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Glass-transition temperatures for soft-contact-lens materials. Dependence on water content

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Abstract

Glass-transition temperatures for three soft-contact-lens (SCL) materials are measured by modulated differential scanning calorimetry as a function of SCL hydration, as determined by thermogravimetric analysis. The SCL materials are: a conventional hydrogel (SofLens® 38, polymacon) with a low water content at saturation; a conventional hydrogel (SofLens™ One Day, hilafilcon A) with a high water content at saturation; and a siloxane–hydrogel (PureVision™, balafilcon A).

Polymacon, hilafilcon A, and balafilcon A turn glassy at 35 °C when their water contents drop below 10.4, 13.5, and 6 wt%, respectively. These water contents correspond to the equilibrium water uptake at 35 °C for polymacon, hilafilcon A, and balafilcon A at relative humidities, RH, of 74, 64, and 57%, respectively. Our results suggest that the outer surface of a soft contact lens worn on the eye may develop a glassy skin when exposed to air at low relative humidity. This glassy skin may alter fluid transport through the soft contact lens, and influence SCL-wear comfort.

Keywords: Soft contact lenses; Modulated differential scanning calorimetry; Glass transition

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1. Introduction

A fully hydrated soft contact lens (SCL) is rubbery both at ambient and at physiological temperatures because the imbibed water acts as a plasticizer, conferring ‘softness’ to the contact-lens material. However, in the event of partial SCL dehydration, for example, when the SCL is exposed to an environment at low relative humidity, the soft-contact-lens material can undergo a rubber-to-glass transition. A soft contact lens on the eye is normally bathed in the tear film at the beginning of a blink cycle. When the eye is open, however, the pre-lens tear film (PrLTF) covering the SCL front surface partially ruptures after a few seconds, and the front surface of the soft contact lens is exposed to environmental air for the remaining part of the blink cycle [1–4]. During this interval of time, evaporation draws water from the SCL toward the environment, and the SCL partially dehydrates [5]. Therefore, a gradient of water content is established between the posterior and anterior surfaces with the front surface the most dehydrated. If the local water concentration on the front surface of the SCL decreases sufficiently, the anterior surface of the SCL may experience a glass-to-rubber transition.

Water plasticization has been observed for a variety of synthetic, commercial polymers [6–10], and biopolymers [11–16]. However, investigations of the physical state of a soft contact lens as a function of hydration are rare [17–19]. In this work, we obtain the glass-transition temperatures, T_g, of three soft-contact-lens hydrogels as a function of their water content using modulated differential scanning calorimetry (MDSC). Water content in the SCL’s is measured by

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thermogravimetric analysis (TGA). Data from these measurements directly give the minimum water content needed to maintain a rubbery SCL at a given environmental temperature.

2. Experimental

2.1. Materials

Commercial SCL materials were kindly provided by Bausch and Lomb as flat, rectangular sheets (7×9.5 cm) synthesized between two glass plates. Three soft-contact-lens materials were used in this study: two conventional hydrogels, polymacon (commercial name: SofLens® 38), and hilafilcon A (SofLens™ One Day); and a last-generation siloxane–hydrogel, balafilcon A (PureVision™). Balafilcon A sheets were not subjected to surface oxygen-plasma treatment, unlike the commercial product [20]. Polymacon is a hydrogel of poly(2-hydroxyethyl methacrylate), (i.e. poly(HEMA)), crosslinked with ethylene glycol dimethacrylate (EGDM); hilafilcon A is a copolymer of HEMA and *N*-vinyl-pyrrolidone (NVP), crosslinked with EGDM; balafilcon A is a crosslinked copolymer of NVP with tris-(trimethylsiloxy)-silyl-propylvinyl carbamate [21], a vinyl carbonate functional polydimethylsiloxane (PDMS) macromer, and a vinyl carbamate derivative of alanine [22].

Table 1 gives properties of the SCL materials. Water content at saturation, w_{10}, reported by Bausch and Lomb, is defined as the weight percent of water in a wet contact lens that has been water-saturated in a sterile isotonic solution at room temperature. The conventional hydrogel hilafilcon A has a high water content at saturation ($w_{10}=70\%$), much larger than that for polymacon ($w_{10}=38\%$). Balafilcon A's water content is $w_{10}=36\%$. Wet thicknesses (L_0) of the SCL membranes were measured using a micrometer (Mitutoyo MDC 0-1″ PF, accuracy ±1 μm) at different locations. The average thickness is reported in Table 1 along with the standard deviation.

Saturated aqueous salt solutions were used to establish a constant relative humidity (RH) environment; the SCL polymers were equilibrated in this environment before MDSC measurements. Magnesium chloride ($MgCl_2$), potassium carbonate (K_2CO_3), sodium chloride (NaCl), and potassium chloride (KCl) were purchased from EM Science. Ammonium nitrate (NH_4NO_3) was obtained from Sigma-Aldrich and potassium nitrate (KNO_3) from Mallinckrodt Inc. All salts are A.C.S. grade. Distilled/deionized water was obtained from a MilliQ™ purification system with a water resistivity greater than 18 MΩ cm.

Table 1
Soft-contact-lens (SCL) properties

SCL	Lot #	Material	w_{10} (%)[a]	L_0(μm)
SofLens® 38	2319LS292	polymacon	38	195 (±3)
SofLens™ One Day	Unspecified	hilafilcon A	70	189 (±9)
PureVision™	2362-LS-273A, RD1503	balafilcon A	36	181 (±3)

[a] w_{10} indicates the water content for a wet SCL that has been water-saturated in a sterile isotonic solution at room temperature.

2.2. Preparation of wet SCL samples

Water-saturated SCL sheets were cut into small 5 mm diameter disks matching that of the MDSC hermetic pan used for glass-transition-temperature measurements. The SCL disks were dried for at least 24 h in a vacuum oven fluxed with nitrogen. Drying temperature was 120, 180, and 80 °C for polymacon, hilafilcon A, and balafilcon A, respectively. 4–10 mg of dry SCL disks were fit into the bottom half of MDSC hermetic pans and stored for at least 2–3 weeks in desiccators containing a particular saturated aqueous salt solution to establish a constant relative-humidity environment. Saturated salt solutions were prepared by mixing 50–100 mg of distilled/deionized water with an amount of salt equal to 1.5–2 times the salt solubility limit at room temperature. Table 2 presents the salt solubilities in water at room temperature and the corresponding relative humidities at 25 °C of the vapor phase above the salt solution [23].

Once the SCL disks were water saturated at a given RH, each desiccator was opened inside an inflatable glove-bag filled with air at the same RH as that of the desiccator. To minimize any variation in SCL water content during the sealing procedure, the hermetic pans containing the SCL disks were sealed airtight with a crimper while inside the glove-bag.

2.3. Measurements of glass-transition temperatures

The glass-transition temperature T_g of each dry and wet SCL material was measured with a modulated differential scanning calorimeter (Modulated DSC 2920, TA Instruments) coupled with a refrigerated cooling system. Nitrogen was used as a purge gas at a flow rate of 35 ml/min, and as a cooling gas at a flow rate of 100 ml/min. An empty pan of the same kind as that containing the SCL disks (hermetic aluminum pan) was used as a reference. Temperature and

Table 2
Salt solutions: saturation concentration (c_{sat}) in water at 25 °C and relative humidity (RH) of corresponding vapor phase [23]

Salt	c_{sat} (g salt/100 g H_2O)	RH (%)
$MgCl_2$	56.0	32.8
K_2CO_3	111.4	43.2
NH_4NO_3	212.5	62.2
NaCl	36.0	75.3
KCl	35.5	84.3
KNO_3	38.3	93.6

heat-flow calibrations were performed using pure indium as standard. For this standard, the melting temperature and heat of fusion are 156.61 °C and 28.71 J/g, respectively. Heat capacity was calibrated with sapphire (aluminum oxide). All calibrations were performed at the same heating rate and temperature range as those used for T_g measurements.

Two samples were analyzed for each SCL/salt solution combination, and for each SCL sample, the MDSC experiment was repeated at least twice. A typical MDSC run consisted of a heating ramp followed by a cooling ramp over the same temperature range. Along each ramp, the heating/cooling rate was 2.5 °C/min and was modulated by a sinusoid with amplitude 1 °C and period 60 s. The lower limit of the spanned temperature range was -30 °C for all three polymers, whereas the upper limit of the heating step was tailored to each dry/wet SCL polymer. One constraint to the maximum heating temperature was thermal degradation of the polymer. Also, for the wet SCL disks, an additional constraint on the maximum working temperature was set by requiring an airtight seal of the hermetic pans during the entire MDSC run.

Four separate tests were performed to verify that there was no significant water evaporation from the wet SCL samples during MDSC runs. First, a preliminary test was performed to establish the maximum temperature for which the pan seal remains airtight. A drop of distilled/deionized water was placed into a hermetic pan and sealed using the same procedure as that for a wet SCL sample. First, the hermetic pan containing water was heated at 2.5 °C/min from room temperature to 300 °C in a thermogravimetric cell (TG/DTA 220 SSC/5200 Seiko Instruments). A seal-break temperature was determined by the onset of mass loss. Second, the mass of each SCL sample was measured before and after each MDSC run to establish whether any mass variation occurred during an MDSC experiment. Third, each wet SCL sample was run at least twice. The measured glass-transition temperatures in both heating and cooling steps were compared to verify data reproducibility and consistency. Any water loss during a heating ramp was revealed by a higher glass-transition temperature in the subsequent cooling ramp and/or in a repeated MDSC experiment. Finally, non-reversing heat flow (NRHF) signals were also analyzed for broad endothermic peaks that may be caused by water evaporation during the MDSC heating ramp [10].

Unlike the wet SCL materials, dry SCL disks were placed in punctured non-hermetic pans to facilitate residual-water elimination during heating in the first MDSC run. T_g for each dry SCL disk was obtained from the second MDSC run. All glass-transition temperatures were determined from the inflection point in the reversing-heat-flow signal (RHF) with TA Instrument Analyzer Software.

2.4. Measurement of water content

Thermogravimetric analysis (TG/DTA 220 SSC/5200 Seiko Instruments) was performed to determine the water content of the SCL materials equilibrated at fixed RH. The SCL disks were removed from the hermetic pans after a MDSC experiment and immediately placed into the TGA cell to minimize any water loss before data collection. SCL disks were heated at a rate of 2.5 °C/min from 25 to 300 °C under a 200 ml/min nitrogen flow. The first plateau in the weight vs temperature measurements, near 80–130 °C, was identified as evaporated water as explained in Section 3. The water content was obtained from the weight loss of the wet SCL disk corresponding to this first plateau.

Thermogravimetric analysis was also used to determine the thermal stability of the soft-contact-lens materials. The experimental procedure was identical to that used for the water-content determination. Thermal decomposition was identified from a sudden weight loss after the first plateau in the weight-vs-temperature signal.

3. Result and discussion

Figs. 1(a) and (b) show the weight-vs-temperature signal

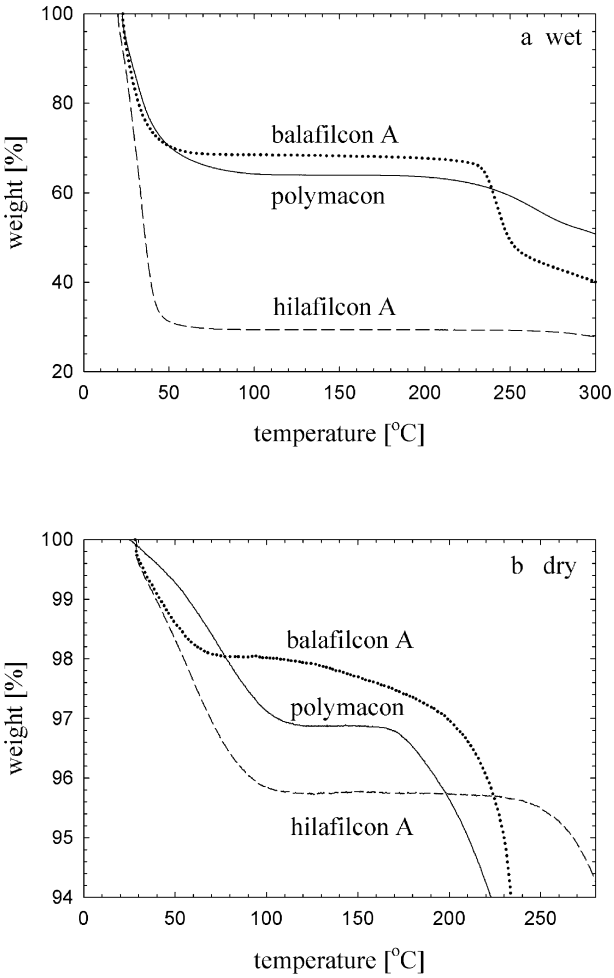

Fig. 1. Thermogravimetric analysis for polymacon (solid line), hilafilcon A (dashed line), and balafilcon A (dotted line) materials. Sample weight is plotted as a function of temperature for (a) water-saturated samples and (b) samples dried under vacuum for 5 days at ambient temperature.

from a TGA-experiment for water-saturated and dry SCL materials, respectively. For this experiment, the SCL disks were initially dried at room temperature under vacuum (300 mmHg) for 5 days. All signals show a rapid weight loss before reaching a plateau at approximately 120–130 °C for polymacon and hilafilcon A, and at 80–90 °C for balafilcon A. At the plateau, the water loss measured for the water-saturated SCL materials (36, 70, and 32 wt% for polymacon, hilafilcon A, and balafilcon A, respectively, from Fig. 1(a)) compare very well with reported SCL hydration at saturation (i.e. 38, 70, and 36 wt%) [24]. These results indicate direct association of the plateau mass loss in Fig. 1(a) with complete water evaporation from the SCL disks.

Fig. 1(b) shows that when dried for 5 days under vacuum at room temperature, the SCL disks contain about 2–4% residual water. Fig. 1(b) also provides information about the thermal stability of the SCL polymer. After the plateau corresponding to complete SCL drying, the onset of an additional weight loss was observed at 170 and 230 °C for polymacon and hilafilcon A, respectively. Balafilcon A shows a very narrow plateau from 80 to 110 °C; after that, the SCL mass decreases initially slowly and, later, progressively faster. Similar behavior was observed for each wet SCL sample analyzed after a MDSC run. The onset of this second mass loss most likely indicates the beginning of thermal degradation. Because water evaporation and thermal degradation occur in two separated temperature ranges, TGA measurements can be used with confidence to determine the water content of wet SCL disks. To avoid thermal degradation, the SCL materials here were dried at 120, 180, and 80 °C for polymacon, hilafilcon A, and balafilcon A, respectively, before equilibration with a fixed RH vapor phase.

Fig. 2 shows water loss from a particular sealed hermetic pan containing distilled/deionized water as a function of the heating temperature in a TGA experiment. A sudden drop of water mass is observed at 140–150 °C, most likely due to the rupture of the airtight seal for the hermetic MDSC pan. The pan was visibly deformed after the TGA run. According to the manufacturer, the maximum internal pressure sustained by the hermetic pans is 3 bar. This pressure corresponds to the vapor pressure of water at 135 °C, in good agreement with our TGA results. Accordingly, the maximum upper limit of the spanned temperature range during a MDSC experiment was 130 °C for polymacon and hilafilcon A to prevent loss of the airtight seal, and 80 °C for balafilcon A to prevent thermal degradation.

Fig. 3 shows two typical MDSC runs on the same wet SCL sample for both reversing and non-reversing heat flows [25]. In the first run (Fig. 3(a)), the reversing heat flow shows one inflection point in the heating ramp and one in the cooling ramp, both at 43–44 °C. At the same temperature, the non-reversing heat flow presents a small peak that is typically associated with polymer chain relaxation when first heated above the glass-transition temperature of the wet polymer [26–28]. In the second run of Fig. 3(a), the

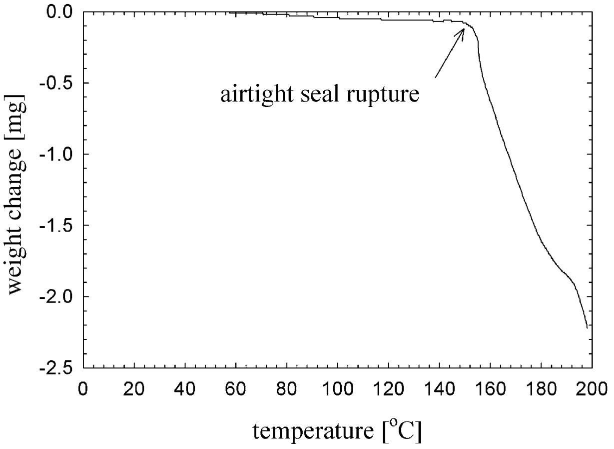

Fig. 2. Thermogravimetric weight vs temperature test for airtight seal of an MDSC hermetic pan. The hermetic pan contains distilled/deionized water and is heated at constant rate in a TGA cell. Seal rupture occurs at the onset of the sudden weight loss (140–150 °C).

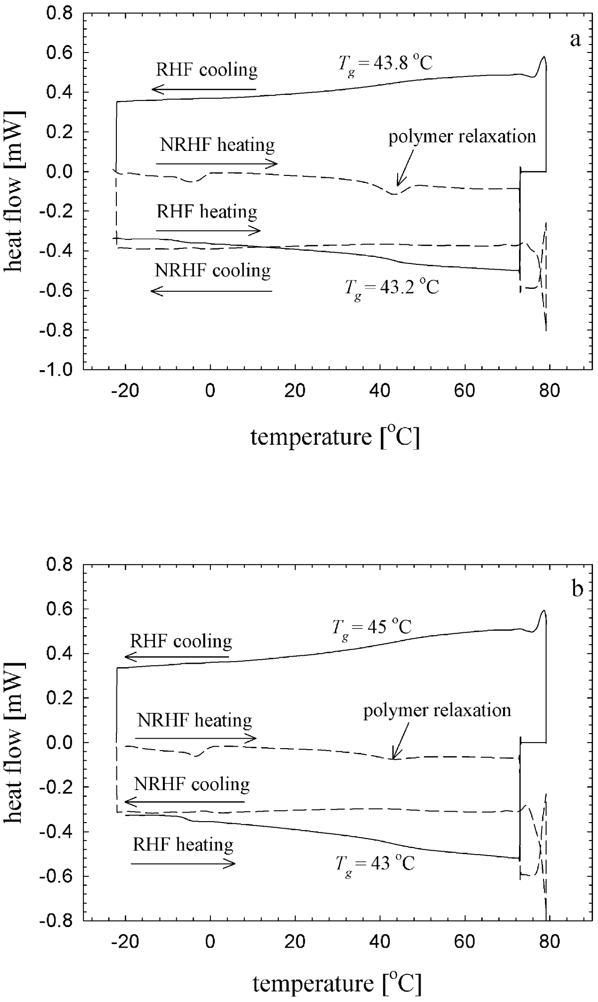

Fig. 3. Reversing (solid lines) and non-reversing (dashed lines) heat-flow signals in an MDSC experiment for balafilcon A with 4.8% water content (corresponding to RH = 48% at T = 35 °C): (a) first run, (b) repeated run for the same sample.

polymer-relaxation peak in the NRHF signal was much smaller, and the inflection points for heating/cooling ramps of RHF were again 43–45 °C. Because the glass-transition temperatures during cooling are the same as those in heating for both runs, we conclude that no significant amount of water was lost during the MDSC run. This conclusion was also confirmed by measuring the sample weight before and after the MDSC experiment. Similar features were observed for each analyzed sample. Therefore, the measured T_g indeed corresponds to the SCL water content subsequently measured by TGA. For comparison, Fig. 4 shows RHF and NRHF for an SCL sample when temperature was raised above the limit to prevent pan-seal rupture. In this case, T_g from the cooling ramp is significantly higher than that from the heating ramp. A large, broad peak was observed in the NRHF before the cooling step, most likely due to water evaporation from the sample pan. Gravimetric mass loss was confirmed after the MDSC run.

Fig. 5 gives experimental glass-transition temperatures for all SCL (polymacon, hilafilcon A, and balafilcon A) samples as a function of water content. Results are shown from both heating (filled symbols) and cooling (empty symbols) ramps, and also from repeated runs for the same sample. Heating and cooling ramps and repeated runs give essentially the same glass-transition temperatures, indicating no significant water evaporation from the SCL samples. Fig. 5 demonstrates that sorption of water markedly lowers the glass-transition temperature for all SCL hydrogels studied. This effect is largest for the balafilcon A siloxane–hydrogel material, as shown by the large (negative) slope of T_g vs water content. The glass-transition temperature of dry balafilcon A appears to lie above the thermal stability limit for the material and, therefore, was not measured.

In most cases, the glass transition was sharper and easier to detect in the heating ramp. Moreover, well above room temperature, both the heating and cooling modulated heat-flow profiles presented no distortion. However, some modulation asymmetry was observed in the cooling ramp near room temperature, becoming more evident at lower temperatures. To avoid artifacts, Fig. 5 does not show results for wet samples with measured glass-transition temperatures lower than 25 °C (except one point for polymacon). Such results were not considered in our analysis.

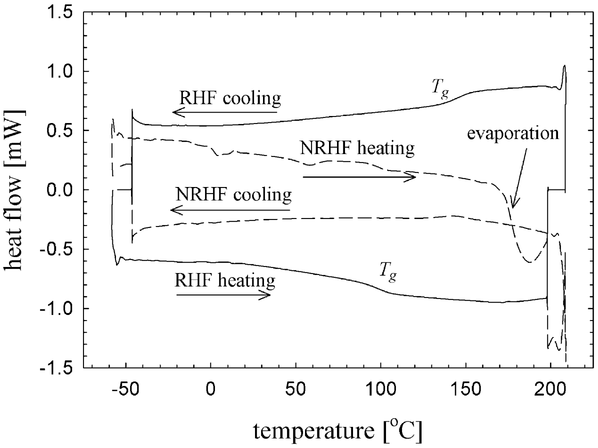

Fig. 4. Reversing (solid lines) and non-reversing (dashed lines) heat-flow signals in an MDSC experiment for hilafilcon A equilibrated with the vapor phase of an aqueous saturated $MgCl_2$ solution. No care was taken to prevent pan seal rupture.

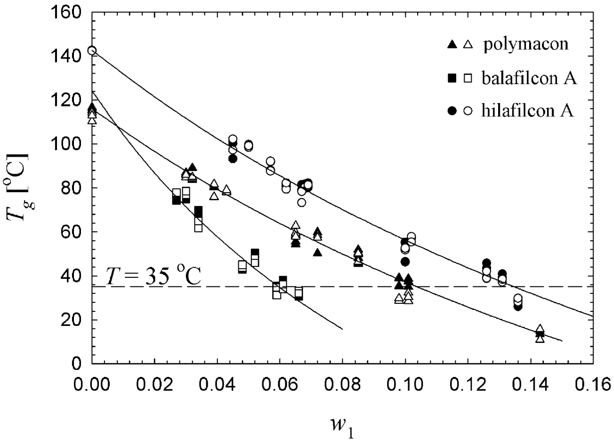

Fig. 5. Glass-transition temperature as a function of water content for polymacon (triangles), hilafilcon A (circles), and balafilcon A (squares) materials. Filled symbols indicate results obtained from the heating ramp, whereas open symbols indicate results determined from the cooling ramp. Repeated MDSC runs are not distinguished because they give essentially the same T_g. Also shown are curves obtained with the Gordon–Taylor Eq. (1) by best fitting the plasticization constant, k.

The change in T_g due to plasticization induced by water sorption is described by the Gordon–Taylor equation [29]:

$$T_g = \frac{k w_1 T_{g1} + w_2 T_{g2}}{k w_1 + w_2} \qquad (1)$$

where w_i is the weight fraction of component i, and T_{gi} is the glass-transition temperature of i; subscripts 1 and 2 indicate water and polymer, respectively, and k is an empirical parameter that gauges the strength of water plasticization. T_{g1} for water is 138 K [30]. For polymacon and hilafilcon A, k was fit to the measured glass-transition temperatures determined from the heating ramp. Because the glass-transition temperature of dry balafilcon A cannot be measured, T_{g2} was also fit to the experimental data for wet balafilcon A. Solid lines in Fig. 5 give the fitting results of Eq. (1); k values are shown in Table 3. Water has essentially the same plasticization effect on polymacon and hilafilcon A ($k=4.1$ for both SCL materials). The larger value of k for balafilcon A ($k=8.3$) indicates stronger water plasticization for the siloxane–hydrogel material.

Setting $T_g=308$ K in Eq. (1), we calculate the minimum water content required for SCL materials to remain in the rubbery state at the average on-eye temperature, as illustrated by the horizontal dashed line in Fig. 5. The resulting minimum water contents, w_1^*, are 10.4, 13.5, and

Table 3
Parameter k of Gordon–Taylor Eq. (1) fitted to glass-transition temperatures measured in MDSC heating ramps

SCL	k
polymacon	4.11
hilafilcon A	4.07
balafilcon A	8.28[a]

[a] T_{g2} was also fitted to the experimental points; $T_{g2}=397.4$ K, where subscript 2 refers to the dry polymer.

6 wt% for polymacon, hilafilcon A, and balafilcon A, respectively.

Table 4 reports the equilibrium water uptake of our SCL materials as a function of the external relative humidity, RH, at 35 °C, as obtained by a gravimetric sorption technique [31]. These measurements show that an environmental relative humidity of at least 74, 64, and 57% is needed to maintain water contents larger than w_1^* for polymacon, hilafilcon A, and balafilcon A, respectively. A recent study using atomic-force microscopy (AFM) [18,19] has demonstrated that the surfaces of some conventional HEMA-based soft contact lenses become rigid when the external RH is less than 60%, a consequence of a rubber-to-glass transition. Our bulk T_g measurements are, therefore, consistent with the surface AFM measurements and demonstrate that a soft contact lens exposed long enough to a RH < 55–75% dehydrates enough to undergo a rubber-to-glass transition.

The implications of such rubber-to-glass transitions for on-eye wear of SCLs are the following. When an SCL is worn on-eye, the anterior surface locally dewets whenever the pre-lens tear film, PrLTF, ruptures [5]. Usually, dewetting does not occur over the entire surface of the lens, but in growing specific spots or streaks [1,32]. The regions of the lens that remain covered by the tear film may supply water to the dewet spot by diffusion. Also, the lens surface is at least partially rewetted within a few seconds when a new PrLTF is deposited on the lens upon blinking [33,34]. Because on-eye dehydration of a soft contact lens requires water transport through the lens toward the environmental air and, because water transport is affected by the air-side mass-transfer resistance [35,36], the RH of the air immediately adjacent to the SCL surface is, in general, larger than that of the bulk environment. Moreover, the presence of other tear components such as salt, proteins, and lipids both in solution and deposited on the surface of the lens may affect both the evaporation rate and surface dehydration and, therefore, may alter the dependence of the physical state of an SCL surface on the environmental RH. Finally, the transition of the lens from a rubbery to a glassy state occurs in a time scale that depends on air-side mass-transfer resistance, lens diffusional resistance, external relative humidity, and polymer relaxation rate. The anterior lens surface becomes glassy only if this time scale is short compared to the interval of time for which the lens anterior surface is directly exposed to environmental air.

Consequently, we cannot claim that the anterior surface of an SCL on-eye develops a glassy skin or glassy spots at the critical RH reported in Fig. 5 for our SCL materials when equilibrated with wet air in the absence of other tear components. Nevertheless, our measurements suggest that the SCL anterior surface may locally turn rigid and glassy in dry environments or in the presence of strong wind. A glassy anterior lens surface may affect the interaction between the soft contact lens and the upper eye-lid, compromising comfort [37]. Moreover, a glassy surface may influence on-eye movement as well as the mass-transport properties of the lens, e.g. water, ions, and oxygen permeabilities. All these factors are critical for good on-eye performance of a soft contact lens [20,22,38].

4. Conclusions

We have investigated the physical state of typical soft-contact-lens (SCL) materials as a function of water content by measuring glass-transition temperatures, T_g, via modulated differential scanning calorimetry (MDSC). The water content of SCL materials was measured by thermogravimetric analysis after equilibration with a constant RH atmosphere provided by saturated salt solutions. Great care was taken to create experimental conditions that avoid SCL polymer thermal decomposition, hermetic-pan seal rupture, and water evaporation during heating in a MDSC run.

Measured glass-transition temperatures decrease

Table 4
SCL water content, w_1, as a function of relative humidity, RH, at 35 °C [31]

polymacon		hilafilcon A		balafilcon A	
RH (%)	w_1 (%)	RH (%)	w_1 (%)	RH (%)	w_1 (%)
7.7	0.6	11.3	3.1	15.3	1.5
19.6	1.7	28.4	6.1	26.1	2.4
29.3	2.4	40.7	8.3	35.9	3.3
39.1	3.7	50.2	10.1	46.3	4.3
50.2	5.2	60.6	12.4	55.9	5.6
60.2	7.1	70.2	15.8	65.9	7.2
69.9	9.3	79.3	20.4	75.3	9.2
79.9	12.9	83.9	25.1	85.0	12.4
85.4	16.0				

significantly with rising SCL water content. Water plasticization was largest for balafilcon A siloxane–hydrogel (commercial name: PureVision™), while the glass-transition temperatures for hilafilcon A (SofLens™ One Day) and polymacon (SofLens® 38) decline at the same rate with rising bulk hydration, as shown by nearly identical Gordon–Taylor *k* parameters. Our SCL materials become glassy at the average on-eye temperature (35 °C) when the water content falls below 10.4, 13.5, and 6 wt% for polymacon, hilafilcon A, and balafilcon A, respectively. This critical water content corresponds to the equilibrium hydration of polymacon, hilafilcon A, and balafilcon A, when exposed to a RH of 74, 64, and 57%, respectively.

Although our results do not establish definitely that SCL's materials on-eye form glassy regions on the front surface when exposed to an environmental relative humidity lower than the critical, the strong water plasticizing effect suggests that a local, surface rubber-to-glass transition may occur in dry environments [18,19]. Change of the physical state of a soft contact lens may affect several significant factors for on-eye lens performance, including comfort, on-eye lens movement, and transport of water, ions and oxygen in the contact lens.

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