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Surface Modification of UV-Cured Epoxy Resins by Click Chemistry

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ABSTRACT: A novel method for surface modification of UV-cured epoxy network was described. Photoinitiated cationic copolymerization of a bisepoxide, namely 3,4-epoxy cyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EEC) with epibromohydrine (EBH) by using a cationic photoinitiator, [4-(2-methylpropyl)-phenyl]4-methylphenyl-iodonium hexafluorophosphate, in propylene carbonate solution was studied. The real-time Fourier transform infrared spectroscopic, gel content determination and thermal characterization studies revealed that both EEC and EBH monomers take part in the polymerization and epoxy network possessing bromomethyl functional groups was obtained. The bromine functions of the cured product formed on the glass surface were converted to azide functionalities with sodium azide. Independently prepared alkyne functional poly(ethylene glycol) (PEG) was subsequently anchored to azide-modified epoxy surface by a "click" reaction. Surface modification of the network through incorporation of hydrophilic PEG chain was evidenced by contact angle measurements.

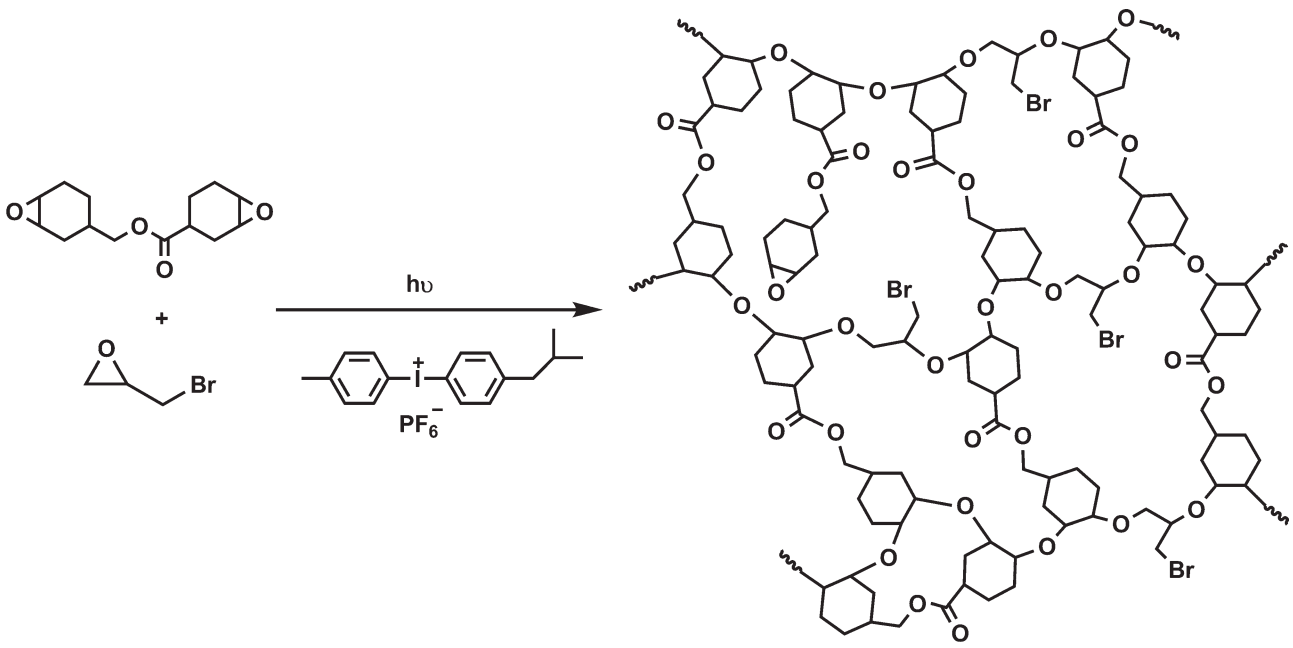
KEYWORDS: click chemistry; epoxy resin; hydrophilicity; hydrophilic polymers; modification; photopolymerization; surface modification; UV curing

INTRODUCTION The ability to control surface hydrophilicity and hydrophobicity of a solid surface has many important applications on industrial processes as well as in our daily life.[1] The hydrophilicity of a surface can be enhanced by a chemical modification that increase the surface energy and decrease the contact angle of a water drop. Wettability of solid surfaces with liquids is a very important property depending on the chemical properties and the microstructure of the surfaces. As the microstructure of a surface is concerned, the hydrophobic and hydrophilic properties are well known to be enhanced by fine roughness.[2] Superhydrophobicity[3] and superhydrophilicity[4] are the two extreme examples of surface wettability.

Epoxy resins are an important class of industrial polymers and largely used in coating applications. In fact, the cationic photocuring of epoxides is becoming increasingly popular in specific technological and industrial fields,[5] mainly in the production of films, inks, and coatings on a variety of substrate, including paper, metal, and wood. Moreover, varieties of high-tech applications, such as the coating of optical fibers and the fabrication of printed circuit boards, have been developed. This technology allows obtaining a quick transformation of a liquid monomer into a solid polymer having tailored physical-chemical and mechanical properties. The main advantage on using UV radiation, to initiate the chain reaction, lies in the very high polymerization rates that can be reached under intense illumination, so that the liquid to solid change takes place within a fraction of a second.[6] Besides, the solvent-free formulation makes UV curing an environmental friendly technique. Another distinct feature of light-induced reaction is that polymerization will occur only in the illuminated areas, thus allowing complex relief patterns to be produced after solvent developments.[7] In the UV-curing process, radical or cationic species are generated by the interaction of the UV light with a suitable photoinitiator. The cationic photo-induced process present some advantages compared with the radical one[8] such as a lack of inhibition in the presence of oxygen, low shrinkage, good adhesion, and high mechanical performance of the UV-cured materials. Moreover, the monomers used are generally characterized by being less toxic and irritant with respect to acrylates and methacrylates, largely used in radical photopolymerization.

Extensive work has been performed to investigate the photocuring of epoxy monomers, focusing mainly on the reaction kinetics and the properties of the cured material.[9–14] For the past two decades, our interest centered on the development of photoinitiating systems for cationic polymerization acting at near UV and visible range and their use in synthesis of complex macromolecular and nanostructures.[9,15–18]

Chemical reactions can be used to subsequently modify surfaces if reactive groups are present. Recent development in the field of surface functionalization is the incorporation of "click" chemistry into surface modification strategies. The Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions between



SCHEME 1 The structure of epoxy network containing bromine groups.

an azide and an alkyne, known as "click reactions"[19,20] have gained a great deal of attention due to their high specificity, relatively mild reaction condition and nearly quantitative yields in the presence of many functional groups. This coupling process has been widely used for the modification of polymeric materials.[21–29] In our laboratory, copper-catalyzed Huisgen 1,3-dipolar azide/alkyne as well as Diels-Alder cycloaddition click reactions have been successfully used for functionalization of polymers,[30,31] microsphere,[32] clays,[33] and silsesquioxanes[34] with thermal-,[35–37] photo-,[30] and electro-active[34] groups. The azide–alkyne click reaction has also been used to modify surfaces of various solid supports including silica spheres,[38,39] carbon nanotubes,[40] even electrode.[41]

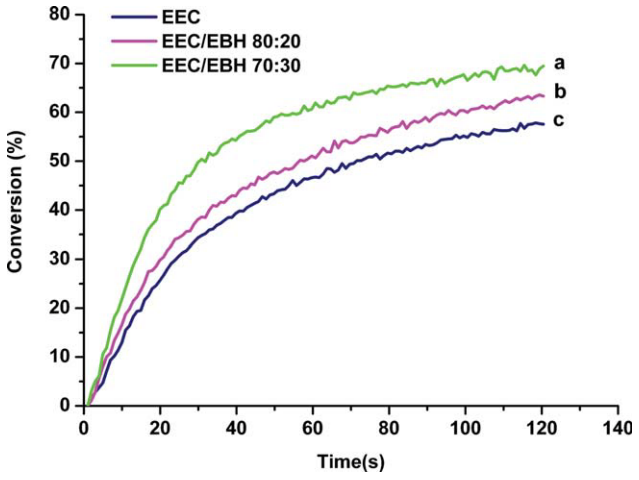


FIGURE 1 RT-FTIR conversion curves as a function of irradiation time for 3,4-epoxy cyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EEC) pristine epoxy resin (a), and for the formulations containing 20 wt % (EEC/EBH 80:20) (b) and 30 wt % (EEC/EBH 70:30) (c) of epibromohydrine (EBH). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

After the first example introduced by Lummerstorfer and Hoffmann,[42] this chemistry has been frequently used for the preparation of functional surfaces.[43,44] Surface monolayers of properly designed terminal alkyne functional diblock copolymers were prepared by Rengifo et al.[45] The alkyne groups provide sites for further surface derivatization reactions or bioconjugation reactions with peptides, proteins, and DNA.[46] Moreover, Sun et al.[47] have published the applicability of sequential Diels-Alder and azide–alkyne click chemistry for the immobilization of carbohydrates and proteins onto a solid surface. In addition to conventional way, the use of microwaves irradiation as an alternative synthetic approach was also reported[48] very recently.

In this study, surface modification of epoxy-cured network for enhancing of surface hydrophilicity via click chemistry was described. The UV-induced polymerization reaction was

TABLE 1 Properties of Cured Films Obtained by Irradiation of 3,4-Epoxy Cyclohexylmethyl 3,4-Epoxycyclohexanecarboxylate (EEC) and Different Concentrations of Epibromohydrine (EBH)

Sample	Conversion (%)[a]	Gel Content (%)[b]	T_g (°C)[c]
EEC	57	100	214
EEC/EBH 90:10	59	98	202
EEC/EBH 80:20	63	98	173
EEC/EBH 70:30	70	100	165

[a] Determined by real-time FTIR.
[b] Determined by solvent extraction.
[c] Determined by dynamic mechanical thermal analysis.

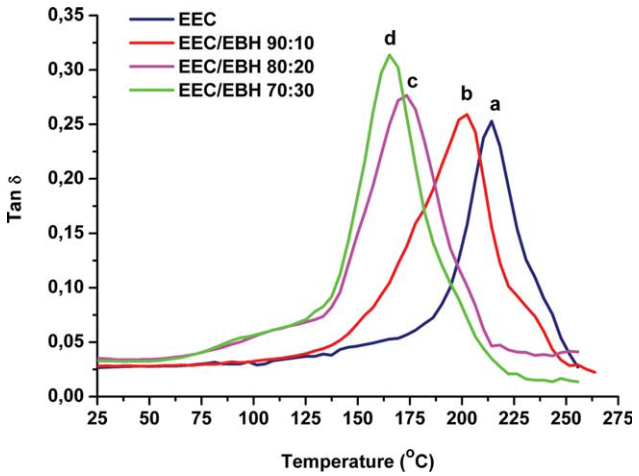


FIGURE 2 Temperature and tan δ values for the UV-cured films obtained by irradiation of 3,4-epoxy cyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EEC) pristine resin (a) and containing 10 wt % (EEC/EBH 90:10) (b), 20 wt % (EEC/EBH 80:20) (c), and 30 wt % (EEC/EBH 70:30) (d) epibromohydrine (EBH).

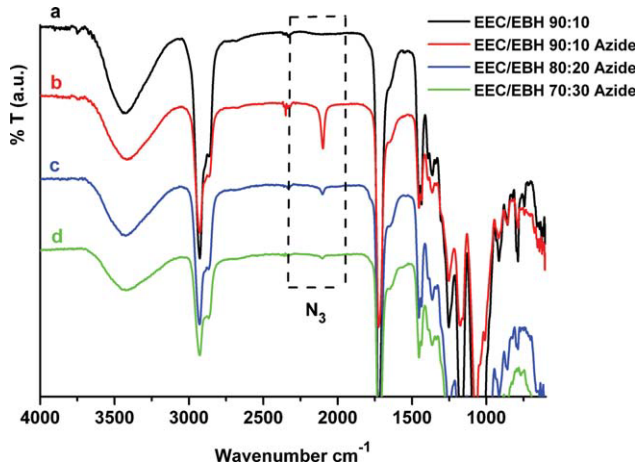
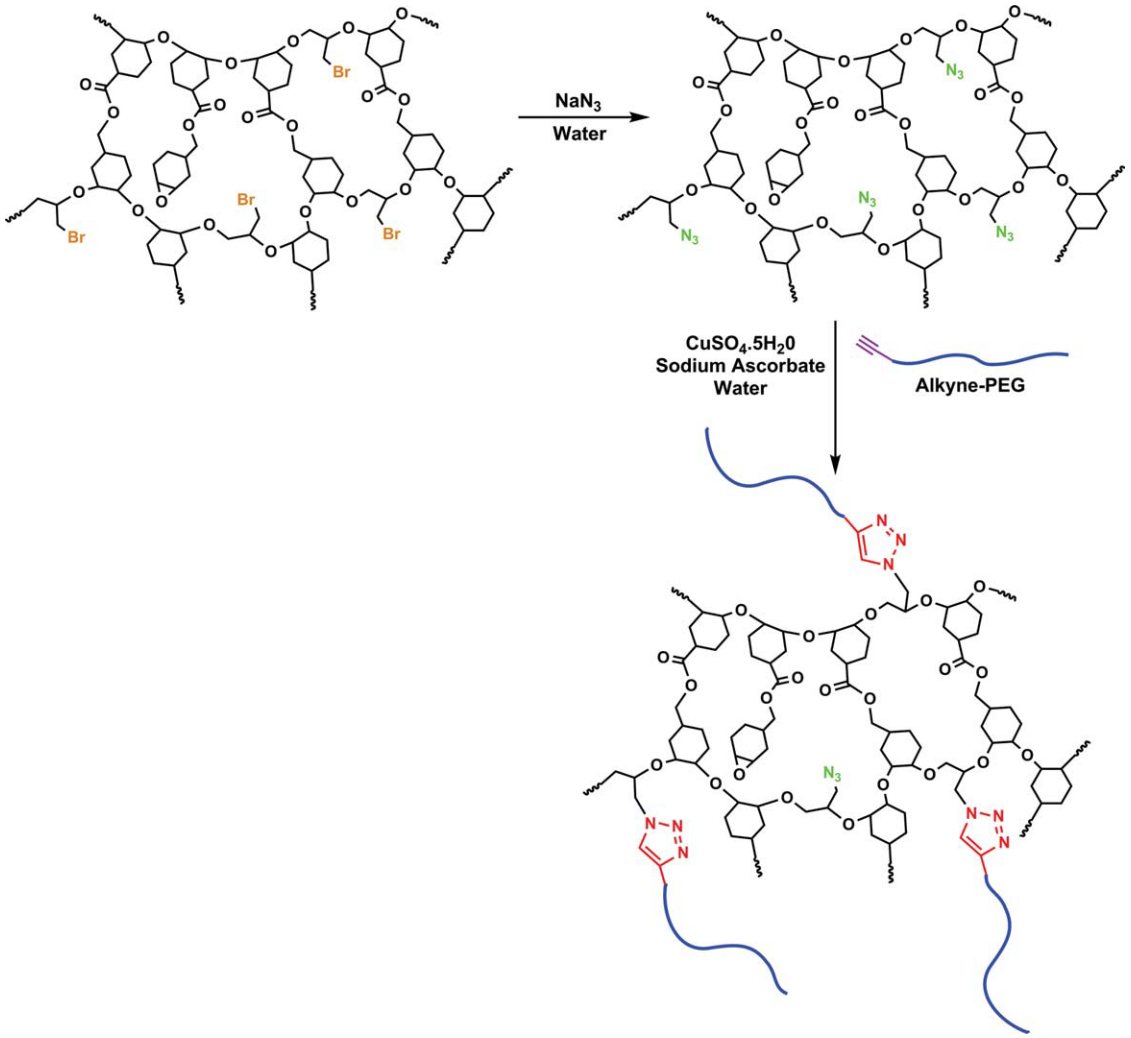


FIGURE 3 FT-IR spectra of epoxy network containing 10 wt % of epibromohydrine (EEC/EBH 90:10) (a), azidated epoxy network with different epibromohydrine content; 10 wt % (EEC/EBH 90:10) (b), 20 wt % (EEC/EBH 80:20 Azide) (c), and 30 wt % (EEC/EBH 70:30) (d).



SCHEME 2 Surface modification of UV-cured epoxy film via click chemistry.

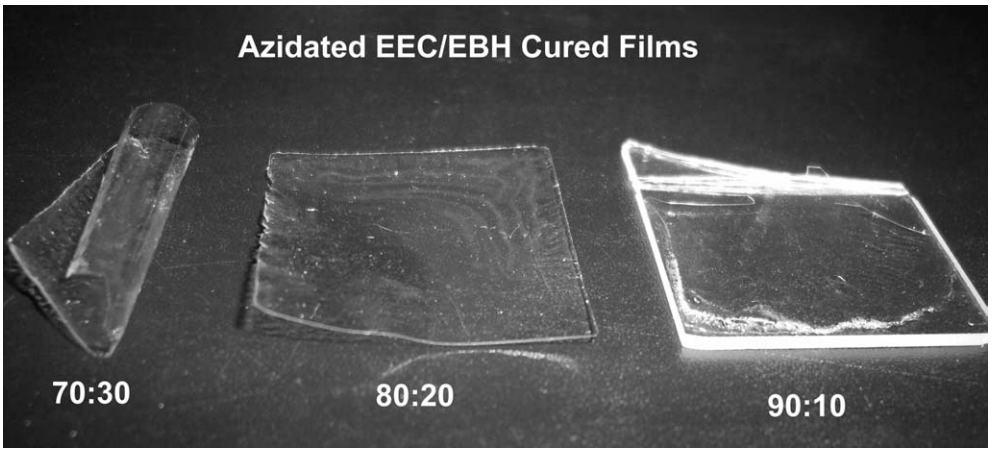


FIGURE 4 The pictures of azidated epoxy network on glass surfaces with different epibromohydrine (EBH) content.

used to introduce bromomethyl groups on the surface of the cured network, through copolymerization between an epoxy resin, 3,4-epoxy cyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (EEC), and epibromohydrine (EBH). They can ultimately form crosslinked networks containing bromomethyl group due to the two epoxy groups of EEC. These groups located at the surface permitted further modification of network for the click reaction. The azide functionality was introduced to structure directly by simple organic reactions using sodium azide (NaN_3). The click reaction between alkyne functional poly(ethylene glycol) (PEG) and azide functional surface-yielded PEG-grafted epoxy network. To the best of our knowledge; this is the first example the application of copper-catalyzed click reaction to epoxy-cured surface obtained by photopolymerization.

EXPERIMENTAL

Materials

The epoxy resin EEC and the EBH were purchased from Aldrich and used as received without further purification. The photoinitiator [4-(2-methylpropyl)phenyl]4-methylphenyl-iodonium hexafluorophosphate in propylene carbonate solution at 75/25 w/w (Irgaqure 250, Ciba Specialty Chemicals, Switzerland) was used with an actual content of photoinitiator of 2 wt %. *N*,*N*′-Dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Acros), 4-pentynoic acid (99%, Aldrich), $CuSO_4$ (Merck), L-ascorbic acid sodium salt (99%, Acros), poly(ethylene glycol) monomethylether (Me-PEG, M_n: 2000, Fluka), and NaN_3 (99%, Acros) was used as received. Dichloromethane (CH_2Cl_2, 99%, J. T. Baker) was dried and distilled over and P_2O_5.

Preparation of Epoxy Network

The UV-curable formulation containing EEC, EBH, and [4-(2-methylpropyl)phenyl]4-methylphenyl-iodonium hexafluorophosphate in propylene carbonate solution was coated on a glass surface and cured by means of UV light, by using a medium pressure mercury lamp. The light intensity on the surface sample was about 30 mW cm^{-2} as measured with an EIT radiometer.

Preparation of Alkyne Functional PEG (Alkyne-PEG)

PEG (M_n: 2000 g/mol, 3.0 g, 1.5 mmol) was dissolved in 25 mL of CH_2Cl_2. 4-Pentynoic acid (0.22 g, 2.25 mmol) and DMAP (0.18 g, 1.5 mmol) were successively added to the reaction mixture. After stirring 5 min at room temperature, a solution of DCC (0.46 g, 2.25 mmol) in 15 mL of CH_2Cl_2 was added to the reaction mixture and stirred overnight at room temperature. After filtration of the salt, the solution was concentrated and product was purified by column chromatography over silica gel eluting with CH_2Cl_2/ethyl acetate mixture (1:10) and then with CH_2Cl_2/MeOH (10:1). Finally, concentrated solution of alkyne-PEG was precipitated in diethyl ether and filtered (yield: 2.81 g, M_{nGPC}: 2400, M_w/M_n: 1.08).

Azidation of Bromine Functional Epoxy-Cured Glass Surface

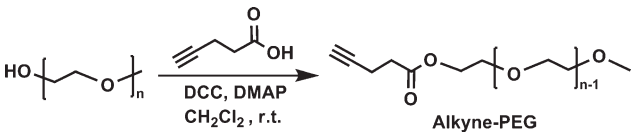
Bromine functional UV cured epoxy resin coated on the glass surface (1 cm^2) was immersed in excess NaN_3 solution in water and stirred at room temperature for overnight. At the end of the reaction, glass surface was kept in water for several minutes and then washed again with distilled water.

Preparation of PEG-Grafted Surface via Click Reaction

Alkyne-PEG (1.5 g, 0.62 mmol), copper (II) sulfate pentahydrate (46 mg, 6 mM), and sodium ascorbate (285 mg, 30 mM) dissolved in 48 mL of water under N_2 atmosphere. Above prepared azide functional epoxy network was immersed in this solution and stirred for 4 days at ambient temperature. After this period, the glass surface was kept for half an hour in water and washed several times with distilled water.

Characterizations

^1H NMR spectra of 5–10% (w/w) solutions in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 250 MHz on a Bruker DPX 250 spectrometer. Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector, and Viscotek a differential refractive index detector. Tetrahydrofuran (THF) was used as an eluent at flow rate of 1.0 mL min^{-1} at 30 °C. Molecular weight of the alkyne-PEG was determined with the aid of polystyrene standards. Fourier transform infrared



SCHEME 3 The synthesis of alkyne functional PEG.

(FTIR) spectra were recorded on a Perkin-Elmer FTIR Spectrum One B spectrometer. The kinetics of the photopolymerization was determined by real-time FTIR spectroscopy, using a Thermo-Nicolet 5700. The liquid formulations were coated onto a silicon wafer with a thickness of 25 μm. The sample was exposed simultaneously to the UV light, which induces the polymerization, and to the IR beam, which analyzes *in situ* the extent of the reaction. Because the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. Epoxy group conversion was followed by monitoring the decrease in the absorbance due to epoxy groups in the region 760–780 cm^{-1}. The gel content was determined on the cured films by measuring the weight loss after 24-h extraction with chloroform at room temperature, according to the standard test method ASTM D2765-84. The cured films showed high gel content values in every case indicating the absence of extractable monomers or oligomers. Dynamic mechanical thermal analyses were performed with a Rheometric Scientific MKIII (UK) instrument, at a frequency of 1 Hz in the tensile configuration. The T_g is evaluated as the maximum of tan δ curves.

RESULTS AND DISCUSSIONS

The overall strategy, as presented in Scheme 1, is based on the preparation of cured epoxy resin with predecessor functionality for the click reaction. The UV-induced polymerization of appropriate formulation containing EEC and EBH monomers was conducted on the glass plate. While the bifunctional cycloaliphatic monomer was responsible for the crosslinking, EBH acted as the source to introduce bromine functional groups on the surface of the network. This bromines groups are suitable for the further surface derivatization reactions.

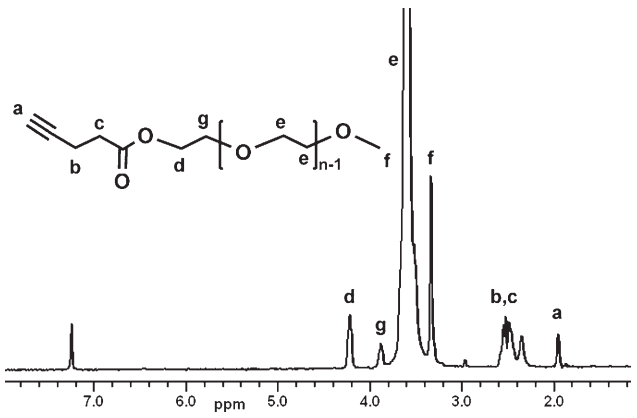


FIGURE 5 ^{1}H NMR spectrum of alkyne functional PEG.

TABLE 2 Advancing Contact Angle With Water for Cured Films Based on EEC Resin With Increasing Content of EBH- and PEG-Modified Films

Samples	Advancing Contact Angle Before Modification (°)	Advancing Contact Angle After Modification (°)
EEC	64	–
EEC/EBH 90:10	72	59
EEC/EBH 80:20	75	63
EEC/EBH 70:30	85	70

Since absorbance of glycidyl and cyclohexane groups are quite close and overlap, epoxy group conversion was followed by monitoring the decrease of the absorbance peak centered at 760–780 cm^{-1} and results are shown in Figure 1 as a function of irradiation time. As can be seen, the polymerization is quite efficient and almost completed after 2 min of irradiation. Also, it is evident that increasing the amount of EBH in the photocurable formulation causes an increase in the epoxy group conversion. This behavior can be attributed to the increased mobility of the reactive species by the retardation of network vitrification arising from the reduction of crosslinking density as the monofunctional monomer content in the formulation increases.

Table 1 shows that all the cured films showed a gel content around 100%, indicating high efficiency of the photopolymerization process and the absence of extractable monomers or oligomers. Moreover, the decreasing of the T_g values of the cured films by increasing the amount of EBH in the photocurable formulations was also noted from the table. The tan δ curves are reported in Figure 2. It is evident from the figure that increasing the amount of EBH in the photocurable formulations results in a significant shift of the maximum of tan δ toward lower temperature range, which is in agreement with the kinetic data previously discussed.

The bromine containing epoxy coatings were used as the starting point for "click" modification by conversion to an azide-functional surface through nucleophilic substitution. The substitution reaction is carried out overnight by exposing the bromine-terminated substrates to a saturated solution of NaN_3 in water (Scheme 2). The sample was then washed several times with distilled water. Azidation of bromine-containing epoxy networks were investigated by using FTIR spectroscopy (Fig. 3). The peak at 2099 cm^{-1} was observed clearly after the azidation processes. Interestingly, the intensity of azide peak in FTIR spectrum did not proportionally increased with increasing bromine content of cured product. This is probably due to the restricted penetration of the reactants in water caused by the increased hydrophobicity with EBH on the surface, which also causes bending of the films (Fig. 4). The thickness of the films can also contribute to the observed bending.



FIGURE 6 Static contact angle of water on the EEC/EBH 80:20 cured film (θ value 75°) and static contact angle of water on EEC/EBH 80:20-*g*-PEG (θ value 63°).

For the subsequent click modification, alkyne-PEG was synthesized by the esterification reaction between 4-pentynoic acid and monohydroxyl functional PEG in CH_2Cl_2 (Scheme 3).

Alkyne end functionality was confirmed by the observation of a signal at 2.06 ppm in the ^{1}H NMR spectrum represented in Figure 5. Moreover, methylene protons of 4-pentynoic acid were observed at 4.23 and 3.89 ppm as an additional evidence for the successful reaction.

Click reaction for the surface modification was performed in water by using sodium ascorbate/$CuSO_4$ system. The solutions of the alkyne-terminated polymers were prepared in water. Then, the azide-terminated substrates were exposed to the polymer solutions for several days in the presence of $CuSO_4{\cdot}5H_2O$ and sodium ascorbate. Water was selected as a solvent for this click reaction because organic solvents such as *N*,*N*-Dimethylformamide (DMF) and THF were spoiling the network surface. At the end of the grafting processes, the intensity of the azide peaks decrease significantly but not completely disappeared. As mentioned above, the azidation reaction is more efficient than the PEG-grafting process due to the mobility of small compound.

A clear evidence for successful grafting process was obtained by the advancing contact angle measurements with water on the cured films at various stages. As can be seen from Table 2, an increase on advancing contact angle was observed by increasing EBH content in the curable formulation. These contact angel values decreased after the grafting PEG on the surface as a result of the increased hydrophilicity. Typical change of contact angle with introducing the PEG onto cured surface is demonstrated in Figure 6.

It should also be noted that the surface-modified films achieved by click reaction showed similar T_g values indicating that this process did not alter the bulk properties of the cured films.

CONCLUSIONS

In summary, we have demonstrated a novel method for the surface modification of photochemically cured epoxy resins. This method pertains to the use of bromomethyl functional epoxide monomer, EBH in cationic UV-curable formulations followed by the azidation through these functions. The subsequent click reaction with hydrophilic PEG possessing antagonist functional group enhances surface hydrophilicity of the crosslinked network. The simplicity and possibility to introduce other functional low molar mass molecules or polymers in a similar manner imply that the present method may find applications in various areas requiring modification of epoxy-based UV coatings.

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