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Characterisation of low molar mass siloxanes extracted from crosslinked polydimethylsiloxanes exposed to corona discharges

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Abstract

Crosslinked polydimethylsiloxanes were exposed to corona discharges in dry air at normal pressure. Short-time solvent extraction and subsequent analysis of the extractables, by gas chromatography, mass spectrometry and size exclusion chromatography showed that, oligomers consisting mainly of cyclics with 4–9 repeating units were formed during corona exposure. The size distribution of the oligomers was independent of the crosslink density and corona exposure time. The amount of oligomers located at the surface increased, with increasing storage time, after the corona exposure in qualitative agreement with the ongoing hydrophobic recovery process. Longer extractions penetrated deeper into the samples, and, in addition to the cyclic oligomers, higher molar mass species ($\sim$50,000 g mol^{-1} for unexposed samples) were detected. Samples exposed to corona, treated in this way, showed a broadening of the high molar mass peak towards lower molar masses.

Keywords: Polydimethylsiloxane; Corona discharges; Degradation products

1. Introduction

Silicone rubber based on polydimethylsiloxane (PDMS) is used as an insulating material in out-door electric power applications, replacing glass and porcelain [1,2]. The benefits are lower weight, easier processing and water-repellent surface properties. Under certain conditions, electrical discharges may impinge on the surface of the insulation, thereby causing a loss in hydrophobicity. Deposition of pollutants, e.g. particles, salts etc., on the surface may also cause a loss in hydrophobicity. The remarkable feature of PDMS is that, after a relatively short period of rest, after the discharge activity or pollution deposition, typically from hours to a few days, the hydrophobicity is recovered. The suggested mechanisms of hydrophobic recovery are, diffusion of low molar mass siloxanes from the bulk to the surface, covering the oxidised surface [1–7] and reorientation of oxidised groups from the surface [4,8]. The low molar mass siloxanes originate from the polymerisation processes, or from the addition of silicone liquids as processing aids. They can also be formed when PDMS is exposed to UV, electrical discharges, or heat. When linear PDMS is heated in an inert atmosphere, chemical reactions occur producing almost exclusively, cyclic oligomers of dimethylsiloxanes (ODMS), of the general formula $D_n = [(CH_3)_2SiO]_n$ [9–14]. Due to the random coil conformation of PDMS [15], an intermediate structure formed either by intermolecular or intramolecular mechanism, has been suggested [16]. In either case, silicon atoms utilise their vacant 3d orbitals to form the intermediate, where two siloxane bonds break, while two new siloxane bonds form simultaneously, and no net energy is thus required during the depolymerisation process [16].

In terms of the kinetics of polymer degradation, this process resembles an initiation by random chain scission, but, is not followed by a propagation step (Fig. 1(a)) [11,17]. The kinetics of the randomly initiated depolymerisation, is independent of the molar mass of the polymer [16] and of the type of terminal group [11]. Trimethylsilylated [16], hydroxyl-terminated [17] and vinyl-terminated [18] linear PDMS have demonstrated this behaviour. The main product formed during depolymerisation at elevated temperatures (>450°C) is D_3 [16–18]. Silanol-terminated PDMS can also be depolymerised by an end-initiated ('unzipping') process starting at temperatures well below the true (random) depolymerisation temperature (Fig. 1(b)). The rate of the end-initiated depolymerisation decreases with increasing molar mass of the polymer [16]. In the presence of potassium ions, a catalytic unzipping of linear PDMS at

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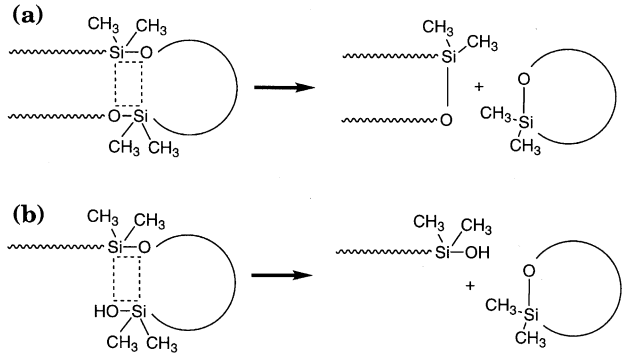

Fig. 1. Siloxane bond rearrangements (depolymerisation) via an intermediate, forming cyclic low molar mass siloxanes: (a) random, (b) end-initiated.

250°C occurred, rather frequently at the fourth, fifth, etc. siloxane unit in the chain, starting from the chain end [11]. The proportion of higher cyclics ($\geq D_4$) then increased. This was explained by the considerable strain prevailing in the D_3 ring, making it thermodynamically unstable at lower temperatures [11]. Branched PDMS formed a mixture of cyclics and polycyclic structures during pyrolysis [19]. The mechanism of degradation of ethylene crosslinks in hydrosilylated PDMS networks shows some resemblance to the degradation of poly(dimethyl-sil-ethylene)siloxane [11]. At lower temperatures (200°C), the cyclic monomer 2,2,6,6-tetrametyl-1-oxa-2,5-disila-cyclohexane was formed [11]. This siloxane-type degradation was accompanied by free radical type splitting of the alkylene segment at temperatures above 400°C [11]. Ageing of PDMS in the presence of oxygen results in oxidative crosslinking, which is initiated at lower temperatures than thermal depolymerisation [16]. However, these two processes occur in parallel, in certain temperature regions [16]. The oxidative crosslinking results in a loss of methyl groups and the formation of an inorganic surface structure with a large number of oxygen bridges [10,20].

It has previously been shown that, when silicone rubbers were exposed to electrical discharges in the presence of oxygen, a hydrophilic silica-like surface layer was formed, which retarded the hydrophobic recovery [3,6,7,21,22]. In a parallel paper [23], the effect of corona discharges on the loss and recovery of hydrophobicity is reported, where the same PDMS materials presented in this paper, were studied. The hydrophobic surface properties were lost due to the formation of oxidised silica-like surface layers. If the silica-like layer exhibited surface cracks, an increased rate of hydrophobic recovery was observed. This was explained by the transport of siloxanes of low molar mass to the surface, through the cracks. The low molar mass siloxanes are believed to form a thin film covering the hydrophilic surface layer, thereby restoring hydrophobicity [3,4,6,7,23]. In this paper, data are presented on the nature of the low molar mass siloxanes responsible for the hydrophobic recovery of crosslinked PDMS materials, with different crosslink densities. The structure of the extractables was assessed by gas chromatography–mass spectrometry and size exclusion chromatography.

2. Experimental

2.1. Material preparation

Vinyldimethyl-terminated polydimethylsiloxanes were crosslinked by a hydrosilylation reaction, using a (30–35%) methylhydro-(65–70%) dimethylsiloxane copolymer ($\bar{M}_W = 2100$ g mol^{-1}) as crosslinker. The ratio of hydride to vinyl groups was kept 2:1, in order to obtain fully crosslinked materials [24]. A platinum divinyltetramethyl disiloxane complex was used as a catalyst at a concentration of 30 ppm. The chemicals were purchased from the United Chemical Technologies Inc., USA, and were used as received. The molar mass distributions of the vinyldimethyl-terminated polydimethylsiloxanes were assessed by size exclusion chromatography, using $CHCl_3$ as solvent. PDMS standards, purchased from Polymer Source, Canada, were used for calibration. Sheets of crosslinked PDMS with a thickness of 1 mm and diameter of 210 mm were prepared in a Schwabenthan Polystat 400S compression moulding machine at 135°C at a pressure of 6 MPa for 15°min. Post-curing was performed at 120°C for 12 h in a hot-air oven. Specimens, with a diameter of 30 mm, were cut from the moulded sheets. Low molar mass species were removed from the specimen by Soxhlet hexane extraction for 72 h. The specimens were then slowly deswollen in air, dried in a vacuum-oven, and kept in desiccators. The number average molar mass of the chain segments between the crosslinks ($\bar{M}_c$) of the PDMS networks is assumed to be equal to the number average molar mass ($\bar{M}_n$) of the particular vinyldimethyl-terminated PDMS used. The codes used for the different PDMS networks are as follows: P0.7: $\bar{M}_c = 700$ g mol^{-1}; P8: $\bar{M}_c = 7500$ g mol^{-1}; P12: $\bar{M}_c = 11,600$ g mol^{-1}; P17: $\bar{M}_c = 16,500$ g mol^{-1} and P38: $\bar{M}_c = 38,300$ g mol^{-1}. The polydispersity ($\bar{M}_w/\bar{M}_n$) of the vinyldimethyl-terminated polydimethylsiloxanes were 1.1 (P0.7), 1.5 (P8), 1.6 (P12), 1.9 (P17) and 1.5 (P38).

2.2. Corona

Specimens were exposed to corona discharges in dry (<2% RH) air (pressure 100 kPa) at 22 ± 2°C, using a set-up described by Hillborg and Gedde [7]. The applied 50 Hz AC voltage was 20 kV_{peak} between the electrode, 87 mm in diameter containing 31 needles and the ground plate. The distance between the tips of the needles and the electrode ground plate was 40–42 mm. The integrated corona charge transfer was 2.6 W. The ground plate rotated at 8 rpm in order to obtain a uniform surface treatment. After exposure to a corona discharge for 0.5, 1 or 3 h, the specimens were allowed to recover their hydrophobicity stored in desiccators at 22 ± 2°C.

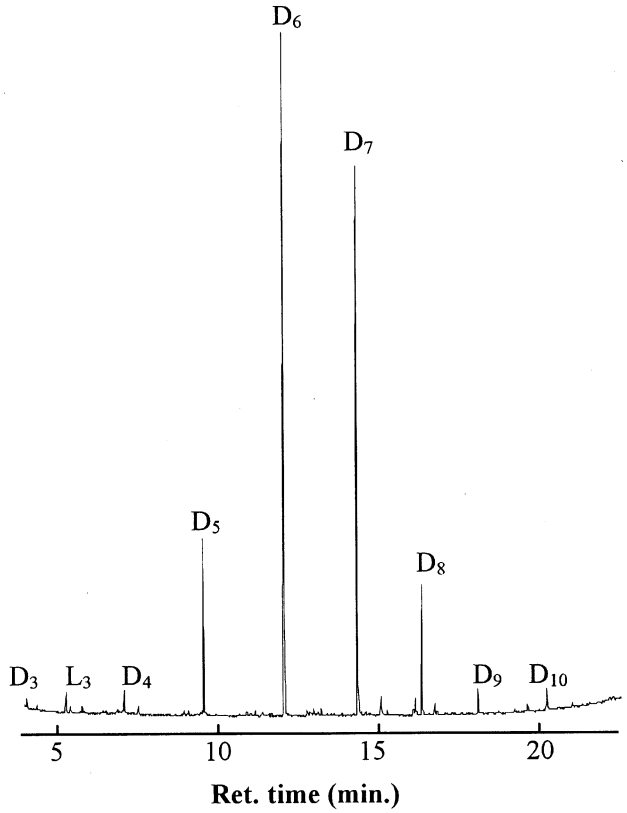

Fig. 2. Gas chromatogram showing the presence of a homologous series of ODMS in the extractables of P12 after exposure to 1 h corona.

2.3. Extraction of low molar mass siloxanes

Films were extracted in weighing bottles at 22°C for 60 s, using 4 ml $CHCl_3$. The solvent was then, removed using a glass syringe, and transferred to glass vials. Since the unexposed sides of the films were attached, firmly to the glassware, the extraction was preferential on the exposed sides. The intention behind using a short extraction time was to dissolve mobile siloxanes in the surface region of the extracted films. A few films were extracted during 20 min for comparison. Materials P0.7, P12 and P38 were allowed to recover to their original hydrophobicity before extraction (storage time: 240 h (P0.7 and P12), 850 h (P38)) whereas P8 and P17 were not extracted until 70–90 h, after corona exposure. The advancing contact angle then ranged between 35–45°, and the receding contact angle between 25–35°, in these cases. The initial advancing and receding contact angles were 100–106 and 74–80°, respectively. Further details can be found in Ref. [23].

Table 1
Contents (wt%) of L_3 in extractables

Material	Exposure time			
	0 h	0.5 h	1 h	3 h
P0.7	0	0	0	0
P8	6	3	4	6
P12	2	3	1	3
P17	9	6	5	5
P38	2	2	2	2

2.4. Size exclusion chromatography (SEC)

SEC was used to assess the molar mass distributions of the extractables. A Waters 717 Plus autosampler and a Waters model 510 apparatus equipped with three PLgel 10 μm mixed-B columns, 300 × 7.5 mm (Polymer Labs.) were used. Chromatograms were recorded using a PL-ELS 1000 evaporative light scattering detector (Polymer Labs). Data were processed using Millenium version 3.20 software. Chloroform was used as the eluent, at a flow rate of 1.0 ml min^{-1}. PDMS standards with narrow molar mass distributions and $\bar{M}_n$ between 2000 and 85,000 g mol^{-1} were used for calibration. The solutions were filtered with 45 μm Teflon filters, before being injected into the column.

2.5. Gas chromatography–mass spectrometry (GC–MS)

The low molar mass fraction was analysed by GC–MS, using a Finnigan GCQ gas chromatograph/mass spectrometer (EI mode). The GC was equipped with a Cp-Sil 8 capillary column (5% phenyl-95%polydimethylsiloxane, 30 m × 0.25 mm, 0.25 μm) from Chrompack, Sweden. Helium was used as the carrier gas. The temperature program of the column was 40°C for 1 min followed by a temperature rise from 40 to 250°C (10°C min_{-1}). The temperature of the injector was kept at 220°C. The electron accelerating voltage used was 70 V. The mass spectrometer was operated at 70 eV. The low molar mass species were identified using standards (D_3–D_5) and by observing the systematic progression in retention times, in the chromatograms. The results were further verified by comparison of the identified species with the NIST database [25]. Using standard solutions of D_4 and D_5 embracing the concentrations of the unknown samples, the amount of cyclics was quantified. A linear relationship between peak area and siloxane concentration was determined with a coefficient of determination $r^2 = 0.994$. These calibrations were based on the assumption that the calibration curves obtained for D_4 and D_5 were also valid for the larger cyclics (D_{6-10}). The total amounts of extractables were then normalised with respect to the areas of the extracted films. The standard deviation of the method was estimated to be 35%. The relative standard deviation between the molar mass distributions of the cyclic ODMS, based on the same type of material and the same dose of corona, was estimated to be 10%.

3. Results and discussion

The extractables of the different PDMS materials were analysed by SEC, and consisted only of low molar mass

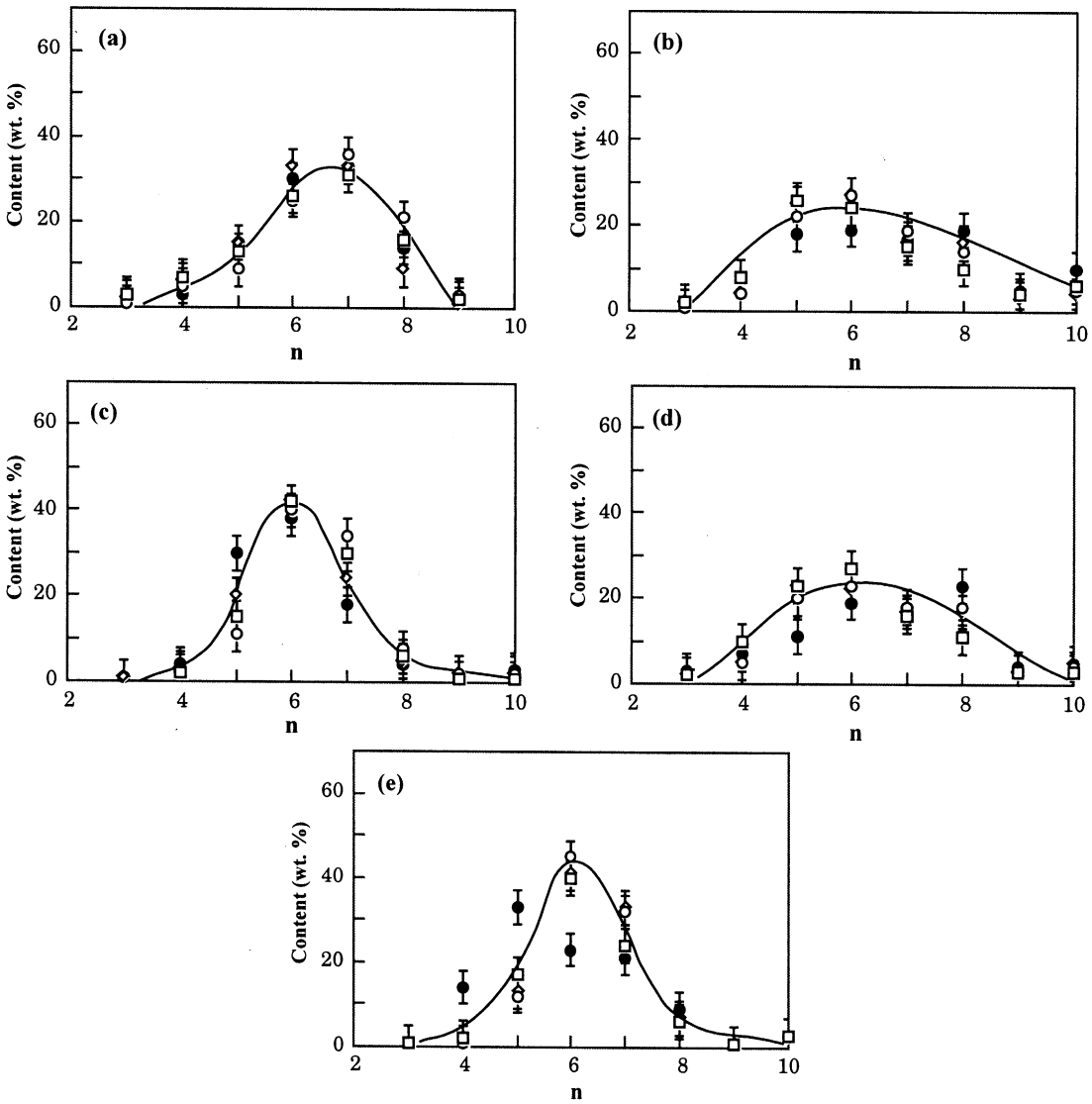

Fig. 3. Number of repeating units (n) of cyclic ODMS, extracted from the surface region of PDMS networks exposed to corona discharges: unexposed (●), 0.5 h corona (◇), 1 h corona (○), 3 h corona (□) for the following materials: (a) P0.7, (b) P8, (c) P12, (d) P17 and (e) P38. The error bars indicate ±5% standard deviation. Lines are drawn as guidance for the eye only.

species (<1000 g mol^{-1}). They were identified by GC–MS as a homologous series of cyclic ODMS, with 3–10 repeating units (Fig. 2).

Traces of linear ODMS with three repeating units (L_3) were also identified (Table 1). Further, low amounts of L_6 (<1 wt%) were found in P38. No trace of the cyclic monomer 2,2,6,6-tetramethyl-1-oxa-2,5-disila-cyclohexane, formed by a siloxane type degradation of the ethylene crosslinks, was found [11]. The absence of fragments from the carbon crosslinks suggests a complete oxidation of these units to volatile species, such as carbon dioxide or methane. Cyclic ODMS, mainly D_5–D_8, were also isolated by extraction from the unexposed materials, although, these species had been carefully extracted prior to the corona exposure. The molar mass distributions of the cyclic oligomers of both unexposed and corona-exposed specimens were independent of the crosslink density (Figs. 3(a)–(e)). Further, the molar mass distributions showed no systematic change with corona exposure time (0.5–3 h).

However, the recovery time after exposure to corona, influenced the molar mass distribution. For the fully recovered materials, the distributions of cyclic ODMS were either identical to that of the extractables of the unexposed molar mass (P0.7) or contained a higher content of larger cyclics, D_6–D_7 (P12 and P38) (Fig. 3). Since these materials were extracted approximately 240 h (P0.7 and P12) and 850 h (P38) after the corona exposure, it is suggested that an equilibrium in the composition of cyclics between the bulk and the surface of the exposed specimen was established. The additional amounts of D_6–D_7 may have been formed during the corona exposure. The materials which were not given sufficient time to fully recover their original hydrophobicity

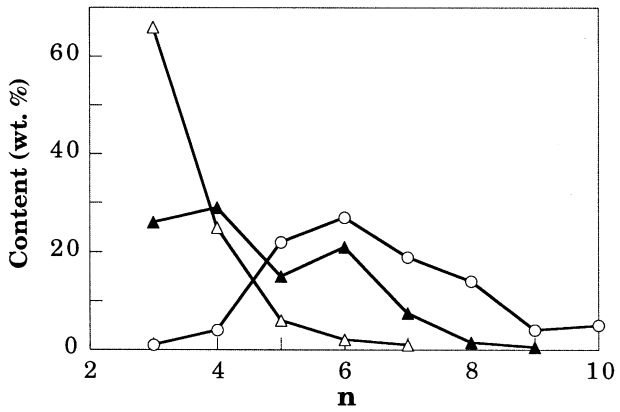

Fig. 4. Comparison of number of repeating units (n) of cyclic ODMS in P8, after 1 h corona (○) with data from Blazsó et al. [11] for pyrolysis products from O^-K^+-terminated linear PDMS in argon at 450°C (△) or 250°C (▲).

(P8 and P17) contained higher proportions of D_4–D_6 in their extractables than the extractables of the unexposed materials. This suggests that the initial hydrophobic recovery (<100 h) was controlled by the transport of these smaller cyclics, whereas the larger cyclics (>D_6) appeared at later stages in the recovery process.

In Fig. 4, data from Blazsó et al. [11] are compared with the molar mass distributions of cyclic oligomers in material P8 after 1 h corona. Pyrolysis at 450°C of O^-K^+-terminated PDMS in argon, yielded 66% of D_3. If the temperature was decreased to 250°C, the amount of D_3 decreased and larger cyclics were formed, due to the increased significance of end-initiated depolymerisation, at the expense of the random depolymerisation. Corona exposure at 22°C then corresponds well to the trend of increasing amount of larger cyclic ODMS, with decreasing temperature, formed by a catalysed end-initiated mechanism. The catalysts may be residues from the Pt-catalyst, or impurities from the solvents

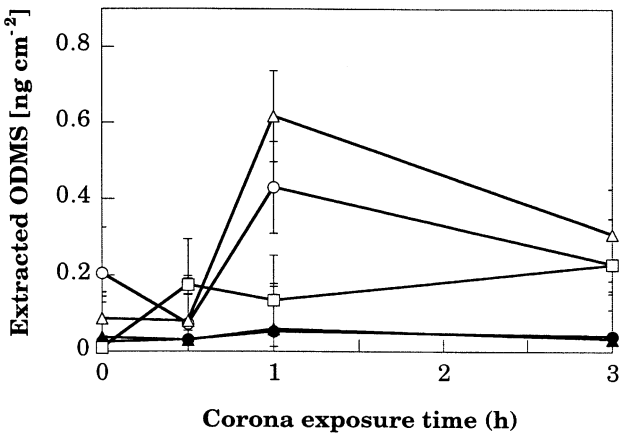

Fig. 5. Total amount of identified low molar mass PDMS per area extracted (ng cm^{-2}) as a function of time of exposure to corona discharges for the PDMS networks: P0.7 (○), P8 (●), P12 (△), P17 (▲) and P38 (□). The error bars indicate a variation of 35% in the amounts found between replicates.

used. The low amounts of D_3 found in the studied systems may be a result of the strained ring structure which makes D_3 thermodynamically unstable at 22°C in favour of larger, unstrained cyclic oligomers, as suggested by Blazsó et al. [11].

The content of L_3 was highest in the extractables of P17, whereas, it was not detected in the extractables of P0.7 (Table 1). Further, the L_3 content was not influenced significantly by exposure to corona, suggesting that, it was present in the virgin networks as a residual structure, which was too short to cyclicise readily, as has been proposed by Thomas and Kendrick [16]. The amount of ODMS increased with increasing dose of corona, especially after more than 0.5 h corona treatment (Fig. 5). Further, the amount of ODMS increased with increasing recovery time after corona exposure (Fig. 5). However, the amounts of ODMS extracted from P8 and P17 before complete hydrophobic recovery were in the same order as in the corresponding unexposed materials. The tendency for ODMS after 3 h corona to be less than after 1 h corona (P0.7, P12) may be due to the scatter in the data.

The total amount of low molar mass siloxanes extracted from the surfaces was considerably lower (maximum 0.5 ng cm^{-2}) than the calculated amount, necessary to form a monolayer of siloxanes (53 ng cm^{-2}) [26]. This strongly suggests that the 60 s extraction was of low efficiency, and that, only a fraction of the free cyclics on the surface, was dissolved. The low yield (average 12% and a standard deviation of 7%) was verified by extraction of known amounts of D_5, which were dissolved in chloroform and adsorbed onto silicon wafers. The wafers were used as received; i.e. oxidised surface layers were present. The purpose of using silicon wafers as test surfaces was the resemblance between the oxidised silicon and the silica-like surface layers formed on PDMS after exposure to corona discharges. ODMS may also have been adsorbed into the oxidised surface layer, making them less susceptible to dissolution, in the non-polar solvent ($CHCl_3$). Furthermore, the low amount of extractable siloxanes suggests that, oxidative crosslinking was the dominant mechanism of degradation of PDMS during corona exposure, rather than the depolymerisation process. The presence of ozone, formed by the ionisation of oxygen during the corona, might as well accelerate the oxidative crosslinking. After extraction of the materials for 20 min, and subsequent analysis using SEC, both prior to and after the exposure to corona discharges, siloxanes of higher molar mass were also found. An example is shown in Fig. 6. Samples of material P38 exposed to corona were extracted after 3100 (1 h corona) and 7000 h (3 h corona) storage time, respectively. The molar mass distribution of unexposed P38 was initially bimodal, consisting of a low molar mass fraction (<1000 g mol^{-1}) and a higher molar mass fraction of $\bar{M}_n = 52,000$ g mol^{-1}, probably originating from residual uncrosslinked PDMS.

When the material was exposed to corona, a broadening

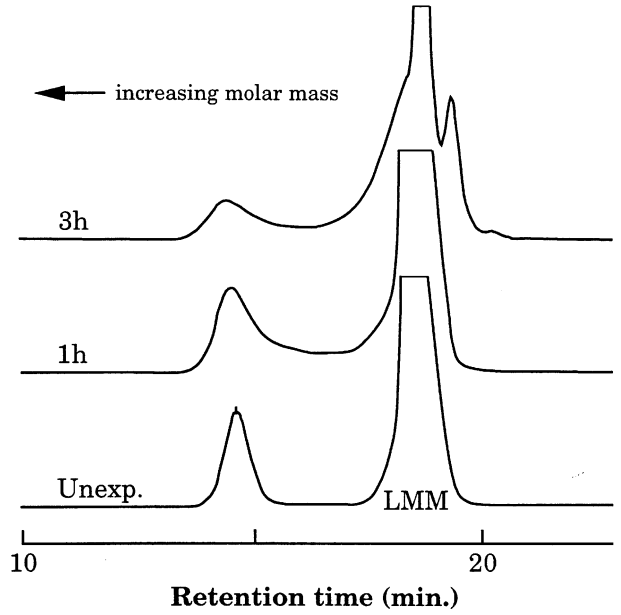

Fig. 6. Molar mass distributions of extractables from P38: unexposed and after exposure to 1 and 3 h corona. Extraction time: 20 min. LMM = low molar mass fraction.

of the peaks was observed, due to the formation of additional amounts of low molar mass siloxanes, resulting in a shift towards longer retention times. Further, siloxane bond interchange reactions resulted in a shift towards higher molar masses [27]. Since these higher molar mass siloxanes were not found in the extractables after the short-time extraction (60 s), it is not believed that these species were involved in the initial hydrophobic recovery (<800 h), after exposure to corona.

The probed extraction depth (r) was estimated from the Einstein relationship [28] for diffusion in one dimension:

$$r = \sqrt{2Dt} \tag{1}$$

where D is the diffusivity of the extractables (oligomers) and t the extraction time. For the unexposed (unoxidised) specimens, the extraction depth can be estimated from the diffusivity data of Gedde et al. [29]: 1×10^{-8} cm^2 s^{-1} (PDMS, $\bar{M}_n = 18,400$ g mol^{-1}) and 20×10^{-8} cm^2 s^{-1} (D_5) to $r = 10$–50 μm (60 s) and $r = 50$–220 μm (20 min). This calculation will tend to overestimate the extraction depth in the specimens exposed to corona, because, these contain a top-layer of oxidised and sometimes vitrified silica-like material [3,6,7,21–23]. The diffusivity of the oligomers through this layer is much lower than that through the unoxidised material. The diffusivity of the oligomer, through the vitrified layer, can be estimated from the Arrhenius diagrams of the hydrophobic recovery of specimens with uncracked silica-like layers presented by Hillborg et al. [23]: $D \approx 10^{-10}$ cm^{2}s^{-1} (D_5); the diffusivity of polymeric penetrants through the vitrified layer should be smaller by several orders of magnitude. The extraction depths for D_5 become ~1 μm (60 s) and ~5 μm (20 min). The extraction depth for a PDMS with $\bar{M}_n = 18,400$ g mol^{-1} should be in order of magnitude smaller, ~100 nm (60 s) and ~500 nm (20 min). These calculations assume that the extraction is controlled only by diffusion. The transport of free oligomers from the surface to the main liquid phase will take some (unknown) time and hence the practical extraction depth should be smaller than the value obtained, according to the above calculation.

4. Conclusions

The low molar mass species produced in crosslinked polydimethylsiloxane on exposure to corona discharges were mainly cyclic oligomers with 4–9 repeating units and smaller amounts of a linear oligomer with 3 repeating units. These are the only species that migrate to the surface, and they account for the larger part of the hydrophobic recovery. The relative proportions of the different species were insensitive to the crosslink density and the corona exposure time.

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