the curing process are shown in Figure 8. The corresponding curing conditions for each epoxy system are listed in Table III. As shown in Figure 8, the surfaces of various epoxy resins are indeed fluorinated by the PTFE substrate, albeit not to the same extent. Their degrees of fluorination, as indicated by the surface [F]/[C] ratio, can vary substantially. As a result of the surface fluorination, the surfaces of the various epoxy resins also be-

Table IIEffect of Soxhlet Extraction onSurface Composition and on Water ContactAngle of Epoxy Resin Molded on PTFESubstrate

Solvent	Surface [F]/[C] Ratio	Water Contact Angle (Deg.)		
None	1.2	120		
Water	1.2	118		
Toluene	1.2	120		
Acetone	1.2	120		
Ethanol	1.2	120		
Dioxane	1.15	117		



Figure 8 The C1s and F1s core-level spectra of various epoxy resin surfaces that were molded against the PTFE sheets during the curing process. The epoxy resins consist of (a) glycidyl end-capped poly(bisphenol A-*co*-epichlorohydrin) and hexamethylenediamine, (b) glycidyl end-capped poly(bisphenol A-*co*-epichlorohydrin) and itaconic anhydride, (c) glycidyl end-capped poly(bisphenol A-*co*-epichlorohydrin) and 1,3-phenyl-enediamine, (d) glycidyl end-capped poly(bisphenol A-*co*-epichlorohydrin) and N,N'-diphenyl-1,4-phylene diamine, and (e) Araldite[®] resin and hardener. The curing conditions are listed in Table III.

came more hydrophobic. Table III lists the surface [F]/[C] ratios, microhardness values, tensile strengths, and water contact angles of these epoxy resins fluorinated by the present method. In general, the high surface microhardness, tensile strength and [F]/[C] ratio are accompanied by the large contact angle.

CONCLUSION

The surfaces of molded epoxy resins have been physically fluorinated with PTFE molecules by curing epoxy resins against a poly(tetrafluoroeth-

Epoxy System	Curing Condition	[F]/[C] Molar Ratio	Microhardness (GPa)	Tensile Strength (MPa)	Water Contact Angle (Deg.)
Epoxy ^a + hexamethylenediamine	120°C, 3 h	1.10	1.40	68	118
Epoxy ^a + itaconic anhydride	150°C, 3 h	0.28	1.38	64	114
Epoxy ^a + 1,3-phenylenediamine	160°C, 3 h	0.13	0.52	50	85
$Epoxy^{a} + N, N'$ -diphenyl-1, 4-phylene diamine	160°C, 3 h	0.64	0.11	58	90
Araldite® resin and hardener	120°C, 3 h	0.38	0.52	54	86

Table III Surface [F]/[C] Ratio, Microhardness, Tensile Strength, and Water Contact Angle of Various Epoxy Resins Fluorinated by PTFE Molds

^a Epoxy stands for glycidyl end-capped poly(bisphenol A-co-epichlorohydrin).

ylene) (PTFE) mold. The fluorinated epoxy surfaces were characterized using contact-angle measurements and X-ray photoelectron spectroscopy (XPS). The XPS analysis indicated that the cured epoxy resin-PTFE assembly was delaminated by cohesive failure inside the PTFE substrate. Because of the failure mode of the cured epoxy resin-PTFE assembly, the PTFE mold can be used repeatedly to fluorinate the epoxy surfaces, giving rise to large contact angles. As demonstrated by the aging tests and the solvent extraction tests, the fluorinated epoxy surfaces were very stable since the PTFE molecules were implanted into or anchored firmly on the epoxy resin surfaces. Results obtained from this study show that the curing of epoxy resins against a PTFE mold represents a valid and feasible method for the surface fluorination of various epoxy resins.

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