Effect of Different Reactive Diluents on PDMS-PEG Hydrogels Properties

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Abstract. Polymethylsilsloxane (PDMS) is commonly used biomaterials for tissue engineering due to inert and nontoxic properties. However, there is the main drawback of PDMS which it is hydrophobic in nature. To overcome this limitation, PDMS was crosslinked with polyethylene glycol (PEG) in order to enhance it hydrophilic property. In this study, the effect of allyl methacrylate (AMA) and PDMS-MA 1K as reactive diluents in the hydrogel fabrication was investigated. Firstly, PDMS-SiH and PDMS-MA that was synthesized and had been confirmed with Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). While for UV-crosslinked hydrogel, contact angle and swelling study were conducted. From the analysis, it was found that increasing in reactive diluents content increased the swelling with insignificant trend for contact angle result. Importantly, from this work the biocompatibility of produced PDMS-based hydrogel was enhanced with the addition of reactive diluents.

1. Introduction
PDMS is an inorganic polymer which is biocompatible, low glass transition temperature, hydrophobic, exhibits excellent gas permeability, and exceptional elasticity when lightly crosslinked. The stability, lack of toxicity, and excellent biocompatibility of PDMS make these materials well suited for use in personal care, pharmaceutical, and medical device applications. (Ratner et al, 2004). Other than that, it is chemically inert, thermally stable, simple to handle and manipulate, exhibits isotropic and homogeneous properties as well as lower cost than silicon (McDonald and Whitesides, 2002). PDMS also shows some drawbacks. One the main drawbacks for cell biology is that PDMS can absorb small hydrophobic molecules like biomolecules and drugs from the solution. Also, many researchers noticed adsorption of proteins on the PDMS surface which has been identified as a major problem for molecular biology. PDMS’s hydrophobicity also has been a noted stumbling block. Although the surface can be made hydrophilic, this is not a natural act for the polymer, and it will revert back to its hydrophobic self in air. The relapse can be a major problem because unwanted phenomena such as adsorption of proteins to the surface start to happen (Guilhem et al, 2010). To overcome this problem, numbers of PDMS treatments have been developed depending on the application. Hence, in this project, PDMS will be blend with other hydrophilic polymer which is PEGDA to overcome its drawback.

Poly(ethylene glycol) diacrylate (PEG-DA) based hydrogels have been extensively utilized as scaffolds for the regeneration of tissues including bone, cartilage, nerve, and vascular tissue. PEG
hydrogels are particularly useful for biomaterial study because of their intrinsic resistance to protein absorption and cell adhesion. PEG chains of any length can be easily synthesized by the controlled polymerization of ethylene oxide or ethylene glycol in aqueous solution. PEG is highly biocompatible and well-suited for use in hydrogels for biological studies. PEG is also non-immunogenic and resistant to protein adsorption, making it suitable for in vivo as well as in vitro studies. In this project, the chemical and physical properties of polydimethylsiloxane (PDMS-MA) hydrogel were tuned by the introduction of PEG-DA. The effect of AMA and PDMS-MAS 1K as reactive diluents on the chemical properties of the PDMS-PEG hydrogels was also evaluated. In addition, the effect of hydrogel composition on physical properties, including, equilibrium swelling, contact angle and biocompatibility was examined.

2. Experimental study

Octamethylcyclotetrasiloxane (98%, Aldrich), 1,1,3,3-Tetramethyldisiloxane (97%, Aldrich), Trifluoromethanesulfonic acid (Aldrich), Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karstedt’s catalyst, 2 wt % in xylene, Aldrich), Poly(ethylene glycol) diacrylate (average Mn 700, Aldrich), photoinitiator 2,2-dimethyl-2-phenylacetophenone (Aldrich), Anhydrous magnesium sulphate (Aldrich), Toluene for analysis (EMSURE® ACS) and Allyl Methacrylate were purchased and used as received. The hydrogels were prepared by photo-polymerization of aqueous mixtures of PEGDA and PDMS-MA solutions. Different composition of PDMS-MA 12k, PEG and reactive diluent were mixed according to the parameters in Table 1 and 2.

Table 1: PDMS with allyl methacrylate (AMA) as reactive diluent (A) with PEG-DA phase

| Item          | Weight ratio (wt%) |
|--------------|--------------------|
|              | PDMS-MA | PEG-DA | AMA |
| PDMS/0A/0PEG | 100      | 0      | 0   |
| PDMS/7.5A/0PEG | 92.5    | 0      | 7.5 |
| PDMS/7.5A/2.5PEG | 90.2   | 2.3    | 7.5 |
| PDMS/7.5A/5.0PEG | 87.9    | 4.6    | 7.5 |
| PDMS/7.5A/10.0PEG | 83.3   | 9.3    | 7.5 |
| PDMS/15.0A/0PEG | 85.0    | 0      | 15.0 |
| PDMS/15.0A/2.5PEG | 82.9   | 2.1    | 15.0 |
| PDMS/15.0A/5.0PEG | 80.8   | 4.3    | 15.0 |
| PDMS/15.0A/10.0PEG | 76.5   | 8.5    | 15.0 |

Table 2: PDMS with PDMS-MA (1K) as reactive diluent (B) with PEG-DA phase

| Item          | Weight ratio (wt%) |
|--------------|--------------------|
|              | PDMS-MA | PEG-DA | PDMS-MA (1K) |
| PDMS/0B/0PEG | 100      | 0      | 0   |
| PDMS/25.0B/0PEG | 75.0   | 0      | 25.0 |
| PDMS/25.0B/2.5PEG | 73.1   | 1.9    | 25.0 |
| PDMS/25.0B/5.0PEG | 71.2   | 3.8    | 25.0 |
| PDMS/25.0B/10.0PEG | 67.5   | 7.5    | 25.0 |
| PDMS/50.0B/0PEG | 50.0    | 0      | 50.0 |
| PDMS/50.0B/2.5PEG | 48.7   | 1.3    | 50.0 |
| PDMS/50.0B/5.0PEG | 47.5   | 2.5    | 50.0 |
| PDMS/50.0B/10.0PEG | 45.0   | 5.0    | 50.0 |

A total 4 wt% photoinitiator DMPA was added into the mixture. Then, the mixture was subjected with magnetic bar stirring for 15 minutes. Planar hydrogel samples (1.00 mm thick) were prepared by
pipetting the precursor solution between two microscope slides (25.4x76.2 mm²) separated by glass spacers. These hydrogels were synthesized via chemical crosslinking method using a UV curing system (Philip UVA). This UV chamber is a controlled radiation source with 6 UV-tubes that provides a spectral range between 315-400 nm at average intensity of 40 W/cm². Further characterization were conducted including FTIR, NMR, swelling, contact angle and biocompatibility test.

3. Results and Discussion

3.1 Fourier-Transform Infrared spectroscopy (FTIR) of PDMS-SiH and PDMS-MA

To determine the polymerisation of PDMS-SiH had completed, the present of Si-H peak was determined from the spectrum. The Si-H group is readily identified by a strong band in the range 2280-2080. As it shown in Figure 1(left), there was a small peak in the range of 2280-2080 for both PDMS-SiH 12k and PDMS-SiH 1k spectrum. The Si-H peak was not obvious in PDMS-SiH 12k and it is due to the very large molecular weight of PDMS 12k with 12000g/mol. Si-H is the functional group of the polymer chain which each chain only contains two Si-H group and make it relatively small and hard to be detected. After synthesized of PDMS-SiH, it needs to be further process to change the functional group from Si-H to MA. Figure 1 (right) show the FTIR spectrum of PDMS-MA 12k and PDMS-MA 1k. Si-H terminal groups were subsequently converted to photo-sensitive methacrylate groups by Pt-catalyzed hydrosilylation with allyl methacrylate. The chemical reaction was confirmed by the disappearance of the Si-H peak (~ 4.5 ppm) in the 1H NMR spectra and Si-H absorbance (~2125 cm⁻¹) in the FTIR spectra to determine the process of changing functional group had completed. C=O is present in methacrylate groups hence after the reaction had completed, C=O peak which is at 1720 had appeared.

![Figure 1](image1.png)

**Figure 1**: FTIR spectrum of PDMS-SiH 12k and PDMS-SiH 1k (left) and FTIR spectrum of PDMS-MA 12k and PDMS-MA 1k (right)

3.2 Nuclear magnetic resonance spectroscopy (NMR) of PDMS-SiH and PDMS-MA

Figure 2 show the NMR spectrum for PDMS-SiH 1k and PDMS-SiH 12k respectively. From the NMR spectrum of PDMS-SiH 1k, it can be seen a little tiny peak at 4.5ppm which representing Si-H peak. In the NMR spectrum of PDMS-SiH 12k, a Si-H peak was not present. It was due to the extremely low Si-H content in the polymer chain. By comparing PDMS 1k and PDMS 12k, the molecular weight is 12 times larger. With just a tiny peak in PDMS 1k, so the probability of not being seen in PDMS 12k is high.
After synthesized of PDMS-SiH, it is then further processed into PDMS-MA. Figure 3 show the NMR spectrum for PDMS-MA 1k and PDMS-MA 12k. The purpose of NMR spectrum was to determine whether PDMS-SiH had been completely changing its functional group to MA. From the disappearance of peak 4.5 ppm in PDMS-SiH 1k and the arising of others AMA peak, it can conclude that AMA had been attached to the PDMS.

3.3 Contact Angle of PDMS-PEG Hydrogels

Figure 4 (left) shows the contact angle of PDMS-PEG hydrogel in various composition of PEG with 7.5 and 15 wt% AMA. From the Figure 4, it showed that AMA had the lowest contact angle with 77°. AMA is hydrophilic in natural which show in its ester bond with can form hydrogen bond with water. Hydrophilic properties also increase the wettability of the hydrogel which explains by the low contact angle of the result. PEG which is also hydrophilic in natural due to its OH functional group which readily for hydrogen bond with water which expected the contact angle to be lower than 90° but in the experiment, the contact angle that obtains is 102°. The value obtained here can be explained by the different surface roughness on PEG surface which due to air entrapment. In the UV crosslinking of PEG, air entrapment had happened between polymer chains as agreed by the surface roughness of PEG throughout the surface. Air entrapment had increased the contact angle of PEG. PDMS-MA 12k is hydrophobic which theoretically had a higher contact angle as compared to PDMS-MA 1k. The end chain of PDMS-MA is hydrophilic but due to steric hindrance effect, the end chain is sealed due to the high molecular weight of PDMS. In term of the concentration of functional group, PDMS-MA 12k had a lower concentration of functional group as compare to PDMS-MA 1k which cause it had a higher contact angle.

Increasing the concentration of AMA and PEG in hydrogel did not give trending effect on the contact angle. Theoretically, increasing in AMA and PEG concentration will decrease the contact angle of hydrogel. AMA and PEG are hydrophilic. Increasing the concentration will increase the hydrophilic properties of hydrogel and hence increase its wettability and decrease in contact angle. But in the experiment, the increased AMA and PEG content show fluctuated result on the contact angle of
hydrogel. The results may be also associated to the better biocompatibility property of the PDMS-PEG hydrogels due to the addition of reactive diluents. In which, the PDMS hydrophobicity overshadowed the AMA and PEG hydrophilicity. Thus, decreased of contact angle results were achieved. The enhanced biocompatibility of PDMS-PEG hydrogels was reflected in the one phase occurrence from visual observation (data is not shown). However, at higher ratio of PDMS-PEG, the occurrence of opaque hydrogel was achieved due to the phase separation existed in the hydrogels.

Figure 4 (right) shows the contact angle for PEG, Pure PDMS-MA 1k and hydrogel at different PDMS 1k and PEG composition. PDMS 1k showed a very high contact angle at 114° which shows it hydrophobicity. The increase of PDMS 1k had an increase in contact angle for all different composition. It is because PDMS 1k is hydrophobic and increasing its content in hydrogel will increase the hydrogel hydrophobicity and thus decrease the wettability and decrease contact angle. Besides, increasing PEG content suppose had a decrease in contact angle. But due to uneven surface, increasing PEG had a fluctuating effect on contact angle.

3.4 Swelling Percentage of PDMS-PEG Hydrogels

Figure 5 (left) shows the swelling percentage of AMA, PEG and the mixture of AMA, PDMS-PEG hydrogels at a different ratio. PEG is hydrophilic which can show in the Figure 5 that it swells at 49%. Although AMA is hydrophilic in nature due to its ester bond that can form hydrogen bond easily with water, it just swells for 1.4% which can be explained by UV crosslinked AMA had high crosslink density which shields the water from the ester bond and makes it swelling percentage to decrease. PDMS is hydrophobic in nature due to its does not have any functional group that can react with water which shows by its limited swelling percentage in distilled water. As the PEG content is increasing, the swelling percentage also increased. This is due to the increasing PEG content which is hydrophilic that act as water absorber. 7.5 wt% AMA with 100 wt% PDMS shows a minimum swelling value in hydrogel due to its composition which is made up of mainly PDMS 12k only which are hydrophobic in natural.

Figure 5 (right) shows the swelling percentage of PDMS 1k and different mixing ratio of PDMS 1k, and PEG. From this figure, it shows that PDMS 1k had a very minimum value in swelling which is 0.3%. While PEG is a very hydrophilic material, the trend is still the same as AMA hydrogel which increasing in PEG content will increase the swelling percentage. It is true for both 25 wt% PDMS 1k and 50 wt% PDMS 1k. At constant 10 wt% PEG, 25 wt% 1k had higher swelling percentage than 501k. It is due to higher PEG content in 25 wt% 1k 10 wt% PEG. For 25 wt% PDMS 1k and 50 wt% PDMS 1k hydrogel, the swelling percentage did not have significant different to each other as indicate by the overlapping of error bar. This can be explained by both PDMS 1k and PDMS 12k are hydrophobic in nature. Thus, it only had a very minimum swelling effect in distilled water.
Figure 5: Swelling percentage of AMA, PEG and hydrogel at 7.5 wt% AMA (left) and swelling percentage of PDMS 1k and different mixing ratio of PDMS 1k, PDMS 12k and PEG

4. Conclusion

All hydrogel was fabricated and characterized to determine the properties of hydrogel at different formulations. The chemical structure of PDMS-SiH and PDMS-MA were confirmed by FTIR and NMR. Different types of reactive diluent which are AMA and PDMS-MA 1k had different effect to the properties of hydrogel. For contact angle of hydrogel, increasing of AMA should decrease the contact angle due to AMA is hydrophilic but from the testing, increasing AMA content had a fluctuating effect and this deviation can be explained by uneven surface of hydrogel which deviated the result. Besides, increasing PDMS 1k had an increasing trend to the contact angle of hydrogel. This is because PDMS 1k is hydrophobic and it decreases the wettability of hydrogel. Furthermore, in swelling test, different reactive diluent which are AMA and PDMS-MA 1k had no significant effect on swelling percentage. This is due to the same hydrophobic nature in crosslinked AMA and PDMS-MA 1k.

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