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ORIGINAL CONTRIBUTION

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Effect of surface polarity on wettability and friction coefficient of silicone rubber/poly (acrylic acid) hydrogel composite

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Abstract Water absorption, surface energetic, and friction coefficient of filled silicone rubber composites containing different amounts of a superadsorbent hydrogel, poly(acrylic acid) (PAA), were investigated. Measurements were performed in two different time windows, 1 and 5 weeks, to study the effect of hydration time on surface polarity of the samples. It was shown that water absorption increased consistently with hydrogel content and that prolongation of hydration time led to a marked increase in surface tension and polarity. Friction, as measured by a solid–solid contact method in phosphate buffer saline, showed strong dependence on polarity of the composite surface. Results demonstrate that the surface of the composite continued to evolve after the bulk had reached equilibrium swelling and the surface tension reached that of PAA after 5 weeks of hydration time.

Keywords Silicone rubber · Hydrogel · Poly(acrylic acid) · Composite · Surface polarity · Friction coefficient

Introduction

Silicone rubber has found widespread applications in plastic and reconstructive surgery [1], as well as in the fabrication of medical devices as balloon catheters, cartilage replacements, vascular grafts, and tubing for feeding and drainage [2, 3]. The relatively strong silicon–oxygen bond in the structure of the silicone rubber imparts chemical stability to the elastomer in a physiological environment, high tear and tensile strength, good elongation and flexibility, and excellent compression set [4]. The surface and bulk properties of silicone rubber can be tailored to fit a particular application by blending [5] or chemical grafting [6]. Surface properties such as contact angle, surface tension, and friction coefficient affect protein adsorption and cell attachment to the surface of silicone rubber [7]. Previous studies report qualitatively that differences in surface wettability lead to different types of foreign body reaction [8] and that protein adsorption is directly related to the types of functional groups present on the surface [9]. However, recent works have emphasized the quantitative relationship between biomaterials' surface energy and foreign body reaction [10].

Hydrogels are three-dimensional crosslinked polymeric structures which are able to swell in aqueous physiological solution and retain a significant fraction of water in their structure without dissolving [11–13]. Structure of hydrogels can be engineered to absorb a given amount of water, providing these materials with excellent biocompatibility [14] and low friction coefficient while they can interact less strongly with immobilized biomolecules than hydrophobic materials [15]. For example, hydrogels absorb very small volumes of fibronectin compared to hydrophobic polymers like silicone rubber [16], and poly(acrylic acid) (PAA)/gelatin interpenetrating polymer networks show reduced foreign body reaction in animal studies [17–19]. This can be explained not only by protein adsorption, which initiates the foreign body reaction, but also by unfolding of the protein on the biomaterial surface. Recent studies have demonstrated that protein adsorption on hydrophobic surfaces, like silicone rubber, is followed by protein unfolding and changes in secondary and tertiary structures

to expose the hydrophobic domains of the protein to the surface [20, 21]. For hydrophilic surfaces, like hydrogels with high water content, the structure of the biomaterial surface resembles that of soft tissues; consequently, the extent of protein unfolding is less on hydrophilic surfaces compared to hydrophobic surfaces. Therefore, the type of foreign body reaction is related to protein unfolding and changes in secondary and tertiary structures of the adsorbed protein, which is related to the surface tension, water content, and hydrophilicity of the composite surface [3]. Hydrogels, due to their high water content, can potentially reduce unfolding of the adsorbed protein on the surface and, as a result, reduce the foreign body reaction.

Composites of silicone rubber and hydrogels can reduce protein adsorption and friction coefficient while retaining the tear and tensile strength of the silicone rubber [22–30]. Poly 2-hydroxyethylmethacrylate and poly-acrylamide hydrogels have moderate swelling characteristics and interact with surfaces by hydrophobic (van der Waals forces) and polar (dipole forces) interactions. On the other hand, superabsorbent hydrogels such as PAA interact with surfaces by acid–base interactions in addition to hydrophobic and polar interactions [12, 13]. Proteins can interact with the surface of biomaterials by hydrophobic, polar, and acid–base interactions. The objective of this work was to determine the effect of polar and acid–base interactions on swelling characteristics, wettability, and solid–solid friction coefficient of silicone rubber composites with PAA hydrogel as the particulate phase. The pKa of PAA is between 4.5 and 5.0, and PAA hydrogels swell significantly at the physiological pH of 7.4 due to ionization of the anionic carboxylic acid groups.

Experimental

Room-temperature vulcanizable (RTV) silicone rubber was obtained from Rhone Poulenc (Cedex, France). The monomer, acrylic acid (AA); the cross-linking agent, ethylene glycol dimethacrylate (EGDMA); the initiator, ammonium persulfate (APS); and the accelerator, sodium bisulfide (SBS), were obtained from Aldrich Chemicals (Milwaukee, WI, USA). AA monomer was distilled under a reduced pressure of 5 mmHg at 30 °C to remove the inhibitor, hydroquinone monomethyl ether. All other reagents were used as received without further purification.

The following procedure was used for the synthesis of AA hydrogel. In a scintillation vial, 7 g of distilled deionized (DDI) water was mixed with 7.4 g of AA (0.1 mol) and varying amounts of EGDMA ranging from 0.01 to 0.05 g, corresponding to 0.05–0.025 mmol, using a vortex mixer. In two separate vials, 0.016 g of APS (0.07 mmol) and 0.008 g of SBS (0.046 mmol) were mixed with 1 ml of DDI water. The three solutions were purged with nitrogen gas to remove dissolved oxygen. Next, the APS solution was added to the polymerizing mixture followed by the addition of SBS. The polymerizing mixture was transferred to a Petri dish, covered with plastic wrap to exclude oxygen, and placed in the oven at 50 °C to react. The crosslinking reaction was allowed to proceed for 1 h followed by postcuring for 12 h at 30 °C. The water content of the hydrogel in the polymerizing mixture was 55% by weight. The molar ratio of AA to APS was 1,500. The molar ratio of AA to EGDMA ranged from 3,500 to 350, corresponding to 0.01–0.08% by weight EGDMA in the solution. After the reaction, the hydrogel was washed twice with DDI water to remove unreacted compounds. The thickness of the hydrogel film before swelling was 1 mm.

For swelling studies, circular disks with a diameter of 20 mm were cut from the hydrogel films using a cork-borer and placed in at least 100 ml of phosphate buffer solution (PBS) with a pH of 7.4. To prepare the PBS buffer, 0.02 g of potassium hydrogen phosphate was mixed with 0.0115 g of disodium hydrogen phosphate, 0.02 g of potassium chloride, and 0.8 g of sodium chloride in 90 ml of DDI water. The pH was adjusted by adding 1 M sodium hydroxide solution dropwise and the final volume was adjusted to 100 ml. The swelling ratio, defined as the difference between the weight of the swollen sample and the dry weight divided by the dry weight, was determined as a function of time. To measure the dry weight, the sample was dried in a vacuum (10 mmHg) at 50 °C for 12 h. At least four samples were used for each measurement and the mean was reported.

The following procedure was used to prepare the silicone rubber/PAA hydrogel composites. The PAA film was dried in vacuum at 30 °C to a water content of 10% w/w, crushed with a mortar and pestle, ball milled, and passed through a 200 mesh sieve twice. The particle size of the dried hydrogel powder was less than 75 μm with an average of 50 μm, as measured with a light microscope. Next, different amounts of the PAA powder, ranging from 5 to 40% w/w, was added to RTV silicone and homogenized with a vortex mixer for 5 min, followed by the addition of the crosslinking agent in the amount of 5% based on the weight of the RTV silicone. The mixture was poured into 8×8-mm, Teflon-coated aluminum molds and allowed to crosslink for 24 h at 30 °C in an oven. The thickness of this mold was 1 mm. The distribution of the dried hydrogel particles in the silicone matrix was uniform, as observed with a light microscope (see Fig. 2).

The contact angle and surface tension of the composite samples were measured using a Kruss 40 (Hamburg, Germany) analyzer. A drop of DDI water with a volume of 10 μl was placed on the composite surface using a microsyringe, and the contact angle was measured after 5 min to allow equilibration of the drop on the surface.

The friction coefficient of the composite hydrogel on a glass surface was measured using a Daven Test Limited (Fairfield, NJ, USA) friction measuring apparatus. An 8×8-cm composite sample swollen to equilibrium in PBS

buffer was placed on a clean glass plate. The glass plate was degreased in a nitric acid/water mixture and dried at ambient conditions. A 100-g weight was placed on the composite surface and the sample was pulled at a constant speed of 10 mm/min. The initial force to pull the sample on the glass plate was measured by the apparatus and the static friction coefficient was calculated from this initial force. The steady force to pull the sample at a constant velocity was also measured to determine the dynamic friction coefficient. All samples were swollen in PBS before measurement.

Results

Figure 1 shows the change in water content of the composite in PBS with 40% by weight PAA (hydrogel was crosslinked with 0.035 w/w EGDMA crosslinker). In general, composite samples reached equilibrium in 5–6 days. It was assumed that samples reached equilibrium when there was less than 2% change in water content with swelling time. Therefore, the changes in surface polarity observed between 1 and 5 weeks of hydration time were due to the dynamics of the composite surface while the bulk of the sample had reached equilibrium water content. The micrograph in Fig. 2 shows a cross-sectional view of the composite surface, hydrated in PBS, with 30% w/w PAA content. This micrograph indicates that the PAA particles had nearly rounded morphology and dispersed homogeneously in a continuous rubber matrix.

The equilibrium swelling ratio of the PAA hydrogel as a function of the concentration of crosslinking agent, EGDMA, is shown in Fig. 3. According to this figure, as the amount of EGDMA was increased from 0.01 to 0.07% w/w, the equilibrium swelling ratio decreased exponentially. This decrease was due to the increase in network density as the concentration of crosslinker was increased, resulting in a decrease in water absorption capacity of the hydrogel. Other factors, such as the pH of the swelling medium, can enhance or suppress the water absorption of the hydrogel. Swelling behavior of the composites was also studied in PBS and a linear relationship was obtained between the composite water content and hydrogel content, as shown in Fig. 4. The hydrophobic silicone rubber seemed to suppress the swelling behavior of the composite, leading to water contents significantly less than that of the PAA hydrogel.

The equilibrium swelling of the PAA hydrogel, in the absence of the silicone rubber matrix, was much greater than the extent of swelling in the composite. For example, the equilibrium swelling ratio of PAA with 0.035 w/w EGDMA was 16.5, corresponding to a water content of 94% by weight. The equilibrium swelling of PAA/rubber composite with the highest PAA fraction of 40% by weight (crosslinked with the same concentration of EGDMA) was 61% (excluding the weight of the rubber matrix). This demonstrates that the swelling capacity of the PAA in the rubber matrix was restricted by the elastic retraction force of the rubber. On the other hand, unrestricted swelling of PAA on the surface of the composite with hydration time

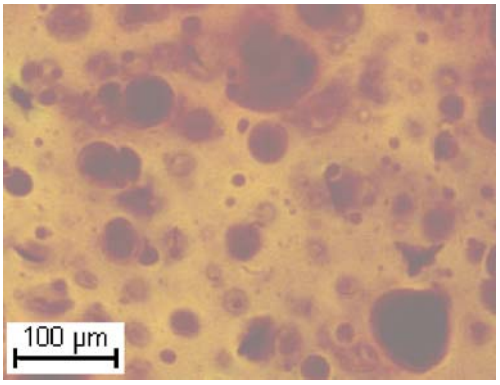

Fig. 2 Light micrograph of the surface of a silicone rubber/hydrogel composite. PAA fraction in the composite was 30% w/w

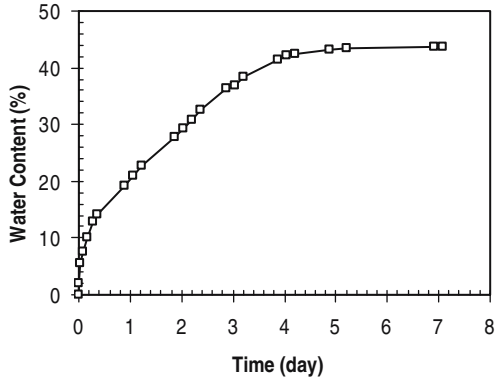

Fig. 1 Swelling kinetics of the silicone rubber/hydrogel composite in PBS solution at 25 °C with 40% w/w PAA content. PAA hydrogel was prepared with 0.035 w/w EGDMA crosslinker

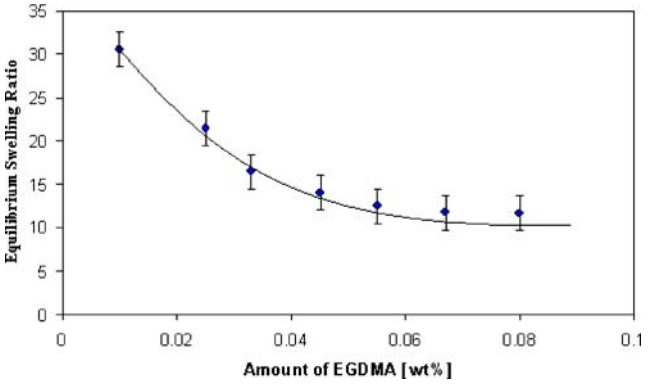

Fig. 3 Equilibrium swelling ratio of PAA in PBS solution at 25 °C as a function of the amount of EGDMA crosslinking agent. The *error bars* are ±1 standard deviation from the mean value of four samples

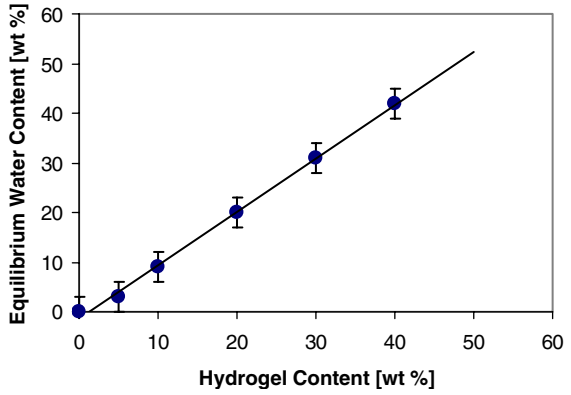

Fig. 4 Equilibrium water content of the silicon rubber/hydrogel composite in PBS solution at 25 °C as a function of the PAA content. PAA hydrogels were prepared with 0.035 w/w EGDMA crosslinker. The *error bars* are ±1 standard deviation from the mean value of four samples

(from 61% water content to as much as 94%) dominated the surface properties of the composite.

Figure 5 shows the change in contact angle of DDI water on the composite surface with hydrogel content after 1 and 5 weeks in PBS. After 1 week, the contact angle did not change significantly with PAA content. After 5 weeks, a sharp drop in contact angle from 98 to 50° was observed when the hydrogel content was increased from 0 to 5%. As the hydrogel content was increased from 5 to 40%, the contact angle decreased from 50 to 41°, respectively. Hydrogel contents of greater than 5% did not seem to significantly change the contact angle of the composites. This implied that the existence of a hydrophilic phase in the bulk did not affect the surface behavior to the same extent. This is reflected in Fig. 6, where changes in surface tension of the composite surface with hydrogel content after 1 and 5 weeks of hydration in PBS are compared. The surface tension increased abruptly with the addition of only 5% PAA and reached a plateau of 65 mN/m for 20, 30, and 40% hydrogel contents.

Dynamic contact angle measurements are important for conditions where the surface is in contact with a flowing liquid and the measurements are typically carried out by moving a rectangular shaped sample against the liquid droplet and converting the force into a contact angle. A trend similar to static measurements is observed in dynamic results as shown in Fig. 7 where a decrease is observed for both advancing and receding contact angles.

Figure 8 shows the effect of hydrogel content on the friction coefficient of the composite in contact with a glass surface. The static friction coefficient was higher than the dynamic coefficient. A peak in friction coefficient was observed for both static and dynamic coefficients at 10% hydrogel content. The addition of hydrogel led to an increase in the polar component of the surface free energy of the composite. Because the glass surface had polar hydroxyl groups, the addition of hydrogel increased polar hydrophilic interactions between the composite and glass surfaces, which, in turn, increased the friction coefficient. As the hydrogel content was increased further to 20, 30, and 40%, the viscosity of the fluid film trapped between the composite and glass surfaces decreased significantly, which caused a decrease in friction coefficient. In other words, at low hydrogel contents, the polarity of the surface overcame the effect of medium viscosity, whereas the inverse effect was observed at higher hydrogel contents. These and other results, on mobilization of surface groups in nanocomposite hydrogels [28], demonstrate that the medium plays a critical role in determining the frictional behavior of the composite surface.

Figure 9 shows the effect of EGDMA concentration on friction coefficient of the composite and glass surfaces. The static friction coefficient did not change significantly as EGDMA was increased. However, a slight increase in the dynamic friction coefficient was observed around 0.05% EGDMA. This observation can be attributed to the increase

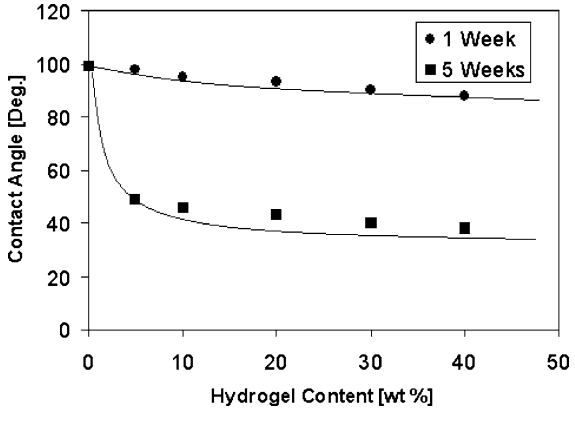

Fig. 5 Variations in contact angle of the composites after 1 and 5 weeks of hydration in contact with PBS solution at 25 °C. PAA hydrogels were prepared with 0.035 w/w EGDMA crosslinker

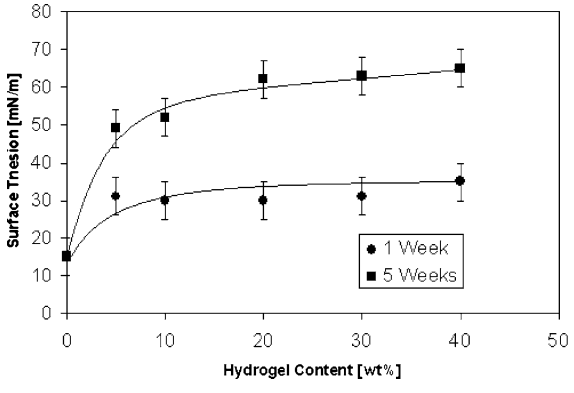

Fig. 6 Variations in surface tension of the composites after 1 and 5 weeks of hydration in contact with PBS solution 25 °C. PAA hydrogels were prepared with 0.035 w/w EGDMA crosslinker. The *error bars* are ±1 standard deviation from the mean value of four samples

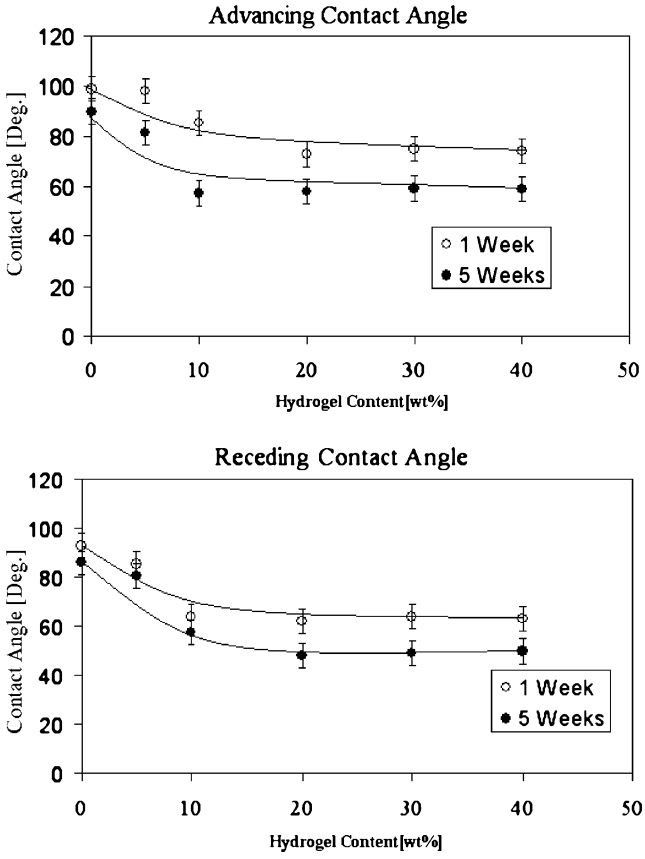

Fig. 7 Advancing and receding contact angles of the composites as a function of hydrogel content in contact with PBS solution 25 °C. PAA hydrogels were prepared with 0.035 w/w EGDMA crosslinker. The *error bars* are ±1 standard deviation from the mean value of four samples

in viscosity of the fluid film trapped between the composite and glass surfaces with increasing amounts of EGDMA. At higher amounts of EGDMA, corresponding to higher network densities, less water was squeezed out of the composite during the friction test, leading to higher dynamic friction coefficients.

Discussion

Composite materials based on silicone rubber and hydrogels are intended to combine the good tensile strength of silicone rubber with hydrophilicity and water permeability of hydrogels. Silicone rubbers have a tensile strength of 1–10 MPa [24], while PAA hydrogels have a tensile strength of 0.1–1 MPa [31]. Lopour and collaborators have studied the effect of the addition of hydrogel to the mechanical properties of silicone rubber/hydrogel composites [32]. When 25% by weight-crosslinked acrylamide hydrogel was added to silicone rubber and mechanical properties were measured in the wet state, tensile strength decreased from 3.1 to 1.1 MPa, breaking elongation increased from 220 to 320%, hardness reduced from 58 to 25 shore A, and resilience increased from 19 to 38%. Our results indicate that PAA hydrogel content of 5% by weight was sufficient to make the surface of the composite hydrophilic. Furthermore, comparison of Figs. 3 and 4 indicates that the swelling of PAA particles in the rubber matrix was restricted by the tensile strength of the rubber matrix (60% water content in the composite compared to 94% in free swelling). Therefore, it can be assumed that, in composites with 5% PAA content, the tensile mechanical strength of the composite is controlled by the silicone rubber phase.

Assuming that the chemical structure of the surface dominates over surface topology [33], the surface tension of the solid can be divided into dispersive (γ^d) and polar (γ^p) components, as suggested by Fowkes [34, 35].

$$\gamma = \gamma^d + \gamma^p \tag{1}$$

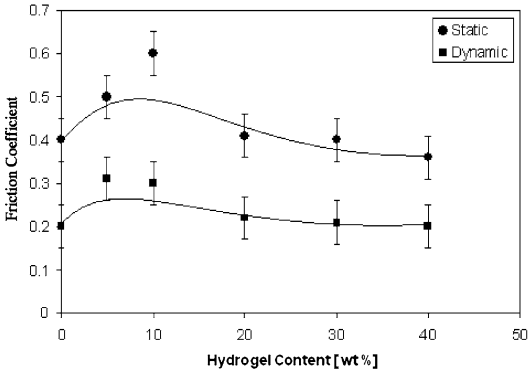

Fig. 8 Static and dynamic friction coefficients of the composites as a function of hydrogel content in contact with PBS solution at 25 °C. PAA hydrogels were prepared with 0.035 w/w EGDMA crosslinker. The *error bars* are ±1 standard deviation from the mean value of four samples

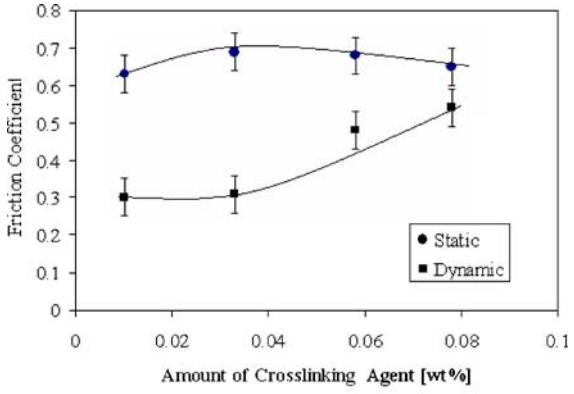

Fig. 9 Effect of EGDMA crosslinker concentration on the friction coefficient of the composites in contact with PBS solution at 25 °C. The hydrogel content of the composites was 10% w/w. The *error bars* are ±1 standard deviation from the mean value of four samples

Neglecting vapor adsorption on the surface, using the geometric mean for calculation of the total surface tension, and assuming the test liquid to be completely dispersive leads to the following form for the Young's equation:

$$(1+\cos\theta)\gamma_L = 2\sqrt{\gamma_S^d \gamma_L} \tag{2}$$

Where θ is the contact angle of a nonpolar test liquid on a polar surface, γ_L is the test liquid surface tension, and γ_S^d is the dispersive component of the surface tension of the solid surface. Knowing the surface tension of the test liquid and obtaining θ from measurement, the dispersive component of the solid surface tension, γ_S^d, can be obtained from Eq. 2. γ_S^p is then calculated using Eq. 1.

Hydrogels like PAA have acid–base interactions with test liquids as well as dispersive and polar interactions [36]. For systems with acid–base or electron donor/acceptor interactions, the solid surface tension is divided into a Lifshitz–van der Walls component, γ^{LW}, representing the dipole–dipole interactions, and an acid/base component, γ^{AB}, representing the electron acceptor/donor effect. Hence:

$$\gamma_L = \gamma_L^{LW} + \gamma_L^{AB} \tag{3}$$

Where:

$$\gamma_L^{AB} = 2\sqrt{\gamma_L^{(+)}\gamma_L^{(-)}} \tag{4}$$

For the case of contact between a test liquid and a solid surface, the Young's equation can be written as:

$$(1+\cos\theta)\gamma_L = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{(+)}\gamma_L^{(-)}} + \sqrt{\gamma_S^{(-)}\gamma_L^{(+)}} \tag{5}$$

In this equation, the two unknowns $\gamma_S^{(+)}$ and $\gamma_S^{(-)}$ can be determined if two test liquids with known acidic and basic components are used for contact angle measurements. We chose water and formaldehyde in this study. The values for γ^{LW}, $\gamma_S^{(+)}$, and $\gamma_S^{(-)}$ for water and formaldehyde are given in Table 1.

Table 1 Acidic (electron acceptor) and basic (electron donor) components of the surface tension of the test liquids used in Eq. 5

Liquid	γ^{LW}	$\gamma^{(+)}$	$\gamma^{(-)}$
Water	21.8	25.5	25.5
Formaldehyde	30	3.92	57.4

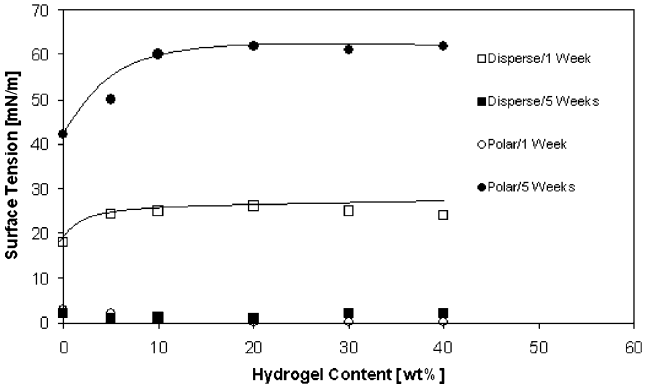

Fig. 10 Dispersive and polar components of the surface tension of the composites after 1 and 5 weeks of hydration as a function of hydrogel content in contact with PBS solution at 25 °C. PAA hydrogels were prepared with 0.035 w/w EGDMA crosslinker

The changes in the dispersive and polar components of the composite surface tension with hydrogel content, calculated by Eqs. (1 and 2), are shown in Fig. 10. There is a noticeable rise in the polar component of the surface tension after 5 weeks of hydration, compared to 1 week. This suggests that the surface tension of the composite surface is a time-dependent process and the polar groups of PAA tend to rearrange on the solid surface if sufficient time is given to react to the changes in the medium. Figure 11 shows changes in the acidic and basic components of the surface tension of the solid surface, calculated using Eqs. (3, 4 and 5), with hydrogel content. The acidic and basic components are significantly less than the polar components of the surface. Furthermore, according to Fig. 11, the basic component of the surface tension was greater than the acidic component. The acid–base component of the surface tension was smaller after 5 weeks of hydration compared to 1 week. These results demonstrate that the polar component of the surface tension of silicone

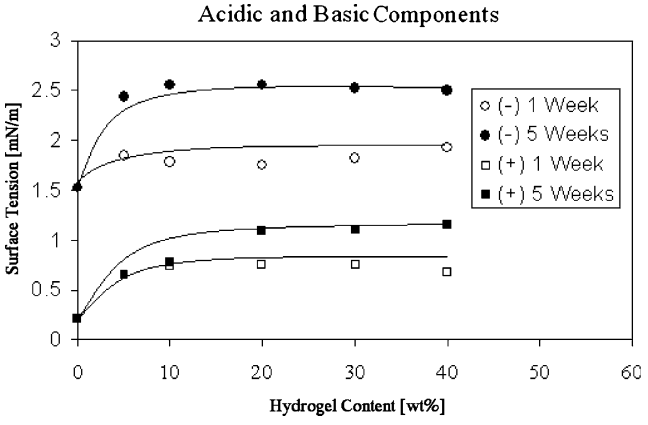

Fig. 11 Acidic and basic components of the surface tension of the composites after 1 and 5 weeks of hydration as a function of hydrogel content in contact with PBS solution at 25 °C. PAA hydrogels were prepared with 0.035 w/w EGDMA crosslinker

rubber/PAA composite is significantly higher than the acid–base component in phosphate buffer saline. The friction coefficient of the composite surface showed better correlation with the polar component compared to the acid–base component.

As shown in Fig. 1, the samples reached bulk equilibrium swelling in 5–6 days but the composite surface continued to show changes in contact angle and surface tension after 5 weeks. The contact angle and surface tension data in Figs. 5 and 6 demonstrate that the surface energy of the composite changed from hydrophobic (contact angle of 90–100°) to hydrophilic after 5 weeks (contact angle of 40–50°). The swelling force of PAA in the bulk of the composite was counterbalanced by the elastic force of the silicone rubber matrix. Therefore, in the bulk, PAA swelled until the swelling force became equal to the elastic force exerted by the silicone rubber matrix. On the sample surface, PAA was free to swell in the direction perpendicular to the surface and was not limited by the matrix stiffness. Therefore, PAA continued to swell and rearrange on the surface and eventually dominated the surface properties of the composite. This is illustrated in Fig. 6, in which the surface tension after 5 weeks approaches the value of 60 mN/m, the value reported for PAA hydrogel [37]. Results demonstrate that the surface of the composite continued to evolve after the bulk had reached equilibrium swelling, and the surface energy reached that of PAA after 5 weeks.

Conclusions

The effect of the addition of PAA hydrogel to silicone rubber on surface properties of the composite depended on hydration time. The equilibrium water content of the PAA hydrogel decreased with increasing density of crosslinks. The addition of higher amounts of hydrogel to the composite led to an increase in water content, a decrease in contact angle, and an increase in surface tension. Hydration time of 5 weeks significantly increased surface tension, as compared to 1 week. The dispersive and polar components of the surface tension were calculated from the experimental data, which demonstrated that the polarity of the solid surface increased with the addition of PAA hydrogel. The observed increase in the friction of the composite surface with the addition of hydrogel can be explained by the changes in surface polarity, but this hypothesis requires further experiments on similar rubber/hydrogel composite systems.

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