Role of Bulky Polysiloxanylalkyl Methacrylates in Oxygen-Permeable Hydrogel Materials

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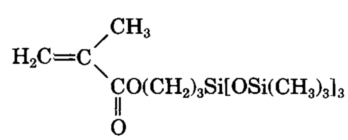
SYNOPSIS

Polysiloxanylalkyl methacrylates, such as methacryloxypropyl tris(trimethylsiloxy)silane (TRIS), have been used extensively in rigid gas-permeable contact lens materials due to their ability to produce high oxygen permeability in the resulting polymeric material. In this study, the role of TRIS was evaluated as a component in silicone hydrogel materials based on polysiloxane-based prepolymers. It was found that it not only gave high oxygen permeability, but also gave hydrogels with better tear strength and lower modulus. These changes in properties are all favorable for applications such as oxygen-permeable hydrogel lenses.

INTRODUCTION

Existing hydrogel materials which are claimed to be useful as contact lens materials are derived almost exclusively from hydrophilic monomers such as 2-hydroxyethyl methacrylate, glycerol methacrylate, or *N*-vinyl pyrrolidone.[1] These hydrogels, in general, have water contents ranging from 38 to 75%. The oxygen permeability of these hydrogel materials, which depends exclusively on water content, falls in the range of 8–40 in Barrer unit (1 Barrer = 10^{-11} cm^2 mL O_2/s mL mmHg). The tensile moduli of these hydrogels are in the range of 20–140 g/mm^2; and tear strengths are in the range of 1–5 g/mm. The water content, modulus, and tear strength of hydrogels depend on the nature of monomers and crosslinking density.[1] Existing hydrogel lenses are, in general, comfortable to wear and suitable for daily wear. However, because of insufficient oxygen transport, they caused excessive corneal swelling in overnight wear due to hypoxia.[2] It was suggested that the oxygen transmissibility of a lens (oxygen permeability divided by lens thickness) should be at least 87×10^{-9} cm mL O_2/s mL mmHg for a human corneal overnight swelling equivalent to a no-lens situation.[3] Attempts to increase oxygen transport, by either using material with higher water or thinner hydrogel lens, did not generate satisfactory results due to other complications.[1] Polysiloxane-based elastomers, or silicone rubber, are known to be highly oxygen permeable. Oxygen permeability as high as 600 Barrers was claimed for polydimethylsiloxane.[4] Because of high oxygen permeability, silicone elastomers have long been considered as a viable contact lens material.[5] In addition to silicone elastomers, monomers and prepolymers containing siloxane groups have been prepared and used in combination with other monomers to give oxygen-permeable polymeric materials. These monomers and prepolymers were claimed to be useful for contact lens applications. For example, bulky polysiloxanylalkyl acrylic esters were incorporated into compositions to fabricate hard lenses in the early 1970s.[6] Since then, this class of silicone–acrylate monomers[7-9] and their styrene,[10] itaconate,[11] and dimer[11,12] analogs, particularly methacryloxypropyl tris(trimethylsiloxy)silane (TRIS, **1**),



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have been used extensively in the development of rigid gas-permeable lens materials.

TRIS or its analogs have seldom been mentioned in patents[8,13] for its use as components of soft hy-

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drogel lenses with improved oxygen permeability. In those cases, TRIS or its methacrylamide analog is used in combination with hydrophilic monomers such as *N,N*-dimethyl acrylamide or *N*-vinyl pyrrolidone to form hydrogels with good oxygen permeability. Recently we incorporated TRIS into compositions containing polypropylene glycol–based polyurethane prepolymer and hydrophilic monomer to obtain hydrogels with improved oxygen permeability.[14,15] In this article, the role of bulky polysiloxanylalkyl methacrylates in silicone hydrogels is discussed using hydrogels derived from methacrylate-based polysiloxane prepolymers and TRIS as examples.

EXPERIMENTAL

Monomers and Prepolymers

TRIS (over 98.5% purity, containing less than 0.02% of dimer) was obtained from Silar Incorporated and used as received. *N,N,*-dimethyl acrylamide and *n*-hexanol, both from Aldrich Chemical Co, and Darocur-1173 (from EM Science) were used as received. The preparations of polysiloxane-based prepolymers, a,w-bis(4-methacryloxyybutyl) polydimethylsiloxanes, M_2D_{25} and M_2D_{50}, have been described elsewhere.[16]

Hydrogel Synthesis

An a,w-bis(4-methacryloxybutyl) polydimethylsiloxane, TRIS, and hydrophilic monomer, in weight ratio chosen to total 100 parts, were mixed with 40 parts of *n*-hexanol and 0.2 part of Darocur-1173. The monomer mix was introduced between two glass plates (10 × 8 cm) and cured under a long-wave ultraviolet (UV) lamp (from UVP) for 2 h. The film thickness was controlled by a Teflon gasket material which gave fairly consistent thickness of 0.25 mm. The films were extracted with ethanol for 16 h, dried in a vacuum oven at 70°C for 16 h, boiled with distilled water for 4 h and swollen to equilibrium in phosphate-buffered saline (with pH 7.30) before characterization.

Characterization of Hydrogel Films

The water contents and the amounts extractable in ethanol were measured gravimetrically.

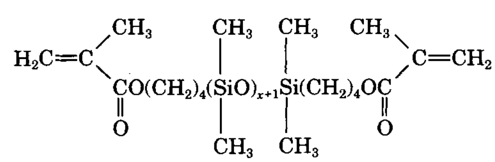
Mechanical testing was conducted in phosphate-buffered saline on an Instron instrument, according to the modified ASTM D-1708 (tensile) and D-1938 (tear) procedures, and were reported in grams per square millimeter (1 MPa = 102 g/mm^2) for tensile strength and modulus and grams per millimeter (1 kN/m = 1020 g/mm) for tear strength. The oxygen permeabilities were measured by the one-chamber method[17] with consideration of edge effect and probe configuration and were reported in units of Barrers (1 Barrer = 10^{-11} cm^2 mL O_2/s mL mmHg).

RESULTS AND DISCUSSION

The effect of a bulky polysiloxanylalkyl acrylate, such as TRIS, on the oxygen permeability of polyurethane hydrogels derived from a polypropylene glycol–based polyurethane prepolymer and a hydrophilic monomer was reported previously.[13] In the non–silicone polyurethane prepolymer–based systems studied, the addition of TRIS increases the oxygen permeability, with the amount of increase in proportion to the TRIS content. In this article, the discussion is centered on the effects of TRIS on the properties of silicone hydrogels derived from polysiloxane-based prepolymers.

Polysiloxane-Based Prepolymers

Polysiloxane-based methacrylate-capped prepolymers, such as a,w-bis(4-methacryloxybutyl) polydimethylsiloxanes, with structure shown as **2** and abbreviated as M_2D_x,



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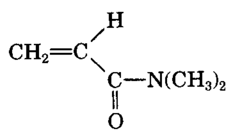
have been claimed to be useful as components for contact lens materials due to high polysiloxane content, which gives high oxygen permeability.[16] In fact, this class of prepolymers has been used successfully as a component for hard-lens materials. However, due to the hydrophobicity of siloxane fragments, it is hard to formulate this class of prepolymers with hydrophilic monomers to create hydrogels with acceptable mechanical properties as well as optical quality required for a contact lens. These hydrogels are, in general, stiff and show poor tear strength. The task of improving the compatibility of M_2D_x with hydrophilic monomers, improving the optical quality, reducing the stiffness, while improving the tear strength of the hydrogels derived is formidable. In the following, it is demonstrated that a bulky polysiloxanylalkyl methacrylate, such as TRIS, can be used in compositions containing a M_2D_x prepolymer and DMA and improve all the properties for hydrogels derived from them.

Hydrogel Compositions

To simplify the discussion, prepolymer M_2D_{25} and M_2D_{50} (x = 25, 50 in structure **1** and *N,N*-dimethyl acrylamide (DMA, **3**),



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were chosen as the siloxane prepolymers and hydrophilic monomer respectively. M_2D_{25} has a molecular weight of 2264 and M_2D_{50} has a molecular weight of 4114. DMA is a very polar hydrophilic monomer. It gives roughly 1% water content to hydrogels formed from it per percentage of its usage. In order to study the effect of TRIS on properties of silicone hydrogels based on polysiloxane-based prepolymers, a varying amount of TRIS was used to replace M_2D_x, while the amount of DMA used was maintained at the same level in order to compare hydrogels with roughly the same water content. For simplicity, DMA was kept at 40 wt %, while the combined amount of M_2D_x and TRIS was 60 wt %.

Improvement of Compatibility among Components with TRIS

Table I lists the compositions used in the study based on M_2D_{25}, TRIS, and DMA, with the amount of TRIS used to replace M_2D_{25} ranging from 0 to 60 parts while DMA stayed at 40 parts. When no TRIS was used, the mixture of M_2D_{25} and DMA was cloudy and separated into two phases upon standing. As TRIS was added gradually, the mixture became clearer and finally turned completely clear when three-quarters or more of M_2D_{25} was replaced by TRIS. Thus, by replacing a higher molecular weight hydrophobic prepolymer with a lower molecular weight hydrophobic monomer, the compatibility of hydrophobic monomers with hydrophilic monomers such as DMA was improved dramatically. Alternatively, the relative compatibility between the hydrophobic, siloxane-based components with DMA can be judged by the amount of a cosolvent, *n*-hexanol, required to bring the hydrophobic–hydrophilic mixture to a clear solution. For a mixture containing M_2D_{25} (60 parts) and DMA (40 parts), it required 45 parts of *n*-hexanol to bring it to a clear solution. However, the amount of *n*-hexanol required to bring a mixture of M_2D_{25}, TRIS, and DMA to a clear solution was decreased as the relative amount of TRIS was increased. It dropped to 14 parts when the mixture contained equal amount of M_2D_{25} and TRIS (at 30 parts each).

For mixtures containing M_2D_{50} and DMA, the effect of TRIS on monomer compatibility was evaluated similarly. It was found that for comparable mixtures, M_2D_{50}-based mixtures required much more *n*-hexanol to turn them into clear mixtures compared to those based on M_2D_{25}. For example, a mixture containing M_2D_{50}, TRIS, and DMA at 15, 45, and 40 parts, respectively, required 50 parts of *n*-hexanol to turn the mixture totally clear, while the comparable mix containing M_2D_{25} is clear without any added solvent.

Preparation of Silicone Hydrogel Films Based on M_2D_x, TRIS, and DMA

To better evaluate the effects of TRIS on properties of silicone hydrogels based on M_2D_x and DMA, hydrogel films of chosen formulations were prepared by, first, UV curing of chosen formulations, followed

Table I Compositions for Silicone Hydrogels Derived from M_2D_{25}, TRIS, and DMA

	By Formulations						
	1	2	3	4	5	6	7
Composition							
M_2D_{25}	60	50	40	30	13	5	0
TRIS	0	10	20	30	47	55	60
DMA	40	40	40	40	40	40	40
Appearance	Cloudy	Cloudy	Cloudy	Cloudy	Clear	Clear	Clear
n-Hexanol[a]	45	40	30	14	0	0	0

[a] Amount needed to add to monomer mix to bring clear solution.

Table II Silicone Hydrogels Derived from M_2D_{25}, TRIS, and DMA

	By Formulation						
	1	2	3	4	5	6	7
Composition[a]							
M_2D_{25}	60	50	40	30	13	5	0
TRIS	0	10	20	30	47	55	60
DMA	40	40	40	40	40	40	40
n-Hexanol	40	40	40	40	40	40	40
Hydrogel films							
Appearance	Weak, cloudy	Weak, pieces	Weak, pieces	Clear	Clear	Clear	Not cured
Properties[b]							
Percent extract	[c]	4.4	8.7	7.0	2.8	8.0	[d]
Percent water	[c]	26	30	29	29	34	[d]
Barrer	[c]	99	104	99	97	85	[d]
Modulus	[c]	386	279	209	89	39	[d]
Tear	[c]	0.7	2.1	3.9	12.0	26.6	[d]

[a] With 0.2 part Darocur-1173 added.
[b] Percent extract was calculated value after excluding effect of solvent. Barrer indicates oxygen permeability. Modulus in units of g/mm^2 and tear strength in g/mm.
[c] Too weak to measure.
[d] No film forming.

by extracting cured films with a solvent, ethanol, and then equilibrating them with a buffered saline. For convenience, 40 parts of *n*-hexanol was used as solvent.

Table II lists those formulations containing M_2D_{25}, TRIS, and DMA and key properties of the silicone hydrogel films derived from them. All formulations were well cured except formulation 7, which contained no crosslinker. The low extractables of cured films with ethanol indicated that the UV curing was efficient. Formulation 1, which contained no TRIS, gave hydrogel films that were weak and cloudy. In fact, these films were too weak to be characterized any further. Formulations 2 and 3, with TRIS at 10 and 20 parts, respectively, gave hydrogel films that were less cloudy but still very weak. When half of M_2D_{25} was replaced by TRIS (formulation 4), the hydrogel films obtained were clear. The water contents of hydrogel films prepared were, within experimental error, the same as ex-

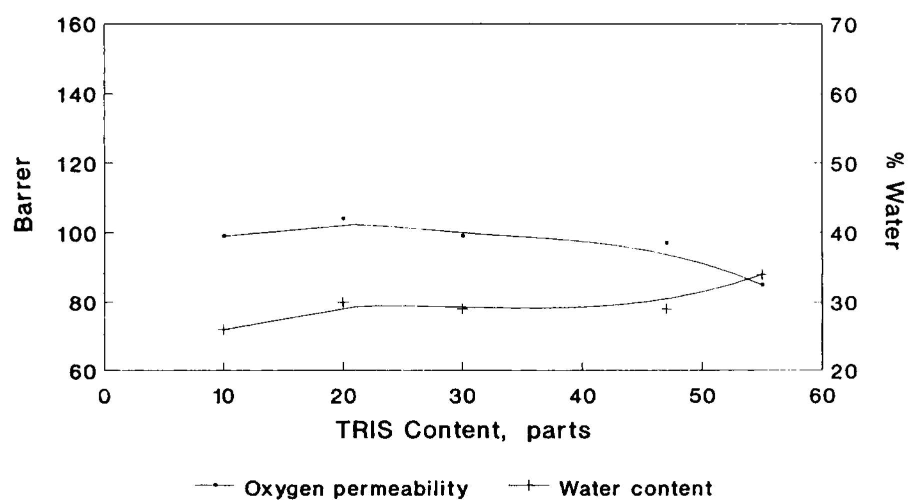

Figure 1 Relationship between oxygen permeability/water and TRIS in hydrogels derived from M_2D_{25}, TRIS, and DMA.

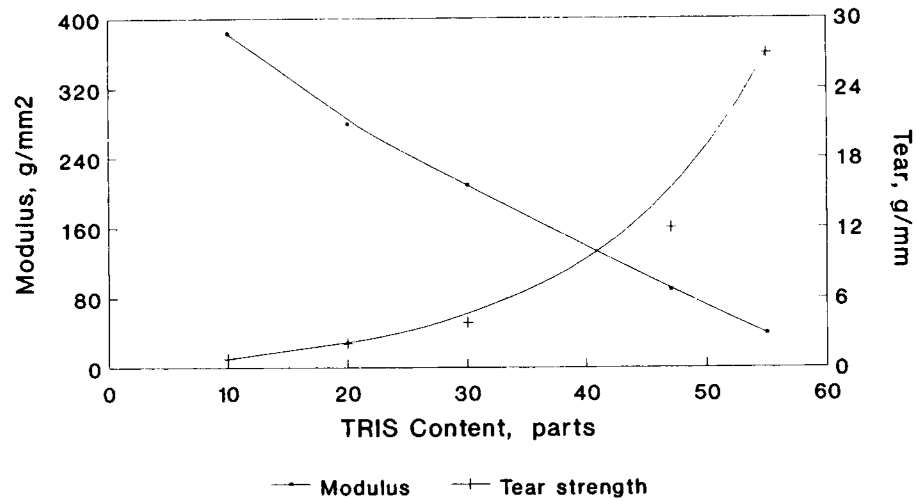

Figure 2 Relationship between modulus/tear strength and TRIS in hydrogels derived from M_2D_{25}, TRIS, and DMA.

pected (26–30%), except for hydrogels derived from a formulation containing almost exclusively TRIS (55 parts) and little M_2D_{25}. This could be due to a change in polarity of the cured films. In the following, the roles of TRIS in silicone hydrogels derived from polysiloxane-based prepolymers and hydrophilic monomers were discussed in terms of its effects on oxygen permeability and mechanical properties.

Effects of TRIS on Properties of Silicone Hydrogels

Oxygen Permeability and Water Content

Table II also gives oxygen permeability and water content data as well as mechanical properties of silicone hydrogels derived from M_2D_{25}, TRIS, and DMA. Figure 1 illustrates the relationship between oxygen permeability/water and TRIS in these hy-

Table III Silicone Hydrogels Derived from M_2D_{50}, TRIS, and DMA

	By Formulations					
	1	2	3	4	5	6
Composition[a]						
M_2D_{50}	50	40	30	15	10	5
TRIS	10	20	30	45	50	55
DMA	40	40	40	40	40	40
n-Hexanol	40	40	40	40	40	40
Hydrogel films						
Appearance	Cloudy, rough	Cloudy, rough	Hazy, good	Clear, good	Clear, pieces	Clear, weak
Properties[b]						
Percent extract	7.8	3.6	5.3	2.4	8.8	25
Percent water	43	38	35	35	33	[c]
Barrer	75	90	92	118	123	[c]
Modulus	173	125	84	26	17	[c]
Tear	0.7	2.7	3.9	9.8	12.5	[c]

[a] With 0.2 part Darocur-1173 added.
[b] Percent extract was calculated value after excluding effect of solvent. Barrer indicates oxygen permeability. Modulus in units of g/mm^2 and tear strength in g/mm.
[c] Too weak to measure.

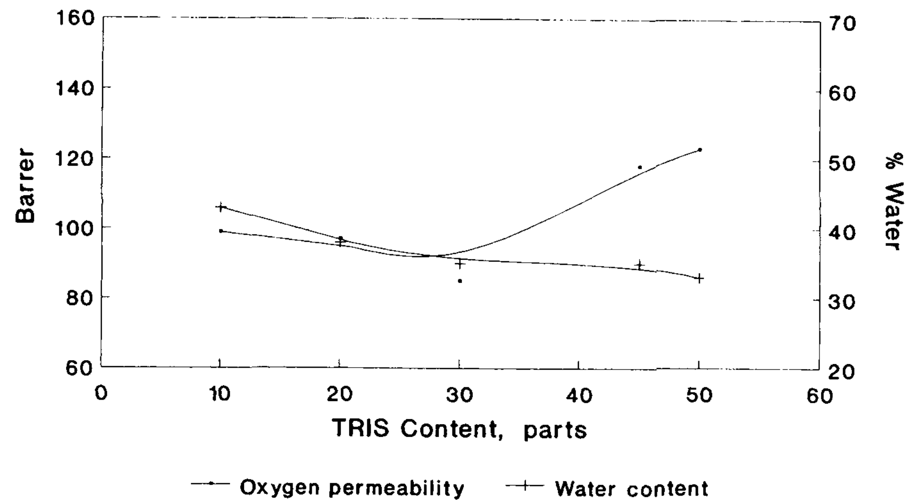

Figure 3 Relationship between oxygen permeability/water and TRIS in hydrogels derived from M_2D_{50}, TRIS, and DMA.

drogels. As expected, the water content showed only minor changes because the same amount of DMA was used in these formulations. These changes in water content, if significant, may be mainly due to the change in polar character of the monomer mix/cured materials as well as the change in the efficiency in incorporating DMA caused by the change in the amount of crosslinker (M_2D_{25}). The oxygen permeabilities of these hydrogels (84–99 Barrers) are about the same for all hydrogels regardless of the amount of TRIS used to replace M_2D_{25}, although there is a difference in silicon content between these two silicon-containing monomer/prepolymer (26.5% for TRIS and 34.1% for M_2D_{25}). The differences in oxygen permeability between these hydrogels are decreased by the weight averaging of these two components in the formulation as well as by the dilution of water in the hydrogels. The resultant silicone hydrogels have about 10.7–12.7% silicon by weight. These oxygen permeability results indicate that, regardless of the difference in structure, both linear polysiloxane and bulky, branched polysiloxane give the same oxygen permeability as long as the silicon content is the same.

In considering the oxygen permeability figures of 84–99 Barrers and the water contents of around 30%, these figures are outstanding as compared to those of traditional, nonsilicone hydrogels. Traditional hydrogels derive their oxygen permeability from water. With a water content of 30%, they give an oxygen permeability below 8 Barrers.[1]

Mechanical Properties

The tear strength and modulus data for hydrogels derived from M_2D_{25}, TRIS, and DMA are tabulated in Table II. Figure 2 further illustrates the relationships between modulus/tear strength and TRIS in these silicone hydrogels. It was observed that, in this series of hydrogels, the tensile modulus decreased as the amount of TRIS used to replace M_2D_{25} was increased. For example, the modulus dropped from 386 to 89 g/mm^2 when the amount of TRIS used was increased from 10 to 47 parts. This is somewhat unexpected since TRIS was used almost exclusively for hard lenses. The reason for these results is that the overall crosslinking density was reduced as the amount of TRIS was increased in the monomer mixture for the hydrogels. On the other hand, the tear strength increased from 0.7 to 12 g/mm with the same change in the amount of TRIS used, as shown in the same figure.

Thus, by replacing part of the polysiloxane prepolymer M_2D_{25} with TRIS in silicone hydrogel compositions, we are not only able to lower the modulus, but also able to increase the tear strength simultaneously for the hydrogels prepared while maintaining the high oxygen permeability nature of these hydrogels. The changes in properties by modifying formulations with TRIS gave hydrogels more suitable for applications such as contact lenses. Normally, hydrogel lenses have modulus in the range of 20–140 g/mm^2 and tear strength in the range of 1–5 g/mm.[1] For practical purposes, tear strength of a hydrogel lens should be 2 g/mm or higher to avoid tearing.

Similar formulation studies were also carried out for M_2D_{50}. Table III lists the formulations and key properties of hydrogel films derived. In this series of hydrogels, DMA used remained at 40 parts, while the combined amount of M_2D_{50} and TRIS was 60

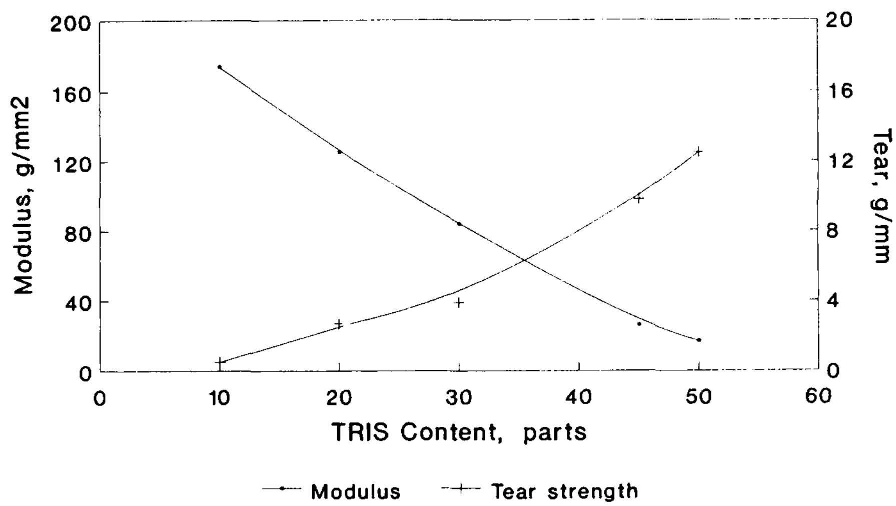

Figure 4 Relationship between modulus/tear strength and TRIS in hydrogels derived from M_2D_{50}, TRIS, and DMA.

parts. Because the molecular weight of M_2D_{50} is about two times that of M_2D_{25}, with the same amount of the M_2D_x prepolymer used, the crosslinking density is lower. This led to less efficiency in curing as compared to films derived from M_2D_{25}. For example, the formulation M_2D_{50}–TRIS–DMA at 5 : 55 : 40 did not cure well, with high extractables (25%), while the formulation M_2D_{25}–TRIS–DMA at the same weight ratio cured well. Figure 3 further depicts the relationship between oxygen permeability, water content, and TRIS content of hydrogels derived from M_2D_{50}, TRIS, and DMA. The decrease in water content and the increase in oxygen permeability as the amount of M_2D_{50} used decreased could be due to the reduction in effective incorporation of DMA. Figure 4 further depicts the relationship between modulus/tear strength and TRIS for hydrogels derived from M_2D_{50}, TRIS, and DMA. Because of the decrease in crosslinking densities, the moduli of the hydrogel films derived from M_2D_{50} were lower than those derived from M_2D_{25}.

Regardless of the difference between those films based on M_2D_{25} and M_2D_{50}, the direction of changes in properties (oxygen permeability, modulus, and tear strength) with added TRIS are the same; i.e., as more TRIS was used to replace M_2D_{50}, the modulus decreased, the tear strength increased, while the high oxygen permeability nature of the silicone hydrogels was maintained.

The relationships of oxygen permeability, modulus, and tear strength with the amounts of bulky polysiloxanylalkyl acrylic monomers, such as TRIS, used to replace polysiloxane-based prepolymer such as M_2D_x in silicone hydrogels make them useful in preparing silicone hydrogels for certain biomedical applications such as contact lenses.

The same effects of TRIS on properties of silicone hydrogels based on other classes of prepolymers were also demonstrated, which will be the subject of future publications.

CONCLUSION

When a bulky polysiloxanylalkyl acrylic monomer, such as TRIS, was used to replace a portion of silicone-based prepolymer in a silicone hydrogel, it helped in improving optical quality, maintaining high oxygen permeability, lowering modulus, and increasing tear strength. These changes in properties make these silicone hydrogels useful for a wider range of applications, including hydrogel contact lenses.

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