Surface Free Energy Analysis of Poly(HEMA)-Poly(Perfluoroacrylate) Copolymer Networks

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ABSTRACT: Copolymer networks of 2-hydroxyethyl-methacrylate (HEMA) and 2-(*N*-ethyl perfluorooctane sulfonamido)ethyl acrylate (FOSEA) were prepared by free-radical polymerization. Ethylene glycol dimethacrylate (EGDM) was used as crosslinker and 2,2′-azobisisobutyronitrile (AIBN) was used as radical initiator. HEMA/FOSEA ratio of the copolymer networks changed from 50/1 to 10/1 (mol/mol). The contact angles of water, ethylene glycol, glycerin, diiodomethane, paraffin, and formamide were measured on copolymer surfaces and results were evaluated in term of surface free energy components using van Oss–Good methodology. It was determined that the Lifshits–van der Waals component (γ_S^{LW}) and total surface tension (γ_S^{TOT}) of networks decreased drastically with the increase of the FOSEA content. However, the electron donor and acceptor components of the surface free energy did not differ that much. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3343–3347, 2006

**Key words:** FOSEA; perfluoroacrylate polymer; HEMA; surface free energy

INTRODUCTION

Polymers based on hydroxyalkyl methacrylates (usually 2-hydroxyethyl methacrylate, HEMA) and their copolymers have been an attractive material for many applications. Owing to the biocompatibility (physiological inertness) and good film-forming characteristics, HEMA-based copolymers have been used in a variety of biomedical applications, including soft contact lenses,[1] drug delivery systems,[2] tissue implantation,[3,4] and protein absorption.[5–7] Since all of these applications are mainly related to the biological systems, cell adhesion and gas permeability properties are of great importance. For improving these properties, the copolymers of HEMA with various polar or nonpolar monomers and their surface characterization have been studied. It was reported by Walker et al. that the copolymers of HEMA and EMA (ethylmethacrylate) possessed increasing protein absorption capability with increasing hydrophilic EMA content.[7] One of the useful way to improve the gas permeability of polyHEMA (PHEMA) is to prepare its copolymers having bulky pendant groups to increase free volume and to improve surface tension.

Perfluoroalkyl acrylate homopolymers with long side chains have extremely low critical surface tension (γc) ranging from 10 to 11 mN/m,[8–10] high water-contact angle, reduced coefficient of friction, biocompatibility, and hydrophobicity. A copolymer having HEMA and perfluoroacrylate units may exhibit considerable difference in favor of the aforementioned properties and may have an importance in the practical application, such as film forming, adhesive property, and gas permeability. They have considerable low solubility in common organic solvents, which makes the preparation of their copolymers difficult.

2-(*N*-ethylperfluorooctanesulfonamido)ethyl acrylate (FOSEA) is a polar fluorocarbon alkyl acrylate monomer. Although it has hydrophobic perfluoro side chains, it is soluble in polar solvents due to polar sulfonamido groups, and therefore has a broad industrial application as surfactant. Besides, copolymer of the FOSEA with other monomer may have application as coating material with good water and oil repellant properties.[11,12] FOSEA is also soluble in supercritical carbon dioxide ($scCO_2$). This may lead to the homogenous synthesis of poly(FOSEA).[13] Taking into the consideration of these attractive properties, incorporation of perfluorooctane sulfonamido groups FOSEA into PHEMA network is expecting to improve its performance of protein absorption and selective gas and liquid permeability.[14–16] Moreover, an application as fluorinated gels for gel-permeation chromatography was developed.[11,17] All these applications indicate that the role of the surface free energy of fluorinated polymers and their copolymers is important. This study is aimed at the evaluation of the surface free energy of HEMA-FOSEA copolymer networks by using van Os-

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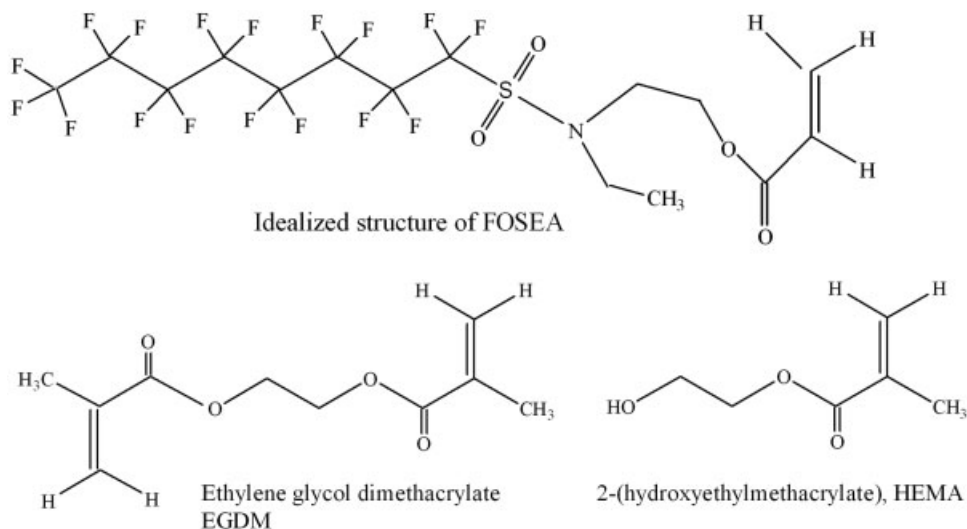
Scheme 1　Chemical formula of the monomers and crosslinker.

s–Good methodology and to follow the change with FOSEA concentration.

EXPERIMENTAL

Materials

The commercially available perfluoroacrylate monomer, FOSEA, is a product of 3M having the trade name of Fluorad FX-13. It was recrystallized from methanol two times before use and dried in dark at room temperature under reduced pressure. White crystals were obtained with melting point of 46°C as determined by using differential scanning calorimetry (DSC) at 10°C/min heating rate. EIMS m/z 626(m$^+$+1), 554(M$^+$-O$_2$CCHCH$_2$), 206(M$^+$-C$_8$F$_{17}$). Other monomer used in copolymerization, HEMA, was supplied from Acros Organics and purified by vacuum distillation. Since HEMA is in equilibrium with ethylene glycol dimethacrylate, EGDM, freshly distilled HEMA was used in copolymerization.[18] The EGDM content of HEMA was determined as 0.34% using gas chromatography and included in copolymerization compositions. The crosslinker, EGDM, was supplied from Aldrich and purified by vacuum distillation. The radical initiator 2,2'-azobisisobutyronitrile (AIBN) was supplied from Aldrich and purified by recrystallization from acetone and dried in dark at room temperature under reduced pressure. Liquid probes, glycerol, ethylene glycol, formamide, diiodomethane, and paraffin oil were used in contact angle measurements. They were supplied from Aldrich and used without further purification. The chemical formula of HEMA, FOSEA, and EGDM are shown in Scheme 1.

Instrumentation

The contact angle measurements were carried out with a Model G-III Contact Angle Meter (Kernco In-strument Co., El Paso, TX). The one-liquid method was applied using polar and nonpolar liquid probes. The EGDM content of freshly distilled HEMA was analyzed using a Fisons model GC8000 series gas chromatography and Fisons model MD800 mass spectrometry. DB5 fused silica column (60 m × 0.25 mm, and with 0.5 μm film thickness) was used with helium at 1 mL/min (0.14 MPa) as carrier gas; GC oven temperature was kept at 40°C for 5 min and programmed to 280°C at heating rate of 5°C/min and kept constant at 280°C for 20 min. The split ratio was adjusted to 1:20, and the injection volume was 0.1 mL. EI/MS of FOSEA was taken at 70 eV ionization energy. Mass range was from m/z 35–450 amu. Scan time 0.5 s with 0.1 interscan delay. The melting point of crystallized FOSEA was determined using a PerkinElmer differential scanning calorimetry (DSC) with Pyris 1 Thermal Analysis System under nitrogen atmosphere at 10°C/min heating rate. DSC system was temperature-calibrated before running.

Preparation of copolymer films

HEMA is a well-known polar monomer and FOSEA has polar sulfonamido groups attached to nonpolar perfluoroacrylate pendant groups. Before use, FOSEA was recrystallized from methanol and mixed well with HEMA. To prepare the copolymer networks, calculated amount of HEMA and FOSEA monomers and the EGDM, as a crosslinker, were mixed in a Payrex reaction tube sealed with a rubber septum. Molar ratios of crosslinker, EGDM, and radical initiator, AIBN, were kept constant in all compositions, as 0.5 and 0.1, respectively, to obtain the same crosslink density. After adding AIBN, the solution was flushed with argon in a sealed tube using gas inlet and outlet needle for 15 min and immediately poured into molds (8 × 8 × 0.3 cm^3). They were kept in the oven at 70°C

TABLE I
Composition of the Copolymers

Copolymer	HEMA/FOSA (mol/mol)	EGDM % (mol/mol)	AIBN % (mol/mol)
Run no. 1	50/1	0.5	0.1
Run no. 2	35/1	0.5	0.1
Run no. 3	20/1	0.5	0.1
Run no. 4	10/1	0.5	0.1

for 4 h. Then, the copolymer films were removed from the molds. The composition of the copolymers is tabulated in Table I.

Contact angle measurements

The surface free energy components of the copolymer networks having various HEMA/FOSEA ratios ranging from 10/1 to 50/1 were determined by measuring the contact angles of various polar and nonpolar liquid drops on the network surfaces. The liquid probes were water, glycerol, ethylene glycol, formamide, diiodomethane, and paraffin oil. Drops of each liquid of 5 μL in size were deposited on the dry surface of the networks with a hypodermic syringe. Contact angles were measured as soon as possible after sessile drops of liquids formed on the surface. Readings on the drop were directly taken using a cathetometer fitted with a ganiometer eyepiece at 20°C. One-liquid method (airdrop, drop-polymer) was used and all measured contact angle values were average of six measurements within ± 2° deviation.

Theory

When a sessile drop is placed on a solid surface, equilibrium is attained between three surface tension under the three phase boundary (i.e., solid, liquid, and vapor). The Young's equation describes the thermodynamic equilibrium of the three surface tensions γ_{SV}, γ_{SL}, and γ_{LV}, existing at the phase boundaries of a drop of liquid at rest on a solid surface,[19]

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL} \tag{1}$$

where, γ is the surface tension (or surface free energy) and the subscripts LV, SV, and SL represent liquid–vapor, solid–vapor, and solid–liquid interfaces, respectively. In this equation, the spreading film pressure of the absorbed vapor (πe) is neglected. The work required to pull the liquid away from the surface leaving the equilibrium absorbed film (i.e., the total work of adhesion on solid surface, W_{SL}^a) is given by following Dupré eq. 20:

$$-\Delta G_{SL}^a = W_{SL}^a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \tag{2}$$

By elimination of γ_{SL} from eqs. (1) and (2), the well-known version of Young-Dupré equation is obtained:

$$-\Delta G_{SL}^a = W_{SL}^a = \gamma_{LV}(1+\cos\theta) \tag{3}$$

Recently, the surface tension theory was developed by van Oss, Good and Chaudhury.[21–23] According to this approach, surface or interfacial tension of macroscopic bodies (solid and liquids) combines two additive components.[21–23]

$$\gamma_{SL} = \gamma_{SL}^{LW} + \gamma_{SL}^{AB} \tag{4}$$

where, γ_{SL}^{LW} is Lifshizt-van der Waals (LW) component comprising polar, dispersion and induction forces; γ_{SL}^{AB} is acid–base interaction component comprising all electron donor–acceptor interactions and hydrogen bonding. When the van Oss–Good theory is applied to the Dupré equation one obtains

$$\Delta G_{SL}^a = (\Delta G_{SL}^a)^{LW} + (\Delta G_{SL}^a)^{AB} \tag{5}$$

According to the van Oss–Good approach and acid–base theory of contact angle[21] the values of $(\Delta G_{SL}^a)^{LW}$ and $(\Delta G_{SL}^a)^{AB}$ are as follows:

$$(\Delta G_{SL}^a)^{LW} = -2(\gamma_S^{LW}\gamma_L^{LW})^{1/2} \tag{6}$$

$$(\Delta G_{SL}^a)^{AB} = -2[(\gamma_S^+\gamma_L^-)^{1/2} + (\gamma_S^-\gamma_L^+)^{1/2}] \tag{7}$$

By combining the eqs. 3, 5, 6, and 7, the following general contact angle equation is obtained.

$$\gamma_{LV}(1+\cos\theta) = 2[(\gamma_S^{LW}\gamma_L^{LW})^{1/2} + (\gamma_S^+\gamma_L^-)^{1/2} + (\gamma_S^-\gamma_L^+)^{1/2}] \tag{8}$$

This equation comprises the Lifshizt–van der Waals and acid–base interaction components of the interaction between a drop of a liquid at equilibrium with a solid surface. In this equation, subscripts L and S refer to liquid and solid respectively. θ is the contact angle of liquid drop on the solid surface, γ_L^{LW} and γ_S^{LW} are the apolar Lifshitz–Van der Waals components of liquid and solid, γ_S^+ and γ_L^+ are the electron acceptor components of surface free energy of solid and liquid, γ_S^- and γ_L^- are the electron donor components of the surface free energy of solid and liquid, respectively.

For an apolar liquid, naturally $\gamma_L^+ = \gamma_L^- = 0$ and $\gamma_L^{LW} = \gamma_L$, hence the last two terms of the right-hand side of the eq. 8 become zero, and therefore, this equation becomes

$$\gamma_L(1+\cos\theta) = -2(\gamma_S^{LW}\gamma_L^{LW})^{1/2} \tag{9}$$

By using the eq. (9) and the data obtained from contact angle measurements for an apolar liquid, γ_S^{LW} of the

TABLE II
Contact Angles Measured with Liquid Probes on Copolymer Network

Liquid probe	HEMA/FOSEA				
	Poly(HEMA)[a]	50/1 (run no : 1)	35/1 (run no : 2)	20/1 (run no : 3)	10/1 (run no : 4)
Water	–	95	102	118	122
Glycerol	–	76	91	108	112
Ethylene glycol	63.7	48	66	88	99
Formamide	39.9	51	66	89	93
Diiodomethane	39.9	60	71	94	106
Paraffin oil	–	45	54	74	86

[a] The contact angle values of PHEMA were obtained from Ref. 28.

solid can be calculated. This calculation was made for two apolar liquids and the values were averaged for single value.

The remaining electron donor and acceptor components of the surface free energy of the solid (γ_S^+ and γ_S^-) can be calculated by simultaneously solving the two different forms of eq. (8). These forms are obtained for three different polar liquid pairs (i.e., water–ethylene glycol, water-formamide, and water–glycerol) with known γ_L^{LW}, γ_L^+, and γ_L^- parameters. The calculated values of γ_L^+ and γ_L^- for each polar liquid pairs are averaged for a single value.[24–27]

RESULTS AND DISCUSSION

Contact angle measurements represent a practical and easy technique to characterize polymer surfaces. In this technique, the liquid probes interact only with the outermost atomic layer of the surface. Therefore, it has been used successfully in determination of the orientation and enrichment of any component on the polymer surface, which strongly depends on the environmental condition.

The surface energy components of the liquids used in the evaluation of the contact angle data of the copolymer samples were obtained from van Oss et al.[22] and are given in Table II. The contact angle values of these liquid probes (water, glycerol, ethylene glycol, formamide, diiodomethane, and paraffin oil) on the surface of the copolymer samples are collected in Table III. They were evaluated using van Oss–Good

TABLE III
Surface Free Energy Component Values of the Liquids Used mJ m^{-2}.[22]

Liquid	γ_L	γ_L^{LW}	γ_L^{AB}	γ_L^+	γ_L^-
Water	72.8	21.8	51.0	25.5	25.5
Glycerol	64.0	34.0	30.0	3.92	57.4
Ethylene Glycol	48.0	29.0	19.0	1.92	47.0
Formamide	58.0	39.0	19.0	2.28	39.6
Diiodomethane	50.8	50.8	0	0	0
Paraffin Oil	28.9	28.9	0	0	0

methodology and the surface free energy components of the copolymer samples are collected in Table IV.

The LW component of the surface free energy of the networks were calculated by incorporating the surface free energy components of apolar paraffin oil and diiodidomethane into eq. (9) and their contact angle data. The values of the LW surface energy components are presented in Table IV. The LW values of the copolymer samples decreased with the increase of the FOSEA content. This is due to the increase of the perfluoro groups in the copolymer composition. γ_S^{LW} component of the surface free energy of PHEMA was 39.7 mJ/m^2, while this was found as 24.8mJ/m^2 for the copolymer sample at the composition of 50/1 HEMA/FOSEA ratio (run no 1). It was reported that the increasing in the length of the perfluoro side groups leads to an increase in the γ_S^{LW} component of the surface free energy,[29,30] where the γ_S^{LW} component of the perfluorinated copolymer samples were found between 5.0 mJ/m^2 and 23.0 mJ/m^2. The γ_S^{LW} values in Table IV are consistent with the results.

γ_S^- and γ_S^+ values were calculated using general contact-angle equation (Equation 8). This calculation was made by individually solving of three equation sets with respect to three different polar liquid pairs (i.e., water–glycerol, water–ethylene glycol, and water–formamide). In this calculation, the apolar γ_S^{LW} values of the solid surface, which was previously calculated with nonpolar liquids, were used in Equation 8. The calculated γ_S^- and γ_S^+ values for the three sets were averaged and listed in Table IV. For each run, the γ_S^+ value was found to be greater than the γ_S^- value. That means all copolymer samples have acidic character (electron acceptor) rather than basic character. However, the change in γ_S^- and γ_S^+ values of the copolymers with increasing FOSEA content is insignificant. In spite of the PHEMA surface has mainly basic character, due to the oxygen atoms of carbonyl and hydroxyethyl groups (Table IV), the surfaces of all copolymer samples are acidic in varying degrees. These results are reasonable due to the enhancement of the long and nonpolar perfluoro groups on the surface in nonpolar environment while polar and ba-

TABLE IV
Surface Free Energy Components of PHEMA and Copolymers at Various HEMA/FOSEA (mJ/m²)

Run no	HEMA/FOSA (mol/mol)	γ_S^{LW} averg. (mJ/m²)	γ_S^- (mJ/m²)	γ_s^+ (mJ/m²)	γ_S^{AB} (mJ/m²)	γ_S^{TOT} (mJ/m²)
	PHEMA[a]	39.7	31.2	-	16.2	55.9
1	50/1	24.8	0.4	4.3	2.6	25.2
2	35/1	20.0	0.6	2.3	2.4	20.6
3	20/1	11.4	0.1	1.1	0.7	12.1
4	10/1	4.5	0.4	1.5	1.6	9.1

[a] The data for PHEMA were taken from Ref. 28.

sic sulfonamido groups of FOSEA and hydroxyl groups of HEMA oriented toward the bulk from the surface. This phenomenon also brings about to decrease in the γ_S^{AB} values of all copolymers than the values of PHEMA.

The total surface tension, γ_S^{TOT}, of all copolymers decreased drastically with the increase of the FOSEA content, which ranged from 25.2 to 9.1 mJ/m² while the value of PHEMA is 55.9 mJ/m². This result shows that a small amount of FOSEA in the copolymer composition causes a sudden decrease in total surface free energy of the PHEMA.

CONCLUSIONS

One-liquid contact angle results were evaluated by using van Oss–Good methodology. It was observed that small amount of FOSEA inclusion of the copolymer networks caused to a drastic decrease in apolar γ_S^{LW} and γ_S^{AB} values. Owing to the surface enrichment of the perfluoro groups of the FOSEA, the total surface free energy values of the copolymers, γ_S^{TOT}, and its apolar LW components, γ_S^{LW}, decreased with the increase of the FOSEA. However, the polar acidity surface tension coefficient γ_S^+ and the basicity surface tension coefficient γ_S^- did not change that much with the increase of the FOSEA content.

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