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Polymer 46 (2005) 4204–4211

polymer

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Characterization of polydimethylsiloxane elastomer degradation via cross-linker hydrolysis

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Abstract

Degradation kinetics based on rheological studies are reported for endlinked silane terminated polydimethylsiloxane (PDMS) networks cross-linked with 2,4,6-triallyloxy-1,3,5-triazine as a function of cross-link density and the relative humidity to which the network is exposed. These unique PDMS networks cure in the absence of water but degrade under humid conditions due to cross-linker hydrolysis. Rheological measurements show an exponential decay of the storage modulus (G') with time under conditions of high humidity (greater than 45%) and a linear decay under conditions of low humidity (lower than 22%). Optical studies show that at high humidity two domains exist wherein a domain of degraded polymer fluid surrounds a central region of a soft elastomer. However, a uniform degradation with absence of any interface is observed under low humidity conditions. Thus a crossover from 'surface' degradation from the edge to 'bulk' degradation is observed between 45 and 22% relative humidity. The time to degrade to half the original modulus ($t_{1/2}$) ranges from a few hours at high humidity to days at low humidity. At high humidity $t_{1/2}$ scales with cross-link density, but it is independent of cross-link density at low humidity. A result that is consistent with 'surface' degradation and 'bulk' degradation, respectively.

Keywords: Polydimethylsiloxane; Elastomers; Cross-linker hydrolysis

1. Introduction

Polydimethylsiloxane (PDMS) is a widely used polymer that has received considerable attention due to its unique properties, such as high thermal stability, low glass transition temperature, outstanding dielectric properties, and physiological inertness [1–3]. Elastomers or networks made from PDMS have been used successfully in applications in the field of biomaterials as drug delivery systems [4], denture liners and biomedical balloons [5,6]. They have also found use in reconstructive plastic surgery [7,8] and as lithographic molds for manufacturing micro-chemical devices [9,10].

A variety of well-characterized PDMS polymeric networks, synthesized from chains with different end groups [11,12] and different cross-linkers [12,13], have been studied previously. Stable viscoelastic properties are the dominant requirement of most applications of PDMS networks. Therefore, work has been carried out to determine the conditions under which PDMS networks might degrade. Network rearrangement in peroxide cured PDMS networks at 250 °C in closed systems is thought to occur due to a siloxane hydrolysis mechanism [14] in the presence of trace amounts of water [15]. Stein and Prutzman [16] have established that the tin catalyst used in room temperature vulcanization of some PDMS networks can cause hydrolysis in the presence of water even at room temperature. Patel and Skinner [17] also showed that these siloxane rubbers aged in a closed system softened with time whereas samples aged open to air did not. Kinetic aspects of thermal [18] and oxidative degradation of PDMS networks [19] under extreme conditions of very high temperatures (>200 °C) have also been investigated. Shim and Isayev [20,21] have reported the ultrasonic devulcanization of filled and unfilled silicone rubber and they have found that the presence of water facilitates devulcanization under similar devulcanization conditions.

For some applications it may however, be desirable to have controlled degradation of a PDMS network under less severe conditions. One method of controlling such a degradation would be uncross-linking end-linked PDMS networks. Little work has been done, however, on a PDMS elastomer that degrades not due to backbone degradation or

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doi:10.1016/j.polymer.2005.02.051

hydrolysis but due to a reaction of the cross-linker. This is partly because of the difficulty in finding a cross-linker that can react in a controlled manner with atmospheric elements such as water or oxygen under ambient conditions. Herz et al. reported failure to cure PDMS networks with certain cross-linkers and speculated that the degradation of the networks was catalyzed by the network curing catalysts [22]. However, there was no further study done to date to confirm the degradation, establish the actual reaction, or characterize the degradation kinetics. In this article, we report the synthesis of 'optimal' end-linked networks with minimal defects made by reacting low polydispersity silane terminated PDMS with the trifunctional cross-linker 2,4,6-triallyloxy-1,3,5-triazine (triallyl cyanurate). The degradation kinetics of these PDMS networks was characterized as a function of PDMS precursor molecular weight and moisture content in the environment. Optical studies were carried out to follow the degradation process.

2. Experimental

2.1. Materials

Low polydispersity bi-functional silane terminated PDMS precursor chains (B_2) were synthesized from hexamethylcyclotrisiloxane (D_3) monomer (Gelest, Inc.) by anionic ring-opening polymerization in a 50 wt% toluene solution at 60 °C using benzyltrimethylammoniumbis(*o*-pheny1enedioxy)phenylsiliconate as a catalyst and dimethylsulfoxide (DMSO) as a promoter. Calculated amounts of water were added to control the molecular weight of the resulting polymer [23]. After the polymerization, pyridine, an acid scavenger, was added to the resulting polymer/toluene mixture. The living chains were end-capped with silane groups by adding dimethylchlorosilane. The polymer samples thus obtained were washed with water, dissolved, and reprecipitated with toluene and methanol, and then dried in a vacuum oven at 60 °C for 3 days. The details of the catalyst preparation and the synthesis of the polymer were described previously [11, 23–24]. PDMS precursor chains were characterized using gel permeation chromatography in toluene, and the M_n were found to be 12 kg/mol and 23 kg/mol with a polydispersity index (PDI) of 1.33 and 1.32, respectively. Networks were formed by end-linking with the optimum amount of trifunctional cross-linker 2,4,6-triallyloxy-1,3,5-triazine in the presence of a platinum catalyst *cis*-dichlorobis(diethyl sulfide)platinum(II) in toluene. The mixtures were first degassed in a vacuum oven and networks were fully cured after 12 h at 70 °C in a dry environment.

As had been reported in earlier studies, 'optimal' networks were obtained by reacting the precursor chains and the cross-linker in a non-stoichiometric ratio [11,12]. For vinyl terminated PDMS and a tetrafunctional silane cross-linker, a value of 1.7 for the mole ratio r of cross-linker junctions to the polymer end-groups was reported [11]. This is thought to be due to kinetic effects [25] as well as possible side reactions that consume the cross-linker [26]. In our systems, we tested *r* ratios of 0.8, 1.0, 1.2, 1.4, 1.6, 1.8 and 2.0, the span of which encompassed the commonly observed range of *r* ratios for siloxane polymers. The equilibrium shear modulus of the network prepared at a ratio of $r = 1.4$ was the highest. If side reactions were mainly responsible for the non-stoichiomteric r ratio, then based on the results of vinyl terminated PDMS and silane cross-linker we would have expected the *r* ratio in the present case of silane terminated PDMS and a vinyl cross-linker to be lower than or close to unity. Since the optimal *r* ratio turned out to be 1.4, this implies that kinetic effects may be playing the major role in these non-stoichiometric effects. All subsequent experiments were conducted at $r = 1.4$.

2.2. Rheology measurements

Viscoelastic properties of the PDMS elastomer were measured using a Rheometrics Dynamic Analyzer RDAII rheometer with 25 mm parallel plates. The degassed reactive mixture of silane terminated PDMS, the cross-linker and the catalyst were placed between the parallel plates of the rheometer and allowed to cure at 70 °C for 12 h. A dynamic frequency sweep between 0.1 and 100 rad/s was first carried out at 70 °C and the value of the storage modulus at 0.1 rad/s was used to characterize the equilibrium shear modulus (G_e/RT). As shown in Fig. 1 the storage modulus is independent of frequency over the range of frequency investigated and is orders of magnitude larger than the loss modulus indicating the formation of a network with minimal defects.

To control the relative humidity around the sample placed between the parallel plates of the rheometer, a Plexiglas® chamber was added as shown in Fig. 2. The relative humidity was controlled through the use of different saturated salt solutions [27]. Concentrated salt solutions reduce the water vapor pressure and lead to a subsequent decrease in the relative humidity within the chamber [27].

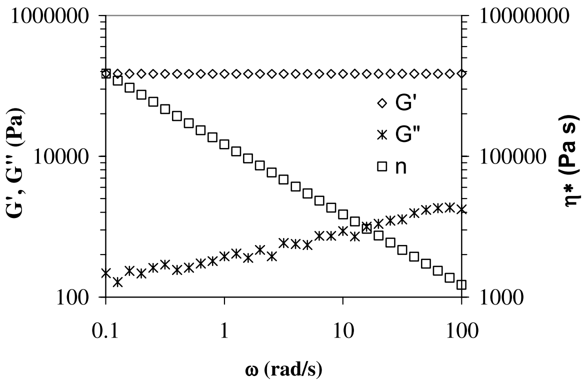

Fig. 1. Storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) of a network made from 23 kg/mol precursor chains at 25 °C just prior to exposure to humid conditions.

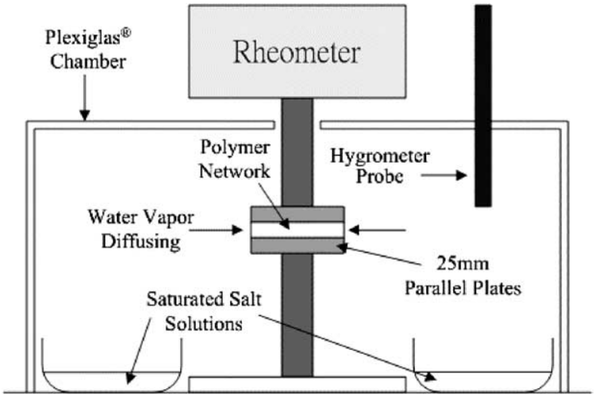

Fig. 2. Chamber for humidity control enclosing the rheometer.

Relative humidity and temperature readings were taken using a Fisher Scientific® Traceable Hygrometer.

After the network had been cured overnight at 70 °C, the heating chamber of the rheometer was first cooled to 25 °C and subsequently opened and replaced by the setup shown in Fig. 2. A dynamic frequency sweep was carried out immediately after the setup was in place. The shear modulus measured at this time represents the shear modulus ($G'(0)$) for the degradation profiles. The air inside the chamber equilibrated to the desired humidity within 15–30 min, which was considered short compared to the degradation time scale. The diffusion of water into the sample occurred only from the exposed edge of the networks. Dynamic frequency sweeps between 0.1 and 100 rad/s were carried out at periodic intervals and the storage modulus at 0.1 rad/s was used to represent the shear modulus.

2.3. Optical analysis

Visual observations of the network along the flat surface of the elastomer discs were not possible with the steel plates of the rheometer, and a separate parallel plate system with two flat, transparent Plexiglas® discs was built to allow for ready observation of the degradation under identical conditions to those in the rheometer. Optical analysis was performed under a Micros Optics IV900 Series microscope and a CCD camera was used to provide a quantitative examination of the degradation kinetics. A digital camera was used to provide qualitative evidence for characterizing the degradation mechanisms occurring over different ranges of humidity based on optical intensity measurements.

3. Results and discussion

3.1. Degradation reaction and network curing

The kinetics of degradation measured via the decrease in storage modulus was found to be extremely sensitive to the humidity in the environment. In particular, very slow degradation kinetics on the order of weeks was observed under near zero humidity conditions at 70 °C, whereas fast degradation kinetics on the order of hours was observed in water-saturated environments as will be shown below. The degradation was irreversible as no curing of the network took place after repeated heating of a degraded sample. We postulate that this irreversibility occurs due to hydrolysis of the cross-linker. The compound 2,4,6-triallyloxy-1,3,5-triazine is known to readily hydrolyze in the presence of dilute mineral acids to give cyanuric acid and three equivalents of allyl alcohol [28]. Based on this reaction we propose the reaction scheme shown in Fig. 3. Such a reaction would render the cross-linker ineffective and explain the irreversibility of the degradation of our PDMS. It would also account for the high sensitivity of the degradation process to water vapor concentration.

Since the reaction in our system happens in the absence of mineral acids we speculate that the cross-linker hydrolysis was catalyzed by the curing catalyst *cis*-dichlorobis(diethylsulfide) Pt(II). This would result in a competition between the curing of the PDMS polymer and the degradation of any partially cured elastomer. The degradation reaction occurred in the presence of water vapor across the range of 20–70 °C. In the presence of water vapor the degradation was generally significant such that the formation of uniform elastomer was not observed even at high temperatures. Also, elevated temperatures appeared to be necessary for the formation of a high modulus network. Unheated formulations stored in closed vials for 5 days showed no sign of curing. Thus to cure the networks both an elevated temperature (∼70 °C) and a water-vapor free environment were required.

3.2. Degradation under different humidity conditions

Experiments were carried out at relative humidity of 100, 75, 45, 22 and 10% for networks made from 23 kg/mol (referred to as 23 k) and 12 kg/mol (referred to as 12 k) PDMS precursor chains. Taking the decrease in the modulus of a network to represent an average degree of degradation of a network, we find that for experiments conducted under conditions of high humidity, the decrease in modulus with time can be fitted to an exponential decay.

$$G'(t) = G'(0)\exp(-kt) \tag{1}$$

where $G'(t)$ is the modulus in kPa at time t; $G'(0)$ is the modulus in kPa when the network was exposed to the humid environment; t represents time in hours and k (h^{-1}) is the characteristic rate constant of decay of the storage modulus. The characteristic time of decrease of the storage modulus is represented by $1/k$. The degradation profiles ($G'(t)/G'(0)$ vs. time) at high humidity values (45–100%) for optimal PDMS networks made from 23 k and 12 k precursor chains are shown in Fig. 4(a). Values of $G'(0)$ and of the rate constants for these networks are listed in Table 1. Fig. 4(b) shows the rate of decrease of the storage modulus as a function of time

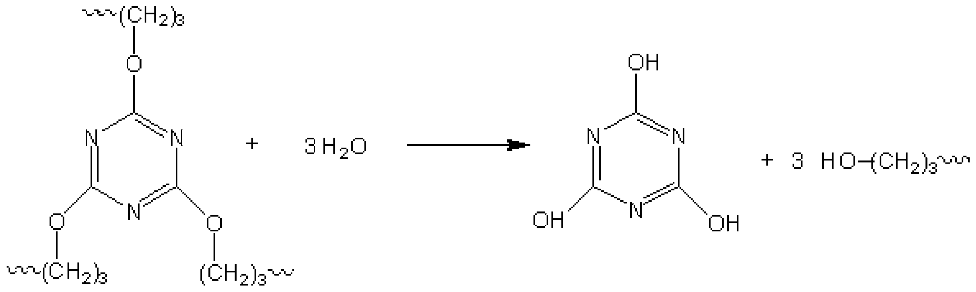

Fig. 3. Cross-linker degradation via hydrolysis.

($dG'(t)/dt$) for the networks made from 12 k and 23 k chains at 100% and 45% humidity. It also shows the ratio of the rates of the network made from 12 k chains to the network made from 23 k. These rates are discussed below.

At a lower humidity value (22%), the decay in storage modulus can no longer be represented by an exponential decay as shown in Fig. 5(a) where a transition from the exponentially decaying profile at 45% humidity to a different decaying profile at 22% humidity is shown. At 22% humidity and lower, the decay of the modulus is well described by a linear decay and represented by Eq. (2):

$$G'(t) = G'(0) - \nu t \tag{2}$$

where $G'(t)$ is the modulus in kPa at time t; $G'(0)$ is the modulus in Pa at time $t=0$; t represents time in hours and ν is the rate of decrease of storage modulus with time. The characteristic time of decrease of the storage modulus is represented by $G'(0)/\nu$. The degradation profiles for PDMS networks prepared at 22% relative humidity, 10% relative humidity at 25 °C and under near zero humidity (achieved by closing the heating chamber around the sample) at 25 and 70 °C are shown in Fig. 5(b). The fitting parameters $G'(0)$ and ν are shown in Table 2. It should be noted that under near-zero humidity conditions, there appears to be a weak dependence of the degradation on temperature as it took

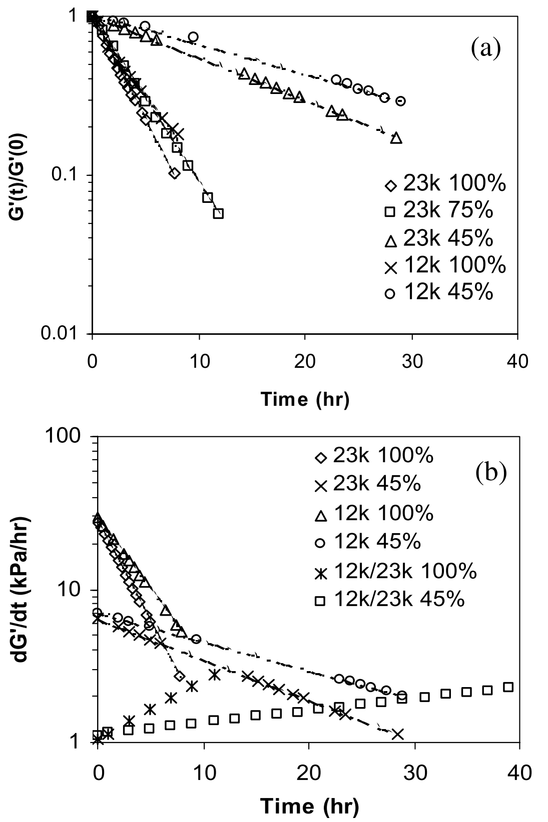

Fig. 4. (a) Decay of normalized storage modulus as a function of time for 23 k and 12 k PDMS at 100, 75 and 45% humidity. (b) Rate of degradation as a function of time for 23 k and 12 k PDMS and the ratio of the two at 100% and 45% humidity.

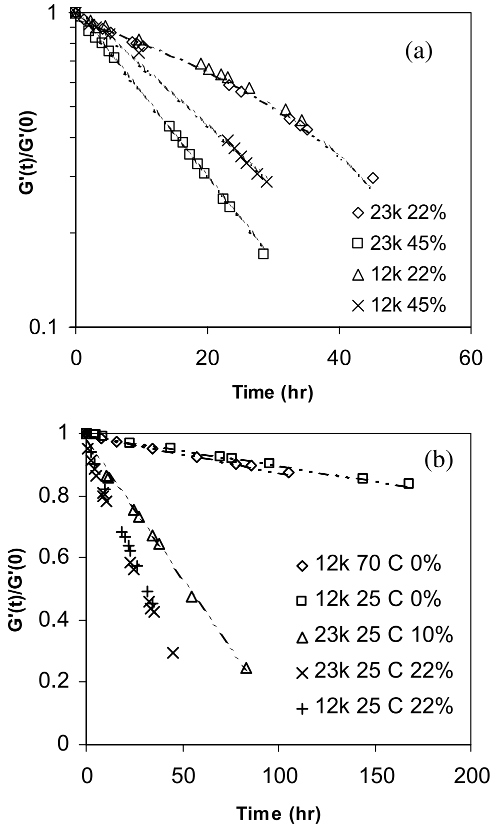

Fig. 5. (a) Decay of the normalized storage modulus for networks made from 23 k and12 k PDMS at 45% and 22% relative humidity showing clearly a transition from an exponential decay to a linear decay at 25 °C. (b) Linear degradation profiles for 12 k and 23 k PDMS under low humidity conditions.

Table 1
Storage modulus $G'(0)$ and rate constant k (h^{-1}) at high humidity (100–45%)

	23 kg/mol			12 kg/mol			Ratio 12 k/23 k	
Humidity	$G'(0)$ (kPa)	k (h^{-1})	$t_{1/2}$ (h)	$G'(0)$ (kPa)	k (h^{-1})	$t_{1/2}$ (h)	$G'(0)$	$t_{1/2}$
100%	92.5	0.30	2.3	137.2	0.21	3.25	1.48	1.42
75%	95.1	0.24	2.9	–	–	–	–	–
45%	105.1	0.06	11.3	162.4	0.04	16.0	1.54	1.41

420 h at 70 °C and 502 h at 25 °C for a 12 k network to degrade to half its starting modulus. When kept in a tightly sealed vial, the networks lasted for more than a year with negligible decline in elastic modulus.

The fact that the data at low relative humidity are accurately represented by a linear fit as opposed to an exponential fit at high relative humidity signifies that a different mechanism governs the degradation under low humidity conditions. The degradation is either governed by the rate of water diffusion, or the rate of reaction with a transition when both rates are comparable. There was a clear visual difference between the networks degraded at high humidity versus those degraded at low humidity. At high humidity (∼100–45%) there were two domains in the degrading sample. One domain of degraded polymer fluid surrounded a central region of soft elastomer, as shown in Fig. 6(a) and (b). The interface between the two domains initially moved dynamically towards the center of the PDMS network in a manner that could be interpreted by a diffusion-limited mechanism. After a certain time (4.5 h in Fig. 7(b)), the movement of the interface appeared to stop, perhaps due to an increased concentration of water in the center region caused by water diffusing in from opposing ends. The center region then degrades slowly with a decay that appeared to be rather uniform. We term the degradation with domain formation to be 'surface' degradation wherein the reaction of the cross-links occurs primarily at the exposed surface of the sample.

At lower relative humidity (∼20%), the two domains observed in the sample under conditions of high humidity were no longer detected and the networks appear to degrade uniformly (Fig. 6(c)). For the network to degrade uniformly, a uniform concentration of water must exist across the network before the reaction begins, which implies that the rate of diffusion or penetration of water must be much greater than the rate of reaction under low humidity conditions. Thus, this 'bulk degradation' in which cross-links are depleted uniformly from the entire sample volume can be interpreted in terms of a reaction rate limited mechanism. Analogous definitions for 'surface and bulk erosion' of degradable polymers exist in the drug delivery literature [29].

Therefore, based on a change in the kinetic degradation profiles and direct visual observation, we can conclude that the mechanism of degradation changes as a function of humidity from 'surface' degradation with interface formation to 'bulk' degradation with uniform degradation across the network.

It is tempting to consider whether for the humidity range of 100–45% wherein a sharp interface is observed, a purely diffusion limited mechanism is at work. This would imply that the rate of reaction or hydrolysis (R_r) is very fast and that as soon as a water molecule reaches the interface an instantaneous reaction occurs [30]. Thus there would be zero concentration of the cross-linker on the side of the interface exposed to the water vapor and the concentration would still be the original cross-link density on the other side of the interface that has still not reacted. For an instantaneous reaction the characteristic rate constants at a particular humidity should be independent of the cross-link density. From Table 1 we see that the characteristic rate constant (k) does depend somewhat on cross-link density implying that a purely diffusion-limited mechanism is unsatisfactory. The exponential decay observed experimentally is thus the result of several effects due to diffusion, the complex dependence of water concentration in the hydrolysis reaction, and the inhomogeneity of the sample on the overall torque measured using the rheometer. A model incorporating all these effects is outside the scope of this paper.

The interface position seen from Fig. 6(a) and (b) was in the range of 2.5 mm (100% humidity) to 4 mm (45% humidity) from the edge. For Fig. 6(a) the photograph is taken after 9 h that corresponds to $2.5t_{1/2}$ for this network

Table 2
Storage modulus $G'(0)$ and rate of decrease of storage modulus ν at low humidity (22–0%)

	23 kg/mol			12 kg/mol			Ratio 12 k/23 k	
Humidity	$G'(0)$ (kPa)	ν (kPa/h^{-1})	$t_{1/2}$ (h)	$G'(0)$ (kPa)	ν (kPa/h^{-1})	$t_{1/2}$ (h)	$G'(0)$	ν
22%	83.4	1.32	31.6	153.3	2.42	31.7	1.83	1.83
10%	78.1	0.71	55.1	–	–	–	–	–
0% 75 °C	–	–	–	154.7	0.18	420.1	–	–
0% 25 °C	–	–	–	100.6	0.10	502.1	–	–

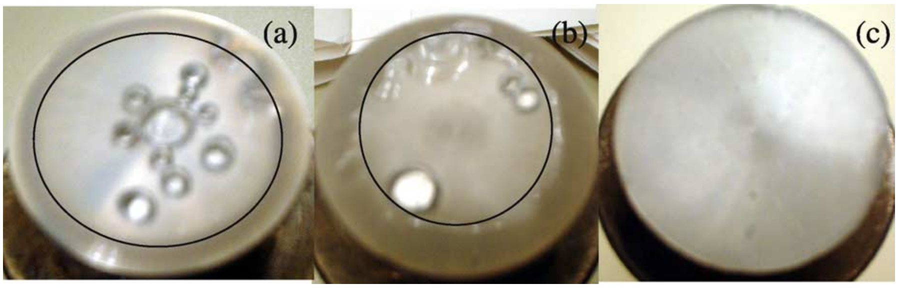

Fig. 6. 12 k PDMS networks at (a) 100% Relative Humidity after 9 h; (b) 45% relative humidity after 48 hr; (c) 23 k network at 22% relative humidity after 178 h. Photographs were taken immediately after removing the elastomer from the rheometer. Defects appear when the sample is detached from the parallel plates after the experiment.

and for Fig. 6(b) the photograph is taken after 48.5 h that corresponds to $3t_{1/2}$. As noted above, since the movement of the interface slows down around $t_{1/2}$, the above interface positions are supposed to reflect closely the interface position at $t_{1/2}$. A purely diffusive half-life of the networks defined as the time it takes to decrease the modulus from $G'(0)$ to $G'(0)/2$, can then be calculated as $t_{1/2}=r^{*2}/D$ where D is the diffusion coefficient of water in PDMS and r^* is the position of the interface from the edge. The literature value of D is reported to be close to 1.45×10^{-5} cm^2/s [31–33]. This gives a half life $t_{1/2}$ in the range of 1–4 h that is comparable but lower than the values reported in Table 1 for the network made from 12 k. This supports the conclusion that even at high humidity where a clear interface is observed, the degradation does not occur via a simple diffusion limited mechanism.

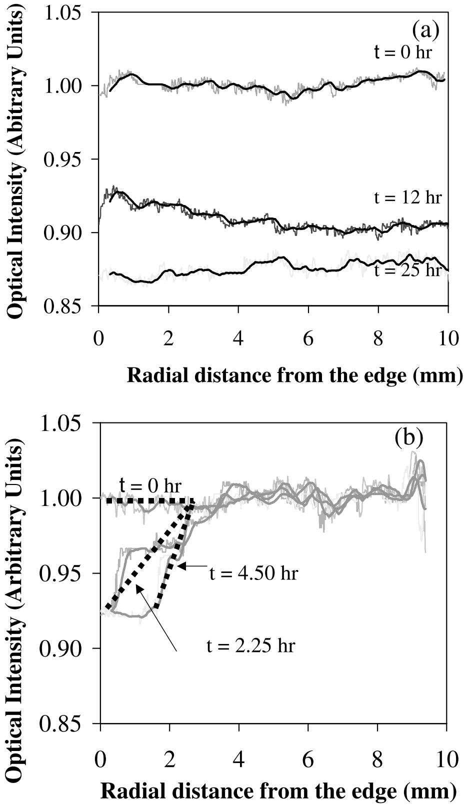

Fig. 7. Optical Analysis of degradation profiles at (a) 20% humidity and (b) 100% humidity.

The ratio of cross-link density of networks made from different precursor molecular weights can be calculated from the ratio of the elastic shear modulus immediately before the networks are first exposed to non-zero humidity. As shown in Table 1, the ratio of cross-link density of networks made from 12 k and 23 k precursor chains is approximately equal to the ratio of time to degrade to half $G'(0)$ at a particular humidity. Thus, the increase in the initial cross-link density leads to a roughly proportional increase in the degradation times. As can be seen in Fig. 4(b) the rate of decrease of storage modulus (dG'/dt) decreases exponentially with time and the rate is greater for the 12 k network than that for the 23 k network. Because the decrease of the storage modulus dG'/dt is initially similar for both the 12 k and 23 k networks (Fig. 4(b)), we argue that the rate at which water penetrates the two types of networks is initially the same. If we assume that the rate of hydrolysis is proportional to cross-link density (which is found to be the case at 22% humidity), then the ratio of the rate of decrease of storage modulus for the 12 k and 23 k networks should be equal to the ratio of their cross-link density. However, the average ratio of the rate of decay for 12 k to 23 k networks (around 1.3) and the ratio of their $t_{1/2}$ times (Table 1) is less than the ratio of cross-link density indicating that both reaction and diffusion mechanisms are at work in the degradation of the networks at high humidity.

The overall rate of degradation for relative humidity of 22% or lower yielded a linear decay profile of the modulus. This result implies that the rate of hydrolysis reaction (R_r) must be an overall pseudo zero-order reaction. But we observe from Table 2 that at 22% humidity the ratio of the rate of degradation of the 12 k to the 23 k network is same as the ratio of their cross-link density and hence $t_{1/2}$ remains the same for these networks under these conditions. This observation points to a first order dependence of the hydrolysis reaction on cross-link density. But, we can also infer that there must be a strong dependence of the hydrolysis reaction on water concentration. At 100% relative humidity and at short times, the diffusion of water at high concentrations around the perimeter drives the hydrolysis reaction and a quick degradation around the edges is observed locally. In contrast, at 20% relative humidity and below, the concentration of water at the network interface is insufficient to push the hydrolysis to appreciable rates as compared to the rate of diffusion.

To reconcile an overall zero order hydrolysis reaction with the fact that the hydrolysis reaction has a first order dependence on cross-link density and a strong dependence on water concentration, we argue that a decrease in the hydrolysis rate due to a decrease in cross-link density produces a compensating increase in water concentration. An increase in water concentration is due to an increase in the hydrophilic nature of the network caused by the release of hydrophilic products, yielding a pseudo-zero order reaction rate. Similar arguments have been proposed by Pitt and Shah [34] to explain the kinetics of hydrolytic cleavage of the *p*-nitrobenzoate ester of 2-hyroxyethyl methacrylate in its copolymer with methoxydiethoxylethyl methacryalte. As the hydrophobic *p*-nitrobenzoate group was lost, they observed a progressive increase in the hydration of the gel resulting in a zero order reaction.

3.3. Optical analysis

While the stable PDMS networks are typically very clear and translucent, the degraded samples became increasingly opaque as the networks were degraded into softer gels during hydrolysis and ultimately turn into a polymer solution (Fig. 6(a)–(c)). As a result, an optical analysis exploiting the changes in optical properties caused by the extent of degradation was conducted for quantitative insights into the competition between reaction-controlled and diffusion controlled mechanisms. As shown in Fig. 7(a), the optical intensity was fairly uniform across much of the radius of a network subjected to a low humidity environment, implying a linearly decaying profile as previously observed. At 100% humidity (Fig. 7(b)), we observe a drop in the optical intensity near the perimeter due to the increased opacity of degraded material. The region of the sharpest decline represented the interface between the degraded material and non-degraded network discussed earlier. It was hence possible to accurately track the movement of the interface as the network was degraded.

Given such quantification of the degree of local degradation, we attempted to perform a numerical integration to correlate the movement of the interface to the decay in G'. However, we were unable to obtain a simple and consistent relationship between the optical intensity and degree of degraded network over time from the Fig. 7. This is due to the fact that the change in optical intensity with time is caused not just by the reaction of water with the cross-linker but also because of the diffusion of the products generated in the reaction within the network. As these products diffuse from regions of high concentration to regions of low concentration they cause a change in the optical intensity making it hard to correlate the change in optical intensity to just the degradation reaction.

4. Conclusion

Optimal PDMS networks were synthesized by end-linking silane terminated PDMS chains with 2,4,6-Triallyloxy-1,3,5-triazine. The decrease in storage modulus of the network measured by a rheometer was used to characterize the degradation kinetics of these networks due to hydrolysis of cross-linkers as a function of precursor molecular weight and relative humidity. Based on rheology and optical studies we demonstrate a crossover of the degradation mechanism from 'surface degradation' with interface formation to 'bulk degradation' between 45 and 22% humidity. We postulate that at high humidity the rate of hydrolysis is higher than rate of diffusion leading to an interface formation. At low humidity the rate of hydrolysis is much slower than the rate of diffusion causing uniform degradation. We show the rate of hydrolysis to be a first order reaction with respect to the cross-link density. At high humidity $t_{1/2}$ scales with cross-link density but is independent of cross-link density at low humidity. This is consistent with a reaction mechanism that goes from a mechanism that is dominated by bulk degradation to a mechanism dominated by surface degradation as a function of increased humidity.

Acknowledgements

We gratefully acknowledge the financial support of NSF polymers program under grant DMR-0349952 and the Cornell Alumni Undergraduate Research Fund. We thank Prof. Steven Mulvaney for the suggestion of using salt solutions to control humidity inside the rheometer chamber. We also thank Dr Shivaun Archer and Mr. Glen Swann for their technical support.

References

[1] Clarson SJ, Semlyen JA. Siloxane polymers. Englewood Cliffs, NJ: Prentice-Hall; 1993.
[2] Noll W. Chemistry and technology of silicones. New York: Academic Press; 1968.
[3] Shimamoto A, Kanemitsu S, Fuginaga K, Takao M, Onoda K, Shimono T, Tanaka K, Shimpo H, Yada I. Ann Thorac Surg 2000;69: 115.
[4] Gao Z, Nahrup JS, Mark JE, Sakr A. J Appl Polym Sci 2003;90:658.
[5] El-Zaim HS, Heggers JP. Polymeric biomaterials. In: Dumitriu S, editor.. New York: Marcel Dekker; 2001. Chapter 3.
[6] McMillin CR. Rubber Chem Technol 1994;67:417.
[7] Alexandrou B, Read R, Li SK. J Med Eng Technol 1978;2:75.
[8] Kheir JN, Leslie LF, Fulmer NL, Edlich RF, Gampper TJ. J Long-Term Eff Med 1998;8:55.
[9] McDonald JC, Duffy DC, Anderson JR, Chiu DT, Wu H, Schueller OJA, Whitesides GM. Electrophoresis 2000;21:27.

[10] Ng JMK, Gitlin I, Stroock AD, Whitesides GM. Electrophoresis 2002;23:3461.

[11] Patel SK, Malone S, Cohen C, Gillmor JR, Colby RH. Macromolecules 1992;25:5241.

[12] Takeuchi H, Cohen C. Macromolecules 1999;32:6792.

[13] Llorente MA, Mark JE. Macromolecules 1980;13:681.

[14] Zeldin M, Qian B-R, Choi SJ. J Polym Sci, Polym Chem Ed 1983;21:1361.

[15] Thomas DK. Polymer 1966;7:99.

[16] Stein J, Prutzman LC. J Appl Polym Sci 1988;36:511.

[17] Patel M, Skinner AR. Polym Degrad Stab 2001;73:399.

[18] Deshpande G, Rezac ME. Polym Degrad Stab 2002;76:17.

[19] Chaudhry AN, Billingham NC. Polym Degrad Stab 2001;73:505.

[20] Shim SE, Isayev AI. J Appl Polym Sci 2003;88:2630.

[21] Shim SE, Isayev AI. Rubber Chem Technol 2001;74:303.

[22] Herz J-E, Belkebir-Mrani A, Rempp P. Eur Polym J 1973;9:1165.

[23] Lee CL, Marko OW, Johannson OK. J Polym Sci, Polym Chem Ed 1976;14:743.

[24] Lee CL, Johannson OK. J Polym Sci, Polym Chem Ed 1976;14:729.

[25] Gilra N, Cohen C, Panagiotopoulos AZ. J Chem Phys 2000;112:6910.

[26] Macosko CW, Saam JC. Polym Bull 1987;18:463.

[27] Spiess WEL, Wolf W. In: Rockland LB, Beuchat LR, editors. Water activity: theory and applications to food. New York: Marcel Dekker; 1987. p. 227.

[28] Smolin EM, Rapoport L. s-triazines and derivates. New York: Interscience Publishers Inc; 1959. p. 81.

[29] Tamada JA, Langer R. Proc Natl Acad Sci USA 1993;90:552.

[30] Tani N, Van Dress M, Anderson JM. In: Lewis DH, editor. Controlled release of pesticides and pharmaceuticals. New York: Plenum Press; 1981. p. 79.

[31] Hofmann D, Fritz L, Ulbrich J, Paul D. Comput Theor Polym Sci 2000;10:419.

[32] Watson JM, Baron MG. J Membr Sci 1995;106:259.

[33] Okamoto K, Nishioka S, Tsuru S, Sasaki S, Tanaka K, Kita H. Kobunshi Robunshu 1988;45:993.

[34] Pitt CG, Shah SS. J Control Release 1995;33:397.